NBO 7.0 Program Manual

Natural Bond Orbital Analysis Programs

compiled and edited by

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PREFACE: HOW TO USE THIS MANUAL

The NBO7 Manual consists of two major divisions:

Section A ("Getting Started") contains introductory and one-time information for the novice user – what the program does, new program functionality, program installation, and a brief tutorial on sample output.

Section B ("NBO User's Guide") is for the experienced user who has an installed program and general familiarity with standard default NBO output. This section documents the many keywords that can be used to alter and extend standard NBO job options, with examples of the resulting output. Section B is mandatory for users who wish to use the program to its full potential. This section describes keyword-controllable capabilities of the basic NBO modules (Sec. B.1-B.6) and *GenNBO* stand-alone program (Sec. B.7), as well as NBO-based supplemental modules (Sec. B.8 *et seq.*).

The NBO website <http://nbo7.chem.wisc.edu/> provides additional tutorials, sample input and output for main program keywords, and explanatory background and bibliographic material to supplement this Manual.

A quick-reference index to NBO keywords and keylists discussed in this manual is presented in Table 1 below. The table lists default (in [brackets]) and optional keywords, indicating whether additional parameters must be provided (Parms? Y = yes; N = no; opt. = optional) with a brief summary of the keyword result and the page number of the Manual for further reference.

Table 1: NBO Keyword/Keylist Quick Summary

Keyword	Parms?	Keyword Description	Page
Main Program Options			
[BEND]	opt.	Hybrid directionality and "bond-bending" analysis	A-25 B-7
CMO	opt.	Bonding character of canonical molecular orbitals	B-142
DIPOLE	opt.	Dipole moment analysis	B-8, 34
[E2PERT]	opt.	2nd-order perturbative estimates of NBO interactions	A-26 B-7
MATRIX	Y	General operator and transformation matrix	B-192
MEMORY	Y	Allocate dynamic memory	B-6
NBBP	opt.	Natural bond-bond polarizability indices	B-103
NBCP	N	Natural bond critical point analysis	B-170
[NBO]	opt.	Natural bond orbital compositions	A-21 B-5
[NBOSUM]	N	NBO summary table	A-27 B-5
NCE	N	Natural coulomb electrostatics analysis	B-181
NCS	opt.	Natural chemical shielding analysis	B-147
NCU	opt.	Natural cluster unit analysis	B-185
NJC	opt.	Natural J-coupling analysis	B-155
NLMO	N	Natural localized molecular orbital compositions	B-5, 32
[NPA]	opt.	Natural population analysis	A-18 B-5
NPEPA	opt.	Natural poly-electron population analysis	B-207
NRT	N	Natural resonance theory analysis	B-82
PROP	Y	General 1e property analysis	B-189

RADICAL	N	Effectively unpaired electron distribution	B-199
RDM2	N	2nd Order Reduced Density Matrix	B-218
RNBO	N	Resonance Natural Bond Orbital	B-222
STERIC	opt.	Natural steric analysis	B-106
Control Options			
AOINFO	N	Write AO basis information to LFN 31	B-14
ARCHIVE	opt.	Write ARCHIVE (FILE47) for stand-alone GenNBO input	B-14, 68
BNDIDX	N	NAO-Wiberg Bond Index and related valency indices	B-14, 39
BOAO	opt.	Fock-Dirac density matrix ("Bond order matrix")	B-16
CYCLES	Y	Limit cycles in NBO search	B-16
DETAIL	N	Additional details of NBO search	B-16
DIST	N	Atomic distance table	B-14
FILE	Y	Specify filestem for PLOT files and other I/O	B-14
FIXDM	N	Correct unphysical occupancies of input density matrix	B-17
MATRIX	Y	Print general matrix operator output	B-192
MOLDEN	opt.	Write geometry and orbitals in Molden format	B-197
MOLUNIT	Y	User-specified molecular units	B-5
MSPNBO	N	Maximum Spin-Paired NBOs (spin-averaged density matrix)	B-5
MULAT	N	Gross Mulliken populations, by atom	B-16
MULORB	N	Gross Mulliken populations, by orbital and atom	B-16
NBOCML	opt.	Write NLS in CML format	B-196
NBODAF	opt.	Write NBO direct access file (DAF) to disk	B-16
NBOMOL	opt.	Write NLS in MDL format	B-196
NOBOND	N	1-center atomic hybrids (no 2-c NBO search)	B-46

NRTCHG	Y	Alter maximum formal charge for candidate NRT structures	B-88
NRTCML	N	Write NRT resonance structures in CML format	B-196
NRTDTL	N	Additional details of NRT search	B-88
NRTE2	Y	Specify delocalization threshold for NRT search	B-86
NRTLST	Y	Print leading $NRTSTR structure specifications	B-87
NRTMOL	opt.	Write NRT resonance structures in MDL molfile format	B-196
NRTPAR	Y	Alter threshold for NRT parent structures	B-86
PLOT	N	Write files for orbital plotting	B-14
PRINT	Y	Heirarchical print control of NBO output	B-15
PRJTHR	Y	Alter projection threshold for NHO search	B-16
PROP	Y	NBO/NLMO analysis of selected operators	B-189
RPNAO	N	Revised pure AO (PAO) to PNAO transformation	B-16
SKIPBO	N	Skip NBO search (NPA only for PRINT=1)	B-5
SVEC	opt.	Print eigenvectors of AO overlap matrix	B-17
THRESH	Y	Alter occupancy threshold for NBO search	B-16
XMOL	opt.	Write XMol-formatted geometry	B-197
Operator Matrix Output			
DI	opt.	Output dipole moment matrix (DIAO, DINAO, etc.)	B-10
DM	opt.	Output density matrix (DMAO, DMNAO, etc.)	B-10
F	opt.	Output Fock matrix (FAO, FNAO, etc.)	B-10
K	opt.	Output kinetic energy matrix (KAO, KNAO, etc.)	B-10
S	opt.	Output overlap matrix (SAO, SPNAO, SPNBO, SPNLMO)	B-10

V	opt.	Output 1-e (N-e attraction) potential matrix (VAO, VNAO, etc.)	B-10
Transformation Matrix Output			
AOPAO	opt.	Output AO to PAO transformation	B-9
AONAO	opt.	Output AO to NAO transformation	B-9
AOPNAO	opt.	Output AO to PNAO transformation	B-9
AONHO	opt.	Output AO to NHO transformation	B-9
AOPNHO	opt.	Output AO to PNHO transformation	B-9
AONBO	opt.	Output AO to NBO transformation	B-9
AOPNBO	opt.	Output AO to PNBO transformation	B-9
AONLMO	opt.	Output AO to NLMO transformation	B-9
AOPNLMO	opt.	Output AO to PNLMO transformation	B-9
AONO	opt.	Output AO to NO transformation	B-9
AOMO	opt.	Output AO to MO (LCAO-MO) transformation	B-9
PAOPNAO	opt.	Output PAO to PNAO transformation	B-11, 16
NAONHO	opt.	Output NAO to NHO transformation	B-9
NAONBO	opt.	Output NAO to NBO transformation	B-9
NAONLMO	opt.	Output NAO to NLMO transformation	B-9
NAONO	opt.	Output NAO to NO transformation	B-9
NAOMO	opt.	Output NAO to MO transformation	B-9
NHONBO	opt.	Output NHO to NBO transformation	B-9
NHONLMO	opt.	Output NHO to NLMO transformation	B-9
NHONO	opt.	Output NHO to NO transformation	B-9
NHOMO	opt.	Output NHO to MO transformation	B-9
NBONLMO	opt.	Output NBO to NLMO transformation	B-9
NBONO	opt.	Output NBO to NO transformation	B-9
NBOMO	opt.	Output NBO to MO transformation	B-9

NLMONO	opt.	Output NLMO to NO transformation	B-9
NLMOMO	opt.	Output NLMO to MO transformation	B-9
NOMO	opt.	Output NO to MO transformation	B-9
Auxiliary Keylists			
$CHOOSE	Y	Specify alternative Lewis structure for NBO search	B-20
$CORE	Y	Modify default NBO core table	B-18
$DEL	Y	Delete selected NBOs, interactions, or blocks of interactions	B-23
$NPEPA	Y	Specify user-selected configurations	B-207
$NRTSTR	Y	Specify reference structures for NRT analysis (also $NRTSTRA and $NRTSTRB)	B-89
Auxiliary FILE47 Keylists			
$BASIS	Y	Atomic centers and angular symmetries of AOs	B-74
$C10	Y	Derivative MO coefficients	B-151
$CONTRACT	Y	Contraction coefficients and orbital exponents of AOs	B-76
$COORD	Y	Job title, atoms, Cartesian coordinates	B-73
$DENSITY	Y	Density matrix in AO basis	B-69
$DIPOLE	Y	Dipole matrix in AO basis	B-69
$FOCK	Y	Fock matrix in AO basis	B-69
$GENNBO	Y	Specify calculation model size, type and units	B-71
$H01	Y	GIAO Hamiltonian first derivatives	B-151
$H11	Y	GIAO Hamiltonian second derivatives	B-151
$KINETIC	Y	Kinetic energy matrix in AO basis	B-69
$LCAOMO	Y	Canonical MOs in AO basis	B-69
$NUCLEAR	Y	Nuclear-electron attraction matrix in AO basis	B-69
$OVERLAP	Y	Overlap matrix in AO basis	B-69

Section A: GETTING STARTED

A.1 INTRODUCTION TO THE NBO 7.0 PROGRAM

A.1.1 What Does the NBO Program Do?

The NBO program performs the analysis of a many-electron molecular wavefunction in terms of localized electron-pair bonding units. The program carries out the determination of natural atomic orbitals (NAOs), natural hybrid orbitals (NHOs), natural bond orbitals (NBOs), and natural localized molecular orbitals (NLMOs), and uses these to perform natural population analysis (NPA), NBO energetic (deletions) analysis, and other tasks pertaining to localized analysis of wavefunction properties, including natural resonance theory (NRT) and natural chemical shielding (NCS) analysis. This section provides a brief introduction to NBO algorithms and nomenclature.

The NBO method makes use of only the first-order reduced density matrix of the wavefunction, and hence is applicable to wavefunctions of general mathematical form. In the open-shell case, the analysis is performed in terms of "different NBOs for different spins," based on distinct density matrices for α and β spin. [Note, however, that electronic structure packages may not provide the spin density matrices for certain types of open-shell wavefunctions (e.g., MCSCF or CASSCF wavefunctions calculated by the GUGA formalism). In this case NBO analysis can only be applied in the "maximum spin-paired" (MSPNBO) formulation.]

NBO analysis is based on a method for optimally transforming a given wavefunction into localized form, corresponding to the one-center ("lone pair") and two-center ("bond") elements of the chemist's Lewis structure picture. The NBOs are obtained as local block eigenfunctions of the density matrix, and are hence "natural" in the sense of Löwdin, having optimal convergence properties for describing the electron density. The set of high-occupancy NBOs, each taken doubly occupied, is said to represent the "natural Lewis structure" (NLS) of the molecule. Delocalization effects appear as weak departures from this idealized localized picture. (For transition metals, a normal-valent Lewis-like structure conforms to a dodectet rule, rather than the normal octet rule for main-group elements.)

The various natural localized sets can be considered to result from a sequence of transformations of the input atomic orbital basis set $\{\chi_i\}$,

$$\text{input basis AOs} \rightarrow \text{NAOs} \rightarrow \text{NHOs} \rightarrow \text{NBOs} \rightarrow \text{NLMOs}$$

[Note that the restriction to starting AOs is not intrinsic. If the wavefunction were not calculated in an atom-centered basis, one could first compute wavefunctions for the individual atoms (in the actual basis set and geometry of the molecular calculation) and select the most highly occupied natural orbitals as the starting "atomic orbitals" for that atom. Indeed, NBOs have now been obtained for a variety of systems in the framework of plane-wave and related grid-type descriptions; see B. Dunnington and J. R. Schmidt, "Generalization of Natural Bond Orbital Analysis to Periodic Systems: Applications to Solids and Surfaces via Plane-Wave Density Functional Theory," *J. Chem. Theor. Comp.* **8**, 1902 (2012); L. P. Lee, D. J. Cole, M. C. Payne, and C.-K. Skylaris, "Natural Bond Orbital Analysis in Linear-Scaling Density Functional Theory Calculations" <http://www2.tcm.phy.cam.ac.uk/onetep/Focus/BiologicalApplications>. However, because atom-centered basis functions are the nearly universal choice for molecular calculations, the NBO program makes no provision for this step.]

Each natural localized set forms a complete orthonormal set of one-electron functions for expanding the delocalized molecular orbitals (MOs) or forming matrix representations of one-electron operators. The overlap of associated "pre-orthogonal" NAOs (PNAOs), lacking only the interatomic orthogonalization step of the NAO procedure, can be used to estimate the strength of orbital interactions in the usual way, based on Mulliken-type approximations.

The optimal condensation of occupancy in the natural localized orbitals leads to partitioning into high- and low-occupancy orbital types (reduction in dimensionality of the orbitals having significant occupancy), as reflected in the orbital labelling. The small set of most highly-occupied NAOs, having a close correspondence with the effective minimal basis set of semi-empirical quantum chemistry, is referred to as the "natural minimal basis" (NMB) set. The NMB (core + valence) functions are distinguished from the weakly occupied "Rydberg" (extra-valence-shell) functions that complete the span of the NAO space, but typically make little contribution to molecular properties. Similarly in the NBO space, the highly occupied NBOs of the natural Lewis structure (NLS) can be distinguished from the "non-Lewis" antibond and Rydberg orbitals that complete the span of the NBO space. Each pair of valence hybrids h_A, h_B in the NHO basis give rise to a bond (σ_{AB}) and antibond (σ^*_{AB}) in the NBO basis,

$$\sigma_{AB} = c_A h_A + c_B h_B$$

$$\sigma^*_{AB} = c_B h_A - c_A h_B$$

the former a Lewis (L, occupied) and the latter a non-Lewis (NL, unoccupied) orbital. The antibonds (valence shell non-Lewis orbitals) typically play the primary role in departures (delocalization) from the idealized Lewis structure.

The NBO program also makes extensive provision for energetic analysis of NBO interactions, based on the availability of a 1-electron effective energy operator (Fock or Kohn-Sham matrix) for the system. [As noted above, the construction of NAOs and NBOs is wholly independent of any such energy operator (or geometry) information.] Estimates of energy effects are based on second-order perturbation theory, or on the effect of deleting certain orbitals or matrix elements and recalculating the total energy. NBO energetic analysis is dependent on the host electronic structure system (ESS) to which the NBO program is attached, as described in the Appendix. Analysis of a DFT calculation is performed analogously to a Hartree-Fock calculation, but uses Kohn-Sham orbitals that incorporate important effects of a correlated electronic distribution that are displayed in details of the NAOs, NBOs, and their occupancies.

The core features included in default NBO analysis output are described in Sections B.1-B.6. However, many additional features can be requested by specific keywords in general `$NBO ...(keywords)... $END` keylist input. These features include natural resonance theory (NRT keyword), natural steric analysis (STERIC keyword), natural energy decomposition analysis (NEDA keyword), natural bond critical point analysis (NBCP keyword), and many others, each described in separate sections of this Manual. *NBO 7.0* now includes additional analysis options for natural polyelectron population analysis (NPEPA keyword), reduced 2nd-order density matrix and cumulant evaluations (RDM2 keyword), and resonance-averaged natural bond orbitals (RNBO keyword). Keyword-requested options build on and extend the capabilities of core NBO analysis, and are described separately in Sections B.8 *et seq.*

NBO 7.0 comes installed in a number of leading ESS packages, and one should follow the instructions provided with the ESS on how to run NBO. However, the *NBO 7.0* program can also be obtained as a binary or source code distribution that, in principle, can be attached to any ESS of the user's choice. The download package for the *NBO 7.0* binary distribution contains specific interfacing routines or instructions to facilitate direct binary-to-binary interactivity with a number of popular *ab initio* packages (currently including Gaussian, GAMESS, Molpro, Orca).

A.1.2 Input and Output

From the user's point of view, input to the NBO portion of an ESS/NBO program consists simply of one or more keywords enclosed in NBO *keylists* in the ESS input file. The main NBO keylist (the $NBO keylist) is of the form:

```
$NBO ...(keywords)... $END
```

Simple examples of such $NBO keylists are

```
$NBO  dipole  nrt  $END

$NBO  file=myjob  archive  naonbo  ncs=0.05  $END
```

Note that keylists are always delimited with $-prefixed identifiers: an identifier such as $NBO to open the keylist and $END to terminate it. Keylist delimiters and keywords are case-insensitive, and the keylist can extend across multiple lines, e.g.

```
$nbo
  file=/home/me/nbo7/myjob
  ARCHIVE
  naonbo
  ncs=0.05,csa
$end
```

Other keylist identifiers include $CORE, $CHOOSE, $NRTSTR, $DEL, and $NPEPA. Keylists cannot be nested, and each new keylist must begin on a new line. The NBO program reads the keywords of each keylist to set various job options, then interrogates the ESS program for information concerning the wavefunction to perform the requested tasks.

Common abbreviations used in naming keywords are:

S	Overlap matrix
DM	Density matrix
F	Fock or Kohn-Sham matrix
K	Kinetic energy matrix
V	1-electron potential energy (nuclear-electron attraction) matrix
DI	Dipole matrix
NPA	Natural population analysis
NAO	Natural atomic orbital
NHO	Natural hybrid orbital
NBO	Natural bond orbital
NLMO	Natural localized molecular orbital

PNAO	pre-orthogonal NAO (omit interatomic orthogonalization)
PNHO	pre-orthogonal NHO (formed from PNAOs)
PNBO	pre-orthogonal NBO (formed from PNAOs)
PNLMO	pre-orthogonal NLMO (formed from PNAOs)

The general form of NBO keylists and the specific functions associated with each keyword are detailed in the User's Guide, Section B. The particular way of including NBO keylists in the input file for each ESS is detailed in the instructions provided by the ESS host.

Principal output from the NBO program consists of the tables and summaries describing the results of NBO analysis, generally written to the ESS output file. Sample default NBO output is described in Section A.3, and sample output for many NBO keyword options is presented in Sec. B.6 and the individual sections for NBO supplementary modules (Sec. B.8 *et seq*).

The NBO program writes transformation matrices and other data to disk files. Two particularly noteworthy files are the NBO direct access file (FILE48) that the program uses to store intermediate results during a calculation, and the archive file (FILE47) that, written on request, can be used with the stand-alone *GenNBO* program to repeat NBO analysis without running the ESS program to recalculate the wavefunction. A description of FILE47 is given in Section B.7.

A.1.3 General Capabilities and Restrictions

Principal capabilities of the NBO program are:

(1) Natural population, natural bond orbital, and natural localized molecular orbital analysis of densities from SCF, Moller-Plesset, MCSCF, CI, coupled cluster, and density functional calculations;

(2) For HF/DFT methods only, energetic analysis of the wavefunction in terms of the interactions (Fock or Kohn-Sham matrix elements) between NBOs;

(3) Localized analysis of molecular dipole moments in terms of NLMO and NBO bond moments and their interactions;

(4) Additional analyses provided by NBO-based supplemental modules (Sec. B.8 *et seq.*), including natural resonance theory, natural steric analysis, bond-bond polarizability indices, natural chemical shielding analysis, natural J-coupling analysis, natural poly-electron population analysis, and natural energy decomposition analysis. New features of *NBO 7.0* are summarized in Sec. A.1.5.

Most NBO storage is allocated dynamically to conform to the minimum required for the molecular system under study. However, certain NBO common blocks of fixed dimensionality are used for storage. These are currently dimensioned to accommodate up to 999 atoms, 5000 basis functions, 2000 basis function shells, and 5000 basis function exponents. These defaults can be modified for users who obtain the NBO source code distribution. The program is not set up to handle complex wavefunctions, but can treat any real RHF, ROHF, UHF, MCSCF (including GVB), CI, CC, or Moller-Plesset-type wavefunction (i.e., any form of wavefunction for which the requisite density matrices are available) for ground or excited states of general open- or closed-shell molecules. Effective core potentials ("pseudopotentials") can be handled, including complete neglect of core electrons as assumed in semi-empirical treatments. The atomic orbital basis functions (including Cartesian *spdfgh* and spherical *spdfghi* functions in angular symmetry) may be of general Slater-type, contracted Gaussian-type, or other general composition, including the "effective" orthonormal valence-shell AOs of semi-empirical treatments. AO basis functions are assumed to be non-orthogonal. Linear dependence in the basis set is handled by discarding subshells of offending functions.

A.1.4 References and Relationship to Previous Versions

The *NBO 7.0* program should be cited as follows:

NBO 7.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI (2018)

NBO 7.0 is an extension of previous versions of the NBO method:

(1) "Version 1.0," the semi-empirical version incorporated in program *BONDO* and distributed through the Quantum Chemistry Program Exchange [F. Weinhold, *Quantum Chemistry Program Exchange No. 408* (1980)];

(2) "Version 2.0," the first *ab initio* implementation, designed for interfacing with Gaussian-82 and distributed through QCPE [A. E. Reed and F. Weinhold, *QCPE Bull.* **5**, 141 (1985)];

(3) Version 3.0, the general-purpose *ab initio* implementation developed for distribution through QCPE, and soon incorporated (as "Version 3.1") into commercial Gaussian distributions [E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold, *QCPE Bull.* **10**, 58 (1990)];

(4) Version 4.0, the subsequent UW/TCI version (under copyright of the University of Wisconsin, Madison) that added NRT, STERIC, NEDA, and other capabilities [*NBO 4.0*. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (1996)];

(5) Version 5.0, the long-running UW/TCI version that maintained link-ready connectivity to leading ESS host systems and added CMO, NCS, NJC, 3CHB, and other capabilities [*NBO 5.0*. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001)].

(6) Version 6.0, the first "link-free" UW/TCI version that employed message-passing for direct binary-to-binary NBO/ESS interactivity, while also introducing new keyword features (NCU, NCE, NBCP) and generalized

provision and labelling for excited states [*NBO 6.0*. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (2013)].

NBO 7.0 should be considered to supercede all these versions.

Principal contributors (1975-2018) to the conceptual development of the NBO methods contained in this program are

T. K. Brunck	J. P. Foster
A. B. Rives	A. E. Reed
R. B. Weinstock	J. E. Carpenter
E. D. Glendening	J. K. Badenhoop
J. A. Bohmann	S. J. Wilkens
C. M. Morales	C. R. Landis
P. Karafiloglou	F. Weinhold

Others who contributed to program development or technical implementation of individual program segments include S. Baker, J. K. Blair, S. H. Feldgus, T. C. Farrar, J. L. Markley, J. Michl, A. V. Nemukhin, J. Sharley, A. Streitwieser, W. M. Westler, S. J. Wright, and H. E. Zimmerman. Many other colleagues and co-workers have provided useful comments and suggestions that are reflected in the final version of the program, and for which we are grateful.

References to the development and applications of principal NAO/NBO/NLMO methods include:

Natural Bond Orbitals:

J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* **102**, 7211-7218 (1980)

Natural Atomic Orbitals and Natural Population Analysis:

A. E. Reed and F. Weinhold, *J. Chem. Phys.* **78**, 4066-4073 (1983)

A. E. Reed, R. B. Weinstock, and F. Weinhold, *J. Chem. Phys.* **83**, 735-746 (1985)

Natural Localized Molecular Orbitals:

A. E. Reed and F. Weinhold, *J. Chem. Phys.* **83**, 1736-1740 (1985)

Open-Shell NBO:

J. E. Carpenter and F. Weinhold, *J. Molec. Struct. (Theochem)* **169**, 41-62 (1988)

Comprehensive Review Articles:

A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* **88**, 899-926 (1988)

F. Weinhold, "Natural Bond Orbital Methods," In, *Encyclopedia of Computational Chemistry* P. v.R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, P. R. Schreiner (Eds.), (John Wiley & Sons, Chichester, UK, 1998), Vol. 3, pp. 1792-1811

E. D. Glendening, C. R. Landis, and F. Weinhold, "Natural Bond Orbital Methods," *WIREs Comp. Mol. Sci.* **2**, 1-42 (2012)

F. Weinhold, "Natural bond orbital analysis: A critical overview of relationships to alternative bonding perspectives," *J. Comput. Chem.* **78**, 2363-2379 (2012).

F. Weinhold, C. R. Landis, and E. D. Glendening, "What is NBO Analysis and How is it Useful?" *Int. Rev. Phys. Chem.* **35**, 399-440 (2016).

E. D. Glendening, C. R. Landis, and F. Weinhold, "NBO 7.0: New Vistas in Localized and Delocalized Chemical Bonding Theory," *J. Comput. Chem.* **40**, 2234-2241 (2019).

Books:

F. Weinhold and C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective* (Cambridge U. Press, 2004), 760pp.

F. Weinhold and C. R. Landis, *Discovering Chemistry with Natural Bond Orbitals* (Wiley-VCH, 2012), 319pp.

Leading references for NBO-based supplementary modules are included in Sections B.8 *et seq*. Further background and bibliographic materials can be found on the NBO website: <http://nbo7.chem.wisc.edu/biblio_css.htm>

A.1.5. What's New in NBO 7.0?

NBO 7.0 includes new capabilities for describing electron correlaton effects and resonance-theoretic aspects of near-equilibrium and reactive species, complementing and extending established NBO/NRT analysis tools. *NBO 7.0* builds on the revised labelling conventions and structural programming model of the preceding NBO6 version (link-free binary-to-binary message passing) to provide new analysis options that expand the range and convenience of NBO analysis technology. Despite numerous changes, *NBO 7.0* was designed to be compatible with earlier versions as nearly as possible. Experienced NBO users should find that familiar features run practically unchanged, allowing smooth and intuitive migration to new keywords and features.

Principal new features include:

Improved NRT and $CHOOSE Algorithms

NBO 7.0 introduces a dramatically improved "solver" (QPNRT algorithm) for variational optimization of NRT resonance weights and bond orders, rendering the non-linear optimizers that were employed in NBO4-NBO6 obsolete. With this improvement, (i) all perturbative approximations of "old-style" NRT are avoided; (ii) *all* resonance structures are treated with full "reference" structure accuracy, in contrast to the former distinction between "reference" and "secondary" structures that often led to numerical discontinuities along a reaction pathway; (iii) the QPNRT algorithm readily allows consideration of *many* structures (hundreds or thousands!) beyond those that could formerly be considered; (iv) the optimal QPNRT solution is provably unique, and is generally obtained with *no* special $NRTSTR input or other user intervention; and (v) converged NRT weightings and bond orders are usually obtained at reduced cost, as well as improved numerical reliability.

The improved QPNRT solver is also combined with a more flexible and robust $CHOOSE algorithm to obtain the density contribution for each idealized resonance bonding pattern . The new $CHOOSE algorithm is closely related to the NBO algorithm for the Natural Lewis Structure, with full optimization of hybridization and polarization parameters for each chosen bonding pattern (rather than presumed perturbative relationship to those of a "parent" precursor).

NEDA for Gaussian

Natural Energy Decomposition Analysis (NEDA) was previously implemented only for the *GAMESS* host system, but *NBO 7.0* now includes the corresponding NEDA implementation for *Gaussian 16, Rev. C.01* and future *Gaussian* versions. As described in Sec. B.11, the numerical NEDA results from *GAMESS* and *Gaussian* are essentiallly equivalent, but the *Gaussian* implementation requires no $DEL-type keylist input and allows more flexible choices of "fragment" charge and spin state.

Natural Poly-electron Population Analysis (NPEPA)

The NEDA module (Sec. B-24) provides a complete numerical implementation of Karafiloglou's "poly-electron population analysis" in localized NAO/NHO/NBO/NLMO basis expansions. This in turn provides a far-reaching generalization of standard NPA and NRT electronic descriptors of "population" and "resonance weighting" to include effects of electron correlation. The latter are beyond the purview of the 1st-order reduced density operator, $\boldsymbol{\Gamma}^{(1)}$, whose matrix elements serve as the fundamental FILE47 input to the NBO program. This density matrix is in turn a "reduced" form of the full *N*-electron wavefunction Ψ or Kohn-Sham electron density $\rho(\mathbf{r})$, sufficient to exactly evaluate any *single*-electron property [i.e., any property whose evaluation depends on $\rho(\mathbf{r})$ alone]. However, $\boldsymbol{\Gamma}^{(1)}$ fails to include the *poly*-electron effects of electron correlation in the full (unreduced) Ψ, which are now made accessible through the NPEPA keyword options of *NBO 7.0*.

NPEPA evaluations can be performed for single-determinant (HF/DFT) or multi-determinant Ψ. The latter requires $WF data list input (Sec. B.7.7), as introduced in NBO6. The NPEPA input conventions are therefore closely tied to $WF wavefunction input, allowing for complete generality of selected electron/hole occupancy patterns in the many-determinant Ψ.

NPEPA evaluations are most succinctly described in the "2nd-quantized" language of NAO- or NBO-based creation and annihilation operators. The Fermi-Dirac anticommutation rules for these operators dictate the exquisite Boolean logic of many-electron Pauli compliancy that is only partially recognizable in the familiar maximum-occupancy constraint ($q_i \leq 1$) for a single spin-orbital φ_i, but is made fully explicit in NPEPA description.

2nd-order Reduced Density Matrix Elements (RDM2)

Still more detailed description of electron correlation effects requires $\Gamma^{(2)}$, the 2nd-order reduced density operator. Numerical values of NBO-based matrix elements of $\Gamma^{(2)}$ are now made available by the RDM2 keyword (Sec. B-25) of *NBO 7.0*. These 2-electron ("geminal") matrix elements are evaluated in the basis of 2×2 Slater determinants of NBOs, providing direct connection to corresponding localized orbital features of $\Gamma^{(1)}$.

As for NPEPA evaluations, $\Gamma^{(2)}$ evaluations can be performed for single- or multi-determinant Ψ, but only the latter can exhibit the characteristic effects of electron correlation. "Pure" *e*-correlation effects are therefore more specifically isolated in matrix elements of the *cumulant* operator Ξ ($\equiv \Gamma^{(2)} - \Gamma^{(1)} \wedge \Gamma^{(1)}$, in symbolic Grassman algebra), which are provided in default RDM2 output for all geminals over doubly-occupied Lewis-type NBOs. These NBOs are expected to exhibit the dominant effects of *e-e* correlation, particularly the "left-right" correlations of 2c/2e bond NBOs as well as secondary "in-out" and "angular" correlations of 1c/2e lone-pair NBOs.

The Ξ values of doubly-occupied NBOs are also closely tied to the exclusion effects of Pauli-compliancy. Default RDM2 output therefore includes numerical evaluation of Pauli-type "*N*-representability" contraints on the NBO-based cumulant values, for comparison with the actual correlated values. However, the RDM2 input options also allow the user to display any desired elements of the $\Gamma^{(2)}$, Ξ matrices for other specialized studies of localized *e-e* interactions.

Resonance Natural Bond Orbitals (RNBO)

NBO 7.0 adds a new "RNBO" orbital-type ("resonance" or "reactive" NBOs) to the NBO family of localized and semi-localized orbitals (Sec. B-26). Whereas the strictly 2c-localized NBOs or semi-localized NLMOs (and their pre-orthogonal counterparts) are primarily intended to display the well-localized bond patterns of stable near-equilibrium species, the RNBOs are designed to better visualize the dynamical *bond-shifting* along a chemical reaction pathway.

Specifically, the RNBOs are constructed from NRT-weighted linear combinations of PNLMOs from the idealized $CHOOSE structures for each contributing NRT bond pattern. Such NRT-weighted semi-localized orbitals are able to evolve smoothly toward one or another bonding pattern along any chosen reaction pathway. RNBOs can thereby display "activation" toward

alternative reaction channels that are available to a reactive species, chosen from an arbitrary starting point on the potential energy surface.

The RNBOs open up a new class of localized animation-type applications, helping to unravel and illustrate the small number of key bond shifts underlying a complex reaction mechanism. However, the non-orthogonal RNBO visualization orbitals can also be symmetrically orthogonalized (ORNBO keyword) to give a highly compact (sub-minimal!) "basis set" that adapts dynamically to any point on a reactive pathway, suitable for wavefunction construction. Furthermore, the bond-shifts represented in RNBO forms are often of simple 3-center (e.g., allylic) type, but the RNBOs can in principle describe higher multi-center bonding motifs. Thus, the RNBOs may also serve a variety of purposes related to optimal "few-center" description of species far from the usual well-localized bonding pattern of the equilibrium limit.

A.2 INSTALLING THE NBO PROGRAM

[*NBO 7.0* comes installed in a number of leading ESS packages. Users of these packages may ignore this section.]

The NBO program is distributed in electronic download form, either as binary executables or source code. Installation instructions differ in these cases. In either case, the final NBO7 binary executables are intended to communicate interactively with a chosen NBO7-compatible host electronic structure system (ESS) or with the *GenNBO* program that takes its input from an archive (FILE47) file.

Windows Binary Executable Distribution

The Windows distribution includes the 32- and 64-bit integer NBO7 executables (nbo7.i4.exe and nbo7.i8.exe), the *GenNBO* executables (gennbo.i4.exe and gennbo.i8.exe), sample FILE47 input files, and a batch script (gennbo.bat) for executing the sample calculations. Instructions for installing and testing these executables are provided with the distribution.

Linux Binary Executable Distribution

Binary executable distributions are available for Linux and Mac OSX operating systems. (Installation for other Unix-based operating systems may require the source distribution described below.) The Linux distribution includes the 32- and 64-bit integer NBO7 executables (nbo7.i4.exe and nbo7.i8.exe), the *GenNBO* executables (gennbo.i4.exe and gennbo.i8.exe), source code or libraries for installing NBO7 in Gaussian-09 and GAMESS, sample FILE47 files, and tcsh and bash shell scripts (gennbo and gennbo.sh) for executing the sample calculations. Instructions for installing and testing these executables are provided with the distribution.

Source Code Distribution

The source distribution consists of the master NBO source code, GNU makefiles, and utility routines for building 32- and 64-bit executables, including the NBO7 executables (nbo7.i4.exe and nbo7.i8.exe) and *GenNBO* executables (gennbo.i4.exe and gennbo.i8.exe). GNU, Portland Group, and Intel Fortran compilers are fully supported by the distribution. Other compilers may successfully build executables too, but are not currently supported by the NBO development team. Consult the “Frequently Asked Questions” link of the

A.2 INSTALLING THE NBO PROGRAM

NBO7 website <http://nbo7.chem.wisc.edu/faq_css.htm> or contact the authors if you encounter undue difficulties when building the NBO executables.

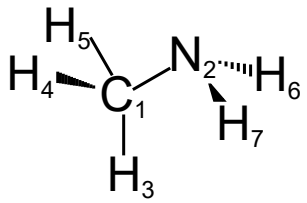
The installation of the NBO programs into your host ESS system generally does not affect the way your system processes standard input files. The only change involves the reading of NBO keylists (if detected in your input file), performance of the NBO tasks requested in the keylist, and return of control to the ESS program in the state in which the NBO call was encountered (unless checkpointing operations were performed; Sec. B.12).

You are encouraged to contact the authors when attempting to interface *NBO 7.0* to an ESS package that is not currently supported by the source code distribution. It may be possible for the authors to assist with this effort. Alternatively, you might consider having the ESS write a FILE47 file that can be used as input to the *GenNBO* stand-alone version of the NBO program. See Section B.7 for a description of this file.

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

A.3.1 Running the Example

This section provides an introductory quick-start tutorial on running a simple NBO job and interpreting the output. The example chosen is that of methylamine (CH_3NH_2) in Pople-Gordon idealized geometry, treated at the *ab initio* RHF/3-21G level. Cartesian coordinates (in Angstroms) of the atoms at this geometry are




```
C       0.745914       0.011106       0.000000
N      -0.721743      -0.071848       0.000000
H       1.042059       1.060105       0.000000
H       1.129298      -0.483355       0.892539
H       1.129298      -0.483355      -0.892539
H      -1.076988       0.386322      -0.827032
H      -1.076988       0.386322       0.827032
```

corresponding to bond lengths of 1.47 (C-N), 1.09 (C-H), and 1.01 Å (N-H) with tetrahedral bond angles and staggered dihedrals. The 3-21G split-valence basis set consists of 28 AOs (nine each on C and N, two on each H), extended by 13 AOs beyond the minimal basis level.

In many cases, you can modify the standard ESS input file to produce NBO output by simply including the line

```
$NBO  $END
```

at the end of the file. This is an empty NBO keylist, specifying that NBO analysis should be carried out at the *default* level. Alternatively, *GenNBO* can be run with the FILE47 archive file (ch3nh2.47) provided with the binary and source distributions to produce the NBO output described here.

Default NBO output produced by this example is shown below, just as it appears in your output file. The start of the NBO section is marked by a standard header, citation, and job title:

```
********************************** NBO 7.0 **********************************
           N A T U R A L   A T O M I C   O R B I T A L   A N D
         N A T U R A L   B O N D   O R B I T A L   A N A L Y S I S
*************************** University of Wisconsin ************************
 (c) Copyright 1996-2018 Board of Regents of the University of Wisconsin System
     on behalf of the Theoretical Chemistry Institute.  All rights reserved.

         Cite this program [NBO 7.0.0 (15-Nov-2018)] as:

         NBO 7.0.  E. D. Glendening, J. K. Badenhoop, A. E. Reed,
         J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou,
         C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute,
         University of Wisconsin, Madison, WI (2018)

Filename set to ch3nh2

Job title:  Methylamine...RHF/3-21G//Pople-Gordon geometry
```

The NBO banner reports the program version (NBO 7.0) and license name ("University of Wisconsin" in this case).

NBO output is formatted to maximum 80-character width for convenient display on a computer terminal or printed page. The NBO heading echoes any requested keywords (none for the present default case). The filename that is reported ("ch3nh2" in this case) is used to open named files, such as the FILE48 direct access file (ch3nh2.48) and FILE47 archive file (ch3nh2.47). (The latter is only produced when the user adds the ARCHIVE keyword to the $NBO keylist.)

A.3.2 Natural Population Analysis

The next four NBO output segments summarize the results of natural population analysis (NPA). The first segment is the main NAO table, as shown below:

```
 NATURAL POPULATIONS:  Natural atomic orbital occupancies

  NAO Atom No lang   Type(AO)    Occupancy      Energy
 ----------------------------------------------------------
    1    C  1  s      Cor( 1s)     1.99978     -11.18023
    2    C  1  s      Val( 2s)     1.09697      -0.20799
    3    C  1  s      Ryd( 3s)     0.00072       1.95620
    4    C  1  px     Val( 2p)     0.88578       0.00427
    5    C  1  px     Ryd( 3p)     0.00128       0.93254
    6    C  1  py     Val( 2p)     1.21480      -0.07273
    7    C  1  py     Ryd( 3p)     0.00063       1.02987
    8    C  1  pz     Val( 2p)     1.24536      -0.08876
    9    C  1  pz     Ryd( 3p)     0.00057       1.01730

   10    N  2  s      Cor( 1s)     1.99983     -15.43232
   11    N  2  s      Val( 2s)     1.43044      -0.59551
   12    N  2  s      Ryd( 3s)     0.00021       2.76110
   13    N  2  px     Val( 2p)     1.29173      -0.16773
   14    N  2  px     Ryd( 3p)     0.00108       1.56674
   15    N  2  py     Val( 2p)     1.82107      -0.33469
   16    N  2  py     Ryd( 3p)     0.00186       1.48620
   17    N  2  pz     Val( 2p)     1.35159      -0.19161
   18    N  2  pz     Ryd( 3p)     0.00067       1.59366

   19    H  3  s      Val( 1s)     0.81261       0.14913
   20    H  3  s      Ryd( 2s)     0.00160       0.95076

   21    H  4  s      Val( 1s)     0.78024       0.16995
   22    H  4  s      Ryd( 2s)     0.00078       0.94567

   23    H  5  s      Val( 1s)     0.78024       0.16995
   24    H  5  s      Ryd( 2s)     0.00078       0.94567

   25    H  6  s      Val( 1s)     0.63851       0.21887
   26    H  6  s      Ryd( 2s)     0.00118       0.99957

   27    H  7  s      Val( 1s)     0.63851       0.21887
   28    H  7  s      Ryd( 2s)     0.00118       0.99957
```

For each of the 28 NAO functions, this table lists the atom to which NAO is attached (in the numbering scheme of the ESS program), the angular momentum type "lang" (*s*, p_x, etc., in the coordinate system of the ESS program), the orbital type (whether core, valence, or Rydberg, and a conventional hydrogenic-type label), the orbital occupancy (number of electrons, or "natural population" of the orbital), and the orbital energy (in the favored units of the ESS program, in this case atomic units: 1 a.u. = 627.51 kcal/mol). [For example, NAO 4 (the highest energy C orbital of the NMB set) is the valence shell $2p_x$ orbital on carbon, occupied by 0.8858 electrons, whereas NAO 5 is a Rydberg $3p_x$ orbital with only 0.0013 electrons.] Note that the occupancies of the Rydberg (Ryd) NAOs are typically much lower than

those of the core (Cor) and valence (Val) NAOs of the natural minimum basis (NMB) set, reflecting the dominant role of the NMB orbitals in describing molecular properties.

The principal quantum numbers for the NAO labels (1*s*, 2*s*, 3*s*, etc.) are assigned on the basis of the energy order if a Fock matrix is available, or on the basis of occupancy otherwise. A message is printed warning of a "population inversion" if the occupancy and energy ordering do not coincide (of interest, but usually not of concern).

The next segment is an atomic summary showing the natural atomic charges (nuclear charge minus summed natural populations of NAOs on the atom) and total core, valence, and Rydberg populations on each atom:

```
Summary of Natural Population Analysis:

                                     Natural Population
           Natural    ---------------------------------------------
 Atom No    Charge        Core      Valence    Rydberg      Total
---------------------------------------------------------------------
   C  1   -0.44588      1.99978     4.44291    0.00319     6.44588
   N  2   -0.89847      1.99983     5.89482    0.00382     7.89847
   H  3    0.18579      0.00000     0.81261    0.00160     0.81421
   H  4    0.21898      0.00000     0.78024    0.00078     0.78102
   H  5    0.21898      0.00000     0.78024    0.00078     0.78102
   H  6    0.36030      0.00000     0.63851    0.00118     0.63970
   H  7    0.36030      0.00000     0.63851    0.00118     0.63970
=====================================================================
* Total *  0.00000      3.99961    13.98785    0.01254    18.00000
```

This table succinctly describes the molecular charge distribution in terms of NPA charges. [For example, the carbon atom of methylamine is assigned a net NPA charge of −0.446 at this level; note also the slightly less positive charge on H(3) than on the other two methyl hydrogens: +0.186 vs. +0.219.]

Next follows a summary of the NMB and NRB populations for the composite system, summed over atoms:

```
                                Natural Population
-------------------------------------------------------------
  Core                      3.99961 ( 99.9903% of    4)
  Valence                  13.98785 ( 99.9132% of   14)
  Natural Minimal Basis    17.98746 ( 99.9303% of   18)
  Natural Rydberg Basis     0.01254 (  0.0697% of   18)
-------------------------------------------------------------
```

This exhibits the high percentage contribution (typically, > 99%) of the NMB set to the molecular charge distribution. [In the present case, for example, the 13 Rydberg orbitals of the NRB set contribute only 0.07% of the electron density, whereas the 15 NMB functions account for 99.93% of the total.]

Finally, the natural populations are summarized as an effective valence electron configuration ("natural electron configuration") for each atom:

Atom	No	Natural Electron Configuration
C	1	[core]2s(1.10)2p(3.35)
N	2	[core]2s(1.43)2p(4.46)
H	3	1s(0.81)
H	4	1s(0.78)
H	5	1s(0.78)
H	6	1s(0.64)
H	7	1s(0.64)

Although the occupancies of the atomic orbitals are non-integer in the molecular environment, the effective atomic configurations can be related to idealized atomic states in "promoted" configurations. [For example, the carbon atom in the above table is most nearly described by an idealized $1s^2 2s^1 2p^3$ electron configuration.]

A.3.3 Natural Bond Orbital Analysis

The next segments of the output summarize the results of NBO analysis. The first segment reports on details of the search for an NBO natural Lewis structure:

```
 NATURAL BOND ORBITAL ANALYSIS:

                            Occupancies       Lewis Structure    Low   High
         Max    Occ      -------------------  -----------------   occ   occ
  Cycle  Ctr   Thresh     Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
 ================================================================================
    1     2     1.90    17.95205   0.04795      2   6   0   1     0      0
 --------------------------------------------------------------------------------

 Structure accepted: No low occupancy Lewis orbitals
```

Normally, there is but one cycle of the NBO search. The table summarizes a variety of information for each cycle: the occupancy threshold for a "good" pair in the NBO search; the total populations of Lewis and non-Lewis NBOs; the number of core (CR), 2-center bond (BD), 3-center bond (3C), and lone pair (LP) NBOs in the natural Lewis structure; and the number of low-occupancy Lewis (L) and "high-occupancy" (> 0.1e) non-Lewis (NL) orbitals. The Lewis structure is accepted if all orbitals of the formal Lewis structure exceed the occupancy threshold (default, 1.90 electrons).

Next follows a more detailed breakdown of the Lewis and non-Lewis occupancies into core, valence, and Rydberg shell contributions:

```
-------------------------------------------------------
   Core                    3.99961 ( 99.990% of   4)
   Valence Lewis          13.95244 ( 99.660% of  14)
  ==================      ============================
   Total Lewis            17.95205 ( 99.734% of  18)
  -------------------------------------------------------
   Valence non-Lewis       0.03903 (  0.217% of  18)
   Rydberg non-Lewis       0.00892 (  0.050% of  18)
  ==================      ============================
   Total non-Lewis         0.04795 (  0.266% of  18)
 -------------------------------------------------------
```

This shows the general quality of the natural Lewis structure description in terms of the percentage of the total electron density (e.g., in the above case, about 99.7%). The table also exhibits the relatively important role of the valence non-Lewis orbitals (i.e., the six valence antibonds, NBOs 23-28) relative to the extra-valence orbitals (the 13 Rydberg NBOs 10-22) in the slight departures from a localized Lewis structure model.

A.3 TUTORIAL EXAMPLE FOR METHYLAMINE

Next follows the main listing of NBOs, displaying the form and occupancy of the complete set of NBOs that span the input AO space:

```
    (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ----------------------------------------------------
  1. (1.99978) CR ( 1) C  1            s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000
  2. (1.99983) CR ( 1) N  2            s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000
  3. (1.97846) LP ( 1) N  2            s( 18.28%)p 4.47( 81.72%)
                                        0.0000  0.4275  0.0002 -0.2715  0.0032
                                       -0.8621  0.0161  0.0000  0.0000
  4. (1.99839) BD ( 1) C  1- N  2
             ( 40.06%)   0.6329* C  1 s( 21.60%)p 3.63( 78.40%)
                                        0.0000  0.4641  0.0237 -0.8836 -0.0298
                                       -0.0479 -0.0100  0.0000  0.0000
             ( 59.94%)   0.7742* N  2 s( 30.63%)p 2.26( 69.37%)
                                        0.0000  0.5535 -0.0010  0.8327  0.0001
                                        0.0120 -0.0103  0.0000  0.0000
  5. (1.99860) BD ( 1) C  1- H  3
             ( 59.80%)   0.7733* C  1 s( 25.91%)p 2.86( 74.09%)
                                        0.0000  0.5090 -0.0068  0.2218  0.0101
                                        0.8316 -0.0052  0.0000  0.0000
             ( 40.20%)   0.6340* H  3 s(100.00%)
                                        1.0000  0.0030
  6. (1.99407) BD ( 1) C  1- H  4
             ( 61.10%)   0.7817* C  1 s( 26.27%)p 2.81( 73.73%)
                                        0.0000  0.5126 -0.0038  0.2903  0.0020
                                       -0.3912  0.0017  0.7070 -0.0105
             ( 38.90%)   0.6237* H  4 s(100.00%)
                                        1.0000  0.0008
  7. (1.99407) BD ( 1) C  1- H  5
             ( 61.10%)   0.7817* C  1 s( 26.27%)p 2.81( 73.73%)
                                        0.0000  0.5126 -0.0038  0.2903  0.0020
                                       -0.3912  0.0017 -0.7070  0.0105
             ( 38.90%)   0.6237* H  5 s(100.00%)
                                        1.0000  0.0008
  8. (1.99442) BD ( 1) N  2- H  6
             ( 68.13%)   0.8254* N  2 s( 25.53%)p 2.92( 74.47%)
                                        0.0000  0.5053  0.0005 -0.3411 -0.0179
                                        0.3578 -0.0064 -0.7070 -0.0092
             ( 31.87%)   0.5645* H  6 s(100.00%)
                                        1.0000  0.0020
  9. (1.99442) BD ( 1) N  2- H  7
             ( 68.13%)   0.8254* N  2 s( 25.53%)p 2.92( 74.47%)
                                        0.0000  0.5053  0.0005 -0.3411 -0.0179
                                        0.3578 -0.0064  0.7070  0.0092
             ( 31.87%)   0.5645* H  7 s(100.00%)
                                        1.0000  0.0020
---------------- non-Lewis ----------------------------------------------------
 10. (0.00008) BD*( 1) C  1- N  2
             ( 59.94%)   0.7742* C  1 s( 21.60%)p 3.63( 78.40%)
             ( 40.06%)  -0.6329* N  2 s( 30.63%)p 2.26( 69.37%)
 11. (0.01531) BD*( 1) C  1- H  3
             ( 40.20%)   0.6340* C  1 s( 25.91%)p 2.86( 74.09%)
                                        0.0000 -0.5090  0.0068 -0.2218 -0.0101
                                       -0.8316  0.0052  0.0000  0.0000
             ( 59.80%)  -0.7733* H  3 s(100.00%)
                                       -1.0000 -0.0030
 12. (0.00757) BD*( 1) C  1- H  4
             ( 38.90%)   0.6237* C  1 s( 26.27%)p 2.81( 73.73%)
                                        0.0000 -0.5126  0.0038 -0.2903 -0.0020
                                        0.3912 -0.0017 -0.7070  0.0105
             ( 61.10%)  -0.7817* H  4 s(100.00%)
                                       -1.0000 -0.0008
```

```
13. (0.00757) BD*( 1) C  1- H  5
              ( 38.90%)   0.6237* C  1 s( 26.27%)p 2.81( 73.73%)
                                        0.0000 -0.5126  0.0038 -0.2903 -0.0020
                                        0.3912 -0.0017  0.7070 -0.0105
              ( 61.10%)  -0.7817* H  5 s(100.00%)
                                       -1.0000 -0.0008
14. (0.00424) BD*( 1) N  2- H  6
              ( 31.87%)   0.5645* N  2 s( 25.53%)p 2.92( 74.47%)
                                        0.0000 -0.5053 -0.0005  0.3411  0.0179
                                       -0.3578  0.0064  0.7070  0.0092
              ( 68.13%)  -0.8254* H  6 s(100.00%)
                                       -1.0000 -0.0020
15. (0.00424) BD*( 1) N  2- H  7
              ( 31.87%)   0.5645* N  2 s( 25.53%)p 2.92( 74.47%)
                                        0.0000 -0.5053 -0.0005  0.3411  0.0179
                                       -0.3578  0.0064 -0.7070 -0.0092
              ( 68.13%)  -0.8254* H  7 s(100.00%)
                                       -1.0000 -0.0020
16. (0.00093) RY ( 1) C  1             s(  0.36%)p99.99( 99.64%)
                                        0.0000 -0.0088  0.0593  0.0283 -0.6937
                                        0.0022 -0.7172  0.0000  0.0000
17. (0.00032) RY ( 2) C  1             s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0149  0.9999
18. (0.00020) RY ( 3) C  1             s( 88.71%)p 0.13( 11.29%)
                                        0.0000 -0.0033  0.9418  0.0268 -0.1978
                                        0.0067  0.2703  0.0000  0.0000
19. (0.00001) RY ( 4) C  1             s( 10.88%)p 8.19( 89.12%)
20. (0.00113) RY ( 1) N  2             s(  1.04%)p95.47( 98.96%)
                                        0.0000 -0.0064  0.1016 -0.0076 -0.0643
                                       -0.0195 -0.9925  0.0000  0.0000
21. (0.00042) RY ( 2) N  2             s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000 -0.0130  0.9999
22. (0.00035) RY ( 3) N  2             s( 53.89%)p 0.86( 46.11%)
                                        0.0000  0.0114  0.7340 -0.0065  0.6782
                                        0.0110  0.0310  0.0000  0.0000
23. (0.00001) RY ( 4) N  2             s( 45.11%)p 1.22( 54.89%)
24. (0.00161) RY ( 1) H  3             s(100.00%)
                                       -0.0030  1.0000
25. (0.00078) RY ( 1) H  4             s(100.00%)
                                       -0.0008  1.0000
26. (0.00078) RY ( 1) H  5             s(100.00%)
                                       -0.0008  1.0000
27. (0.00119) RY ( 1) H  6             s(100.00%)
                                       -0.0020  1.0000
28. (0.00119) RY ( 1) H  7             s(100.00%)
                                       -0.0020  1.0000
```

For each NBO (1-28), the first line of printout shows the occupancy (between 0 and 2.0000 electrons) and unique label of the NBO. This label gives the type ("CR" for 1-center core pair, "LP" for 1-center valence lone pair, "BD" for 2-center bond, "BD*" for 2-center antibond, and "RY" for 1-center Rydberg, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively), a serial number (1, 2,... if there is a single, double,... bond between the pair of atoms), and the atom(s) to which the NBO is affixed. [For example, the first 2-center NBO in the sample output, NBO 4, is the bond (with 1.9984 electrons) between carbon (atom 1) and nitrogen (atom 2), the σ_{CN} bond.] The next lines summarize the natural atomic hybrids h_A of which the NBO is composed, giving the percentage ($100|c_A|^2$) of the NBO on each hybrid

(in parentheses), the polarization coefficient c_A, the atom label, and a hybrid label showing the sp^λ composition (percentage *s*-character, *p*-character, etc.) of each h_A. [For example, the σ_{CN} NBO is formed from an $sp^{3.63}$ hybrid (78.4% *p*-character) on carbon interacting with an $sp^{2.26}$ hybrid (69.4% *p*-character) on nitrogen,

$$\sigma_{CN} = 0.633(sp^{3.63})_C + 0.774(sp^{2.26})_N$$

corresponding roughly to the qualitative concept of interacting sp^3 hybrids (75% *p*-character) and the higher electronegativity (larger polarization coefficient) of N.] Below each NHO label is the set of coefficients that specify how the NHO is written explicitly as a linear combination of NAOs on the atom. The order of NAO coefficients follows the numbering of the NAO tables. [For example, in the first NBO entry, the carbon hybrid h_C of the σ_{CN} bond has largest coefficients for the 2nd and 4th NAOs, corresponding to the approximate description

$$h_C \cong 0.464(2s)_C - 0.884(2p_x)_C$$

in terms of the valence NAOs of the carbon atom.] In the CH_3NH_2 example, the NBO search finds the C-N bond (NBO 4), three C-H bonds (NBOs 5, 6, 7), two N-H bonds (NBOs 8, 9), N lone pair (NBO 3), and C and N core pairs (NBOs 1, 2) of the expected Lewis structure. NBOs 10-28 represent the residual non-Lewis NBOs of low occupancy, led by the valence antibonds (BD*, NBOs 10-15) that are usually of principal chemical interest. In this example, it is interesting to note the slight asymmetry of the three σ_{CH} NBOs, and the slightly higher occupancy (0.0153 *vs.* 0.0076 electrons) in the σ^*_{C1H3} antibond (NBO 11) lying *anti* to the nitrogen lone pair.

[Note that the ordering of NBOs differs slightly from that in earlier NBO program versions, with "Lewis" (L-type; highly occupied) and "non-Lewis" NBOs (NL-type; unoccupied in the formal NLS) more clearly identified in program output. The present ordering always places L before NL, with 1-center (1c; CR, LP) preceding 2-center bonds (2c; BD) and 3-center NBOs in the L-type listing, and with 2c valence antibonds (BD*) or 3-center (3C*) NBOs preceding residual 1c extra-valent Rydberg (RY) NBOs in the NL-type listing. The current ordering of NBOs therefore conforms more closely to the usual priorities of chemical interest, with valence lone pairs (LP) near the top of L-type listing and valence antibonds (BD*) topping the NL-type listing order, followed by the long list of residual RY-type NBOs (required for completeness of the orthonormal NBO set) that are normally of negligible chemical interest.]

A.3.4 NHO Directional Analysis

The next segment of output summarizes the angular properties of the natural hybrid orbitals:

```
 NHO DIRECTIONALITY AND BOND BENDING (deviation from line of nuclear centers at
                                      the position of maximum hybrid amplitude)

         [Thresholds for printing:  angular deviation  >  1.0 degree]
                                    p- or d-character  > 25.0%
                                    orbital occupancy  >  0.10e

                        Line of Centers        Hybrid 1             Hybrid 2
                        ---------------  -------------------  ------------------
           NBO            Theta    Phi    Theta    Phi    Dev   Theta    Phi    Dev
 ================================================================================
   3. LP ( 1) N  2          --      --     90.0  253.1   --      --      --    --
   4. BD ( 1) C  1- N  2   90.0   183.2     --     --    --     90.0    1.1   2.1
   8. BD ( 1) N  2- H  6  145.0   127.8   145.0  133.4   3.2     --      --    --
   9. BD ( 1) N  2- H  7   35.0   127.8    35.0  133.4   3.2     --      --    --
```

The "direction" of an sp^{λ} hybrid is specified in terms of the polar (θ) and azimuthal (φ) angles (in the ESS coordinate system) of the vector describing its *p*-component. For more general $sp^{\lambda}d^{\mu}$ hybrids the hybrid direction is determined numerically to correspond to maximum angular amplitude. The program compares the hybrid direction with the direction of the line of centers between the two nuclei to determine the bending of the bond, expressed as the deviation angle ("Dev," in degrees) between these two directions. For example, in the CH_3NH_2 case shown above, the nitrogen hybrid of the σ_{CN} bond (NBO 4) is bent away from the line of C-N centers by 2.1°, whereas the carbon NHO is approximately aligned with the C-N axis (within the 1.0° threshold for printing). The N hybrids of the N-H bonds (NBOs 8, 9) are bent even further (3.2°). The information in this table is often useful in anticipating the direction of geometry changes resulting from geometry optimization (i.e., the likely reduction in pyramidalization of the $-NH_2$ group in order to relieve the ~4° nitrogen bond bendings found in the idealized tetrahedral Pople-Gordon geometry).

A.3.5 Perturbation Theory Energy Analysis

The next segment summarizes the second-order perturbative estimates of donor-acceptor (bond-antibond) interactions in the NBO basis:

```
 SECOND ORDER PERTURBATION THEORY ANALYSIS OF FOCK MATRIX IN NBO BASIS

     Threshold for printing:   0.50 kcal/mol
                                                                 E(2) E(NL)-E(L) F(L,NL)
      Donor (L) NBO              Acceptor (NL) NBO              kcal/mol   a.u.    a.u.
 ================================================================================

 within unit  1
    1. CR ( 1) C  1           18. RY ( 3) C  1                   0.52   13.01   0.073
    2. CR ( 1) N  2           22. RY ( 3) N  2                   0.68   17.75   0.098
    3. LP ( 1) N  2           11. BD*( 1) C  1- H  3             7.98    1.11   0.084
    3. LP ( 1) N  2           12. BD*( 1) C  1- H  4             1.51    1.12   0.037
    3. LP ( 1) N  2           13. BD*( 1) C  1- H  5             1.51    1.12   0.037
    4. BD ( 1) C  1- N  2     27. RY ( 1) H  6                   0.51    1.80   0.027
    4. BD ( 1) C  1- N  2     28. RY ( 1) H  7                   0.51    1.80   0.027
    5. BD ( 1) C  1- H  3     20. RY ( 1) N  2                   0.84    2.14   0.038
    6. BD ( 1) C  1- H  4     14. BD*( 1) N  2- H  6             2.77    1.34   0.054
    7. BD ( 1) C  1- H  5     15. BD*( 1) N  2- H  7             2.77    1.34   0.054
    8. BD ( 1) N  2- H  6     12. BD*( 1) C  1- H  4             2.87    1.46   0.058
    9. BD ( 1) N  2- H  7     13. BD*( 1) C  1- H  5             2.87    1.46   0.058
```

This is carried out by examining all possible interactions between "filled" (donor, L) Lewis-type NBOs and "unfilled" (acceptor, NL) non-Lewis-type NBOs, and estimating their energetic importance by 2nd-order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, to departures from the idealized Lewis structure description), they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j), the donor-acceptor stabilization energy $E(2)$ associated with $i \rightarrow j$ delocalization is estimated as

$$E(2) = \Delta E_{ij}^{(2)} = q_i \, F(i,j)^2/(\varepsilon_j - \varepsilon_i)$$

where q_i is the donor orbital occupancy (2 for closed-shell, 1 for open-shell), ε_i, ε_j are diagonal elements (orbital energies), and $F(i,j)$ is the off-diagonal NBO Fock matrix element. [In the example above, the $n_N \rightarrow \sigma^*_{CH}$ interaction between the nitrogen lone pair (NBO 3) and the antiperiplanar C_1-H_3 antibond (NBO 11) is seen to give the strongest stabilization, 7.98 kcal/mol.] As the heading indicates, entries are included in this table only when the interaction energy exceeds a default threshold of 0.5 kcal/mol.

A.3.6 NBO Summary

Next appears a condensed summary of the principal NBOs, showing the occupancy, orbital energy, and the qualitative pattern of delocalization interactions associated with each:

```
 NATURAL BOND ORBITALS (Summary):

                                                          Principal Delocalizations
           NBO                  Occupancy    Energy   (geminal,vicinal,remote)
 ================================================================================
 Molecular unit  1  (CH5N)
 ------ Lewis -----------------------------------
    1. CR ( 1) C  1             1.99978   -11.18023  18(g)
    2. CR ( 1) N  2             1.99983   -15.43232  22(g)
    3. LP ( 1) N  2             1.97846    -0.42142  11(v),12(v),13(v)
    4. BD ( 1) C  1- N  2       1.99839    -0.80615  27(v),28(v)
    5. BD ( 1) C  1- H  3       1.99860    -0.65863  20(v)
    6. BD ( 1) C  1- H  4       1.99407    -0.65508  14(v)
    7. BD ( 1) C  1- H  5       1.99407    -0.65508  15(v)
    8. BD ( 1) N  2- H  6       1.99442    -0.76592  12(v)
    9. BD ( 1) N  2- H  7       1.99442    -0.76592  13(v)
 ------ non-Lewis -------------------------------
   10. BD*( 1) C  1- N  2       0.00008     0.57048
   11. BD*( 1) C  1- H  3       0.01531     0.68769
   12. BD*( 1) C  1- H  4       0.00757     0.69687
   13. BD*( 1) C  1- H  5       0.00757     0.69687
   14. BD*( 1) N  2- H  6       0.00424     0.68107
   15. BD*( 1) N  2- H  7       0.00424     0.68107
   16. RY ( 1) C  1             0.00093     0.97549
   17. RY ( 2) C  1             0.00032     1.02058
   18. RY ( 3) C  1             0.00020     1.83014
   19. RY ( 4) C  1             0.00001     1.10413
   20. RY ( 1) N  2             0.00113     1.48473
   21. RY ( 2) N  2             0.00042     1.59198
   22. RY ( 3) N  2             0.00035     2.31944
   23. RY ( 4) N  2             0.00001     2.00963
   24. RY ( 1) H  3             0.00161     0.94870
   25. RY ( 1) H  4             0.00078     0.94508
   26. RY ( 1) H  5             0.00078     0.94508
   27. RY ( 1) H  6             0.00119     0.99805
   28. RY ( 1) H  7             0.00119     0.99805
          -------------------------------
                Total Lewis   17.95205  ( 99.7336%)
          Valence non-Lewis    0.03903  (  0.2168%)
          Rydberg non-Lewis    0.00892  (  0.0495%)
          -------------------------------
               Total unit  1   18.00000  (100.0000%)
              Charge unit  1    0.00000
```

This table allows one to quickly identify the principal delocalizing acceptor orbitals associated with each donor NBO, and their topological relationship to this NBO, i.e., whether attached to the same atom (geminal, “g”), to an adjacent bonded atom (vicinal, “v”), or to a more remote (“r”) site. These acceptor NBOs will generally correspond to the principal “delocalization tails” of the NLMO associated with the parent donor NBO. [For example, in the table above, the N lone pair (NBO 3) is seen to be the lowest-occupancy (1.9784

electrons) and highest-energy (−0.4214 a.u.) Lewis NBO, and to be primarily delocalized into antibonds 11, 12, 13 (the vicinal σ^*_{CH} NBOs). The summary at the bottom of the table shows that the Lewis NBOs 1-9 describe about 99.7% of the total electron density, with the remaining non-Lewis density found primarily in the valence-shell antibonds (0.0390 electrons, mostly in NBO 11).]

The printed summary of NBOs is followed by a corresponding $CHOOSE keylist specification (Sec. B.4) for the corresponding NLS:

```
$CHOOSE
    LONE 2 1 END
    BOND S 1 2 S 1 3 S 1 4 S 1 5 S 2 6 S 2 7 END
$END
```

This can be used as input for a $CHOOSE job or (in slightly modified form) as a resonance structure specification in $NRTSTR keylist input (Sec. B.8).

NBO output concludes by reporting the calculation time and the maximum amount of scratch memory used during the calculation.

Section B: NBO USER'S GUIDE

B.1 INTRODUCTION TO THE NBO USER'S GUIDE AND NBO KEYLISTS

Section B constitutes the general user's guide to the NBO program. It assumes that the user has an installed electronic structure system (ESS) with attached NBO program, a general idea of what the NBO method is about, and some acquaintance with standard NBO terminology and output data. If you are completely inexperienced in these areas, read Section A ("Getting Started") for the necessary background to this Section. The NBO User's Guide describes core NBO options (Sec. B.1-B.6), the GenNBO program (Sec. B.7), and the NBO-based supplementary modules (Sec. B.8 *et seq.*).

The NBO User's Guide describes how to use the NBO program by modifying your input file to the ESS program to get some NBO output. The modification consists of adding a list of *keywords* in a prescribed *keylist* format. Four main keylist ($KEY) types are recognized ($NBO, $CORE, $CHOOSE, and $DEL), and these will be described in turn in Sections B.2-B.5. Other keylists are specific to GenNBO or NBO-based supplementary modules, described in subsequent sections. Some of the details of inserting NBO keylists into the input file depend on the details of your ESS method, and are described in the appropriate Appendix for the ESS. However, the general form of NBO keylists and the meaning and function of each keyword are identical for all versions (insofar as the option is meaningful for the ESS), and are described herein.

The four keylist types have common rules of syntax: Keylist delimiters are identified by a "$" prefix. Each keylist begins with the parent keylist name (e.g., "$NBO"), followed by any number of keywords, and ended with the word "$END"; for example,

```
$NBO   keyword-1   keyword-2   . . .   $END      !comment
```

The keylist is "free format," with keywords separated by commas or any number of spaces. An NBO option is activated by simply including its keyword in the appropriate keylist. The order of keywords in the principal $NBO keylist does not matter, but multiple keylists must be given in the order (1) $NBO, (2) $CORE, (3) $CHOOSE, (4) $DEL of presentation in Sections B.2-B.5. Keywords may be typed in upper or lower case, and will be echoed near the top of the NBO output. A $KEY list can be continued to any number of lines, but all the entries of a $KEY list must appear in a distinct set of lines, starting with the $KEY name on the first line and ending with the closing $END on the last

line (i.e., no two $KEY lists should share parts of the same line). As the above example indicates, any line in the keylist input may terminate with an exclamation point (!) followed by `comment' of your choice; the "!" is considered to terminate the line, and the trailing `comment' is ignored by the program.

Recognized $NBO keylist entries are echoed near the top of NBO output, and unrecognized entries are flagged above the NBO banner.

B.2 THE $NBO KEYLIST

B.2.1 Overview of $NBO keywords

The $NBO keylist is the principal means of specifying NBO job options and controlling output, and must precede any other keylist ($CORE, $CHOOSE, or $DEL) in your input file. Basic keywords that can appear in a $NBO keylist are grouped as follows (other "semi-documented" keywords are described in Sec. B.2.7, and keywords of NBO supplemental programs are described in Sec. B.8 *et seq.*):

Job Control Keywords:

NPA	NBOSUM	NOBOND	SKIPBO	MEMORY
NBO	MSPNBO	3CBOND	NLMO	MOLUNIT

Job Threshold Keywords:

BEND	E2PERT	DIPOLE

Matrix Output Keywords:

AONAO	AONHO	AONBO	AONLMO	AOMO
AOPAO	AOPNAO	AOPNHO	AOPNBO	AOPNLMO
NAONHO	NAONBO	NAONLMO	NAOMO	NHONBO
NHONLMO	NHOMO	NBONLMO	NBOMO	NLMOMO
DIAO	DINAO	DINHO	DINBO	DINLMO
DIMO	DMAO	DMNAO	DMNHO	DMNBO
DMNLMO	DMMO	DMPNAO	FAO	FNAO
FPNHO	FNHO	FPNBO	FNBO	FNLMO
FMO	KAO	KNAO	KNHO	KNBO
KNLMO	KMO	VAO	VNAO	VNHO
VNBO	VNLMO	VMO	SAO	SPAO
SPNAO	SPNHO	SPNBO	SPNLMO	

Other Output Control Keywords:

FILE	DETAIL	BNDIDX	AOINFO
PLOT	ARCHIVE	NBODAF	DIST

Print Level Control:

PRINT=n

B.2 THE $NBO KEYLIST

Keywords are first listed and described according to these formal groupings in Sections B.2.2-B.2.6. Section B.6 illustrates the effect of commonly used $NBO keywords (as well as other $KEY lists) on the successive stages of NAO/NBO/NLMO transformation and subsequent energy or dipole analysis, with sample output for these keyword options.

Some keywords of the $NBO keylist require (or allow) numerical values or other parameters to specify their exact function. In this case, the numerical value or parameter must immediately follow the keyword after an equal sign (=) or any number of blank spaces. Examples:

```
E2PERT=2.5   NBOMO W25
```

(The equal sign is recommended, and will be used in the remaining examples.)

B.2.2 Job Control Keywords

The keywords in this group activate or deactivate basic tasks to be performed by the NBO program, or change the way the NBO search is conducted. Each keyword is described in terms of the option it activates (together with an indication of where the option is useful):

KEYWORD	*OPTION DESCRIPTION*
NPA	Request Natural Population Analysis and printing of NPA summary tables (Section A.3.2). This keyword activates calculation of NAOs, except for semi-empirical ESS methods. Use `NPA=ONLY` when seeking NPA output only.
NBO	Request calculation of NBOs and printing of the main NBO table (Section A.3.3). Use `NBO=NOHYBS` to suppress the printing of the LCNAO-NHO coefficients in the main table.
NBOSUM	Request printing of the NBO summary table (Section A.3.6). This combines elements of the NBO table and 2nd-order perturbation theory analysis table (see below) in a convenient form for recognizing the principal delocalization patterns.
MSPNBO	Request "maximum spin-paired" NBOs from the spin-averaged density matrix (rather than the separate density matrices for α and β spin), as suggested by Michl and coworkers [*J. Am. Chem. Soc.* **114**, 10631 (1992)]. This has no effect for closed-shell systems, but gives an alternative (somewhat less accurate) description of open-shell systems. MSPNBO is useful when the ESS provides no spin information (e.g., as with the GUGA approach).
NOBOND	Request that no bonds (2-center NBOs) are to be formed in the NBO procedure (Section B.6.7). The resulting NBOs will then simply be 1-center atomic hybrids. (Useful for highly ionic species.)
NLMO	Compute and print out the summary table of Natural Localized Molecular Orbitals (Section B.6.2). NLMOs are similar to Boys or Edmiston-Ruedenberg LMOs, but more efficiently calculated. (Useful for `semi-localized' description of an SCF or correlated wavefunction, and activated automatically by NLMO-related keywords such as DIPOLE, STERIC, NCS, NJC.)
MOLUNIT	Specify NBO molecular units by atomic centers. For example, an alternative NBO analysis of methylamine (Section A.3) based on non-bonded methyl and amino groups (i.e. missing CN bond) can be obtained

	using one of the following four examples
	
	`MOLUNIT <1,3,4,5> <2,6,7>`
	`MOLUNIT <1,3-5> <2,6-7>`
	`MOLUNIT <1,3,4,5>`
	`MOLUNIT <2,6,7>`
	
	where atoms 1,3,4,5 are those of the methyl group and 2,6,7 are of the amino group. Atoms not listed in the bracket lists, as in the third and fourth examples, automatically form an additional molecular unit. The four examples are therefore equivalent for a seven-atom system, and yield identical NBO results.
	
	Note that MOLUNIT does not force the NBO search algorithm to bond all atoms of a single bracket list into a molecular unit; the keyword simply ensures that the search will not identify multi-center NBOs involving atoms of one bracket list with those of another.
	
	MOLUNIT gives the user limited control of the bonding pattern for molecular systems without having to fully specify the Lewis structure using the $CHOOSE keylist (Section B.4). MOLUNIT input is ignored when $CHOOSE keylist input is provided.

MEMORY	Allocate dynamic memory in words, megawords (mw), megabytes (mb), or gigabytes (gb). Each of the following allocates one gigabyte:
	
	`MEMORY=134217728`
	`MEMORY=134mw (approximately 1gb)`
	`MEMORY=1024mb`
	`MEMORY=1gb`
	
	By default, NBO allocates 100 megawords of memory. Dynamic memory allocation is only enabled for the 64-bit (i8) integer NBO executables, it is disabled for 32-bit (i4) executables.

NPA=ONLY has higher precedence than other keywords in this list (except for MEMORY), so that keywords with which it is implicitly in conflict (e.g., NBO, NLMO) will be ignored if NPA=ONLY is included in the $NBO keylist.

B.2.3 Job Threshold Keywords

The keywords in this group activate tasks to be performed by the NBO program, but these keywords may be modified by one or more parameters that control the precise action to be taken. (In each case the keywords may also be used without parameters, accepting the default values [in brackets].)

KEYWORD	*parameter(s)*	*OPTION DESCRIPTION*
BEND	ang, pct, occ	Request the NHO Directional Analysis table (Section A.3.4). The three parameters [and default values] have the following significance: ang [1.0] = threshold angular deviation for printing pct [25] = threshold percentage *p/d*-character for printing occ [0.1] = threshold NBO occupancy for printing Parameter may be separated by a space or a comma, e.g.: `BEND=2,10,1.9` This example specifies that the bond-bending table should only include entries for angular deviations of at least 2° (ang) in hybrids of at least 10% *p*/*d*-character (pct) for NBOs of occupancy at least 1.9 electrons (occ). The Directional Analysis table is printed by default in the NBO output. To suppress the printing of this table use `BEND=SKIP`.
E2PERT	eval	Request the Perturbation Theory Energy Analysis table (Section A.3.5), where eval [0.5] = threshold energy (in kcal/mol) for printing Entries will be printed for NBO donor-acceptor interaction energies that exceed the ‘eval’ threshold; for example: `E2PERT=5.0` This example would print only interactions of at least 5 kcal/mol (i.e., only the single interaction of ~8 kcal/mol in the output of Section A.3.5).

DIPOLE	dval	Request the Molecular Dipole Moment Analysis table (Section B.6.3), where dval [0.02] = threshold dipole moment (Debye) for printing The program will carry out a decomposition of the total molecular dipole moment in terms of localized NLMO and NBO contributions, including all terms whose contribution (in vector norm) exceeds the 'dval' threshold, e.g., `DIPOLE=0.1` This example prints out dipole contributions of all NBOs (and their delocalization interactions) of magnitude ≥ 0.1 D.

Both the BEND and E2PERT keywords are activated by default at the standard PRINT level option (see Section B.2.6). Note that the DIPOLE keyword leads to an analysis in terms of both NBOs and NLMOs, so that the NLMO keyword (Section B.2.2) is automatically activated in this case.

B.2.4 Matrix Output Keywords

The keywords in this group activate the printing of various matrices to the output file, or their writing to (or reading from) external disk files. The large number of keywords in this group provide great flexibility in printing out the details of the successive transformations,

input AOs → (PNAOs) → NAOs → NHOs → NBOs → NLMOs → NOs → MOs

or the matrices of various operators in the natural localized basis sets. This ordered sequence of transformations forms the basis for naming the keywords.

Keyword Names

The keyword for printing the matrix for a particular basis transformation, IN → OUT, is constructed by concatenating the acronymns for the two sets (in generic form "INOUT"). For example, the transformation AO → NBO is keyed as "AONBO", while that from NBOs to NLMOs is correspondingly "NBONLMO". The transformations are always specified in the ordered sequence shown above (i.e., "AONBO" is allowed, but "NBOAO" is an unrecognized 'backward' keyword). Keywords are recognized for *all possible* transformations from the input AOs to other sets (NAO, NHO, NBO, NLMO, NO, MO, or "pure" PAO, or the pre-orthogonal PNAO, PNHO, PNBO, PNLMO sets) in the overall sequence leading to canonical MOs, i.e.,

AO basis: AONAO AONHO AONBO AONLMO AONO AOMO
AOPNAO AOPNHO AOPNBO AOPNLMO AOPAO

and from each of the orthonormal natural localized sets to sets lying to the right in the sequence, i.e.,

NAO basis: NAONHO NAONBO NAONLMO NAONO NAOMO
NHO basis: NHONBO NHONLMO NHONO NHOMO
NBO basis: NBONLMO NBONO NBOMO
NLMO basis: NLMONO NLMOMO
NO basis: NOMO

The matrix $T_{IN,OUT}$ for a specified IN → OUT transform has rows labelled by the IN set and columns labelled by the OUT set.

One can also print out the matrix representations of the Fock or Kohn-Sham matrix (F), kinetic energy matrix (K), 1-e potential energy matrix (V), density

matrix (DM), or dipole moment matrix (DI) in the AO or MO set or any of the natural localized sets (NAO, NHO, NBO, NLMO, or NO). The corresponding keyword is constructed by concatenating the abbreviation for the operator (M) with that for the set (SET) (in generic form "MSET"). For example, to print the Fock matrix (F) in the NBO set, use the keyword "FNBO," and to print the dipole matrix in the NLMO basis, use "DINLMO." (For the dipole matrix keywords, all three vector components will be printed.) One can also print out elements of the overlap matrix (S) in the input AO or PAO bases or any of the 'pre-orthogonal' sets (PNAO, PNHO, PNBO, or PNLMO), using, e.g., "SPNAO" for the overlap matrix in the PNAO basis. The Fock operator is also provided in PNHO and PNBO sets (FPNHO, FPNBO) and the density matrix in the PNAO basis (DMPNAO). The list of allowed keywords for operator matrices is:

energy matrices	FAO	FNAO	FNHO	FNBO	FNLMO	FNO	FMO
			FPNHO	FPNBO			
	KAO	KNAO	KNHO	KNBO	KNLMO	KNO	KMO
	VAO	VNAO	VNHO	VNBO	VNLMO	VNO	VMO
density matrix	DMAO	DMNAO	DMNHO	DMNBO	DMNLMO	DMNO	DMMO
		DMPNAO					
dipole matrix	DIAO	DINAO	DINHO	DINBO	DINLMO	DINO	DIMO
overlap matrix	SAO	SPNAO	SPNHO	SPNBO	SPNLMO	SPAO	

Other desired transformations can be readily obtained from the keyword transformations by matrix multiplication.

Keyword Parameters

Each generic matrix keyword ("MATKEY") can include a parameter that specifies the output operation to be performed on the matrix. The allowed MATKEY parameters are of two types (three for AONAO, NAONBO; see below):

MATKEY=P[c] (print out the matrix in the standard output file, 'c' columns)

MATKEY=W[n] (write out the matrix to disk file *n*)

The first (P[c]) parameter is used to control output to the standard output file. When the MATKEY keyword is inserted in the $NBO keylist with no

parameters, the matrix is by default printed (in its entirety) in the standard output file. Thus, "MATKEY=P" would be equivalent to "MATKEY", with no parameters. The complete 'P[c]' form of the print parameter serves to truncate the printed matrix output to a specified number of columns [c]. For example, to print out only the first 16 columns of the NBO→MO transformation matrix, use the form

```
NBOMO=P16          (print 16 columns)
```

For certain transformation matrices, one can also restrict printing to only the valence (VAL) or Lewis (LEW) columns with modified '[c]' specifiers. For the transformations to NOs or MOs, use the form

```
MATKEY=PVAL        (print core + valence NO or MO columns only)
```

where "MATKEY" is AONO, NAONO, NHONO, NBONO, NLMONO, AOMO, NAOMO, NHOMO, NBOMO, NLMOMO, or NOMO (only). This will print out only the occupied and lowest few unoccupied orbitals, e.g., the six lowest virtual orbitals of the methylamine example (Section A.3), although not necessarily those with predominant valence character. Similarly, for the transformations to NBOs, NLMOs, NOs, or MOs, use the form

```
MATKEY=PLEW        (print Lewis NBO, NLMO, NO, or MO columns only)
```

where "MATKEY" is AONBO, NAONBO, NHONBO, AONLMO, NAONLMO, NHONLMO, NBONLMO, NAONO, NHONO, NBONO, NLMONO, NAOMO, NHOMO, NBOMO, NLMOMO, or NOMO. This prints out the Lewis (occupied) orbitals only, e.g., only the nine occupied NBOs or MOs of the methylamine example. Judicious use of these print parameters keeps printed output within reasonable bounds in calculations with large basis sets.

The second type of MATKEY parameter (W[n]) is used to write the matrix (in its entirety) to a specified disk file [n]. Each keyword transformation matrix is associated with a logical file number (LFN), as tabulated below:

matrix	*default* LFN	matrix	*default* LFN	matrix	*default* LFN
PAOPNAO	29	AONHO	35	AOMO	40
NAONBO	30	AOPNBO	36	AONO	41
AOPNAO	32	AONBO	37	DMAO	42
AONAO	33	AOPNLMO	38		
AOPNHO	34	AONLMO	39		

All other matrices are written to LFN 49. When the "MATKEY=W[n]" keyword is inserted in the $NBO keylist with no 'n' specifier, the matrix is by default written out (in its entirety) to this LFN. Thus, "AOPNAO=W" is equivalent to "AOPNAO=W32" for the first entry of the table. Use the "Wn" parameter to direct output to any non-default LFN disk file. For example, the keyword

```
AONBO=W51
```

would write out the AO→NBO transformation to LFN 51 (rather than default LFN 37).

The format of the printed output under the print 'P' parameter differs from that written to an external file under the 'W' parameter. The 'P' output (intended for a human reader) includes an identifying label for each row, and gives the numerical entries to somewhat lesser precision (F8.4 format) than the corresponding 'W' output (F15.9 format), which is usually intended as input to another program. Use the "MATKEY=W6" keyword to route the more precise 'W' form of the matrix to the standard output file, LFN 6.

For the operator matrices (only), one can also request printing of specific *i*,*j* matrix elements, rather than the entire table, by means of a *bracket list*. This is a list of the form $<i_1\ j_1/i_2\ j_2/.../i_n\ j_n>$ that follows the main keyword (separated by at least one space). For example, the command

```
FNBO <6 6/7 13/8 14>
```

would print out only the matrix elements $F_{6,6}$, $F_{7,13}$ and $F_{8,14}$ of the NBO Fock matrix.

For the PAOPNAO and NAONBO matrices (only), one can also include a read parameter (R), e.g.,

```
NAONBO=R[n]
```

which causes the matrix to be input to the program from a file (perhaps written with the "PAOPNAO=W" or "NAONBO=W" keyword on a previous run). This parameter has the effect of 'freezing' orbitals to a set prescribed in the input file (thus bypassing the NBO optimization of these orbitals for the molecular system). For example, the keyword "NAONBO=R30" would have the effect of freezing the NAO → NBO transformation coefficients to the form specified in LFN 30 (perhaps written with the "NAONBO=W30" keyword in a previous calculation on isolated molecules, and now to be used in a calculation

on a molecular complex). Similarly, the keywords "PAOPNAO=R FILE=c2h4" could be used to force the analysis of an excited state to be carried out in terms of the NAOs of the ground state stored in file "c2h4.29" (previously written out with the "PAOPNAO=W" keyword).

A third output option is the *checkpoint* (C) option (of generic form "MATKEY=C"), which allows orbital transformation info to be returned the ESS (Section B.12).

B.2.5 Other Output Control Keywords

The keywords in this group also help to control the I/O produced by a specified set of job options, and thus supplement the keywords of the previous section.

KEYWORD	*OPTION DESCRIPTION*
FILE=*name*	Specify a job*name* stem for NBO file I/O to distinguish NBO output (e.g. PLOT files, FILE47, etc.) for different jobs. *name* can include the directory path. For example, FILE=./ch3nh2 could be used with the PLOT keyword for methylamine, yielding files ch3nh2.31, ch3nh2.32, etc., all in the current directory. Adding an asterisk '*' at the end of *name* forces NBO to attach an integer value to *name* to distinguish the resulting files from others that may already exist in the current directory. For example, "FILE=ch3nh2-* ARCHIVE" will write the file ch3nh2-1.47 (FILE47) to the current directory. If the calculation is run again, and ch3nh2-1.47 has not been deleted or moved elsewhere, the second calculation will write the file ch3nh2-2.47. The string '*name*' can be optionally specified in single quotes, thereby preventing certain ESS host programs (e.g. Molpro) from converting the string to all uppercase.
BNDIDX	Request print-out of the NAO-Wiberg Bond Index array and related valency indices (Section B.6.5).
AOINFO	Request writing the AO basis set (exponents, contraction coefficients, etc.) to an external file, LFN 31. This provides minimal information needed by orbital plotting programs (cf. "PLOT" keyword) .
PLOT	Request writing of plot files required by orbital plotting programs, such as *NBOView*. This activates the AOINFO keyword as well as other matrix output keywords (AONBO=W, etc.).
ARCHIVE=*n*	Request writing the FILE47 archive file (Section B.7) to external file LFN *n*, or, if *n* is not present, to the default LFN 47. This file serves as input to run the GenNBO program in stand-alone mode, to repeat the NBO analysis without repeating the calculation of the wavefunction. If ARCHIVE=ONLY, NBO will only write the archive file, then terminate. 'ONLY' and 'n' may be used simultaneously. For example, ARCHIVE=51,ONLY will write the archive file to LFN 51 (only).
DIST	Print an atomic distance table. This keyword is turned on automatically when BNDIDX or NRT are requested under GenNBO.

B.2.6 Print Level Keywords

The keyword "PRINT=n" (*n* = 0-4) can be used to give flexible heirarchical control of all NBO output in terms of a specified print level *n*. This keyword activates groups of keywords in a heirarchical manner, and thus incrementally increases the volume of output, ranging from *no* NBO output (PRINT=0) to a considerable volume of detail (PRINT=4). The keywords associated with each print level are tabulated below [default value, PRINT=2]:

print level	*additional output or activated keywords*
0	suppress *all* output from the NBO program
1	activate NPA and NBO keywords
[2]	activate BEND, NBOSUM, and E2PERT keywords
3	activate NLMO, DIPOLE, and BNDIDX keywords
4	activate all(!) keywords

For each print level *n*, the NBO output will include items activated by the listed keywords, as well as all items from lower print levels.

When additional keywords are included with a "PRINT=n" keyword in the $NBO keylist, the NBO output includes the additional keyword items as well as those implied by the print level. This can be used to tailor the NBO output to virtually any selection of output items. For example, the keylist

```
$NBO  PRINT=2  NLMO  FNBO=P  NAOMO=P11  $END
```

would add to the standard methylamine output file of Section A.3 an NLMO summary table, the Fock matrix in the NBO basis, and the transformation coefficients for the first 11 molecular orbitals in terms of NAOs. Similarly, to produce the NPA listing only, one could use either form shown below

```
$NBO  PRINT=1  SKIPBO  $END
$NBO  PRINT=0  NPA  $END
```

[There is actually a slight difference between the two examples: The NBOs are determined by default (once the $NBO keylist is encountered), even if all output is suppressed with PRINT=0; in the first example, the keyword SKIPBO bypasses NBO determination, whereas in the second example the NBOs are still determined `in background.']

B.2.7 Semi-Documented Additional Keywords

Some additional keywords are listed below (primarily of use to specialists or program developers):

KEYWORD	*OPTION DESCRIPTION*
THRESH=val	Set the threshold of orbital occupancy desired for bond orbital selection. If this is not included, the default occupancy [1.90] will be used (or values decreasing from 1.90 to 1.50 by 0.01 steps).
CYCLES=val	Set the maximum number of cycles that the default NBO search will perform before terminating. (Each cycle decreases the occupancy threshold by 0.01.) For example, CYCLES=10 will not allow the search to perform more than 10 cycles. The search will cease after the tenth cycle, reporting the Lewis structure obtained during that cycle. CYCLES is particularly useful if the user wants to examine the orbitals obtained during *val*th cycle. Also, see THRESH.
DETAIL	Request additional details of the NBO search. This option (primarily for programming and debugging purposes) records details of the NBO loops over atoms and atom pairs, enroute to the final NBOs.
PRJTHR=val	Set the projection threshold [default 0.20] to determine if a `new' hybrid orbital has too high overlap with hybrids previously found.
MULAT	Print total gross Mulliken populations by atom.
MULORB	Print gross Mulliken populations, by orbital and atom. (This keyword also activates printing the Mayer-Mulliken bond order and valency indices if BNDIDX is active.)
RPNAO	Revises PAO to PNAO transformation matrix by post-multiplying by $\mathbf{T}_{\mathrm{Ryd}}$ and $\mathbf{T}_{\mathrm{red}}$ [A. E. Reed, R. B. Weinstock, and F. Weinhold, J. Chem. Phys. **83**, 735-746 (1985)].
PAOPNAO	Input or output of pure AO (PAO) to pre-NAO (PNAO) transformation. The PAOs are AOs of spherical angular momentum symmetry (rather than Cartesian). This keyword can be used with read (‘R’), write (‘W’, default LFN 29) or print (‘P’) parameters.
BOAO	Print the bond-order matrix (Fock-Dirac density matrix) in the basis set of input AOs. This keyword can be used with write (`W', default LFN 49) or print (`P') parameters.
NBODAF=n	Request writing the NBO direct access file (DAF) to external disk file LFN *n*, or, if ‘n’ is not present, to the default LFN 48.

SVEC	Print the eigenvectors of the overlap matrix in the AO basis.
FIXDM	Massage the input density matrix to remove unphysical occupancies (negative or Pauli-violating values) while preserving integer number of electrons. NBO analysis then begins from a modified density matrix that is “close” to the input density matrix, but is (in principle) N-representable. FIXDM merely camouflages, but does not fundamentally remove, non-physical aspects of certain non-variational densities (e.g., MP2, RhoCI, or CIS density). It should be used with caution.

B.3 THE $CORE LIST

In the Lewis structure picture, the inner core electron pairs are pictured as occupying orbitals having essentially isolated atomic orbital character. In NBO parlance, these core orbitals correspond to 1-center unhybridized NAOs of near-maximum occupancy, which are isolated on each center before the main NBO search begins for localized valence electron pairs. A warning message is printed if the occupancy of a presumed closed-shell core NBO falls below 1.9990 electrons (or 0.9990 in the open-shell case), indicative of a possible core-valence mixing effect of physical significance.

The NBO program contains a table giving the nominal number of core orbitals to be isolated on each type of atom (e.g., 1*s* for first-row atoms Li-Ne, 1*s*, 2*s*, 2*p* for second-row atoms Na-Ar, etc.). At times, however, it is interesting to examine the effect of allowing core orbitals to mix into the bonding hybrids, or to hybridize (polarize) among themselves. This can be accomplished by including a $CORE keylist to specify the number of core orbitals to be isolated on each atomic center, thus modifying the nominal core table. Unlike other NBO keylists, the $CORE list includes only integers (rather than keywords) to specify the core modifications, but the rules are otherwise similar to those for other keylists. The $CORE list (if included) must follow the $NBO keylist and precede the $CHOOSE or $DEL keylists.

The format of the $CORE modification list is:

first line:	The keyword “$CORE”
next lines:	Pairs of integers, one pair for each center. The first integer indicates the atomic center (in the numbering of the main ESS) and the second is the number of core orbitals to be isolated on that atom. Note that atomic centers not included in the CORE list are assigned default cores.
last line:	The keyword “$END”, to indicate the end of core input.

The entire list may also be condensed to a single line, but the word “$CORE” must occur as the first word of the line and “$END” as the last word; that is, the core modification keylist cannot continue on a line that contains other keylist information.

B.3 THE $CORE LIST

The core orbitals are isolated by occupancy, the most occupied NAOs being first selected, and full subshells are isolated at a time. Thus, for example, to select the five orbitals of the $n = 1$ and $n = 2$ shells as core orbitals, it would make no difference to select "3" or "4" (instead of "5"), since all three of these choices would specify a core containing a 1*s*, 2*s*, and all three 2*p* orbitals. The $CORE modification list is read only once, and applies to both α and β spin manifolds in an open-shell calculation.

An example, appropriate for Ni(1)-C(2)-O(3) with the indicated numbering of atoms, is shown below:

```
$CORE
  1   5
$END
```

This would direct the NBO program to isolate only 5 core orbitals on Nickel (atom 1), rather than the nominal 9 core orbitals. In other words, only 1*s*, 2*s*, and 2*p* orbitals will be considered as core orbitals in the search for NBOs of NiCO, allowing the 3*s* and 3*p* orbitals to mix with valence NAOs in bond formation. Since the carbon and oxygen atoms were not included in the modification list, the nominal set of core orbitals (1*s* only) is isolated on each of these atoms.

[The alternative example

```
$CORE   1  0    2  0    3  0   $END
```

(no cores) would allow all NAOs to be included in the NBO search (equivalent to the default treatment in the earliest version of the program).]

B.4 THE $CHOOSE KEYLIST (DIRECTED NBO SEARCH)

A $CHOOSE keylist requests that the NBO search be directed to find a particular Lewis structure ('resonance structure') chosen by the user. (This is useful for testing alternative resonance structure representations of the wavefunction, relative to the optimal Lewis structure returned in a free NBO search.) In the $CHOOSE list, a resonance structure is specified by indicating where lone pairs and bonds (including multiple bonds) are to be found in the molecule.

The format of the $CHOOSE list is:

first line:	The keyword "$CHOOSE"
next line:	The keyword "ALPHA" (only for open-shell wavefunctions)
next lines:	If one-center ('lone') NBOs are to be searched for, type the keyword "LONE" followed by a list of pairs of numbers, the first number of each pair being the atomic center and the second the number of valence lone pairs on that atom. Terminate the list with "END". (Note that only the occupied *valence* lone pairs should be entered because the number of core orbitals on each center is presumed known.) If two-center ('bond') NBOs are to be searched for, type the keyword "BOND", followed by the list of bond specifiers, and terminated by "END". Each bond specifier is one of the following: "S" single bond "D" double bond "T" triple bond "Q" quadruple bond "5" quintuple bond "6" sextuple bond followed by the two atomic centers of the bond (e.g., "D 9 16" for a double bond between atoms 9 and 16). If three-center NBOs are to be searched for, type the keyword "3C", followed by the list of 3-c bond specifiers, and terminated by "END". Each 3-c bond specifier is again one of the letters "S" (single), "D" (double), "T" (triple), "Q" (quadruple), etc., followed by three integers for the three atomic centers (e.g., "S 4 8 10" for a single three-center bond 4-8-10). Multi-center (*n*-c) NBOs for *n*>3 can be searched for analogously using the

	"4C", "5C", "6C" keywords, and so on. For example "4C D 2 4 6 8 END" can be specified to find two (D) 4-c bonds across atoms 2-4-6-8. ["1C" and "2C" can be used instead of the respective keywords "LONE" and "BOND".]
next line:	The word "END" to signal the end of the α spin list.
next line:	The keyword "BETA" (only for open-shell wavefunctions)
next lines:	The input for β spin, using the same format as above.
next line:	The word "END" to signal the end of the β spin list.
next line:	The $END terminator to signal the end of $CHOOSE input.

Three examples serve to illustrate the $CHOOSE format (each is rather artificial, inasmuch as the specified $CHOOSE structure corresponds to the 'normal' structure that would be found by the NBO program anyway):

(1) The closed-shell H-bonded complex FH···CO, with atom numbering F(1)-H(2)···C(3)-O(4), might be specified as

```
$CHOOSE
   LONE  1  3
         3  1
         4  1     END
   BOND  S  1  2
         T  3  4  END
$END
```

This would direct the NBO program to search for three lone pairs on atom F(1), one lone pair on atom C(3), one lone pair on atom O(4), one bond between F(1)-H(2), and three bonds between C(3)-O(4).

(2) The open-shell FH···O_2 complex, with atom numbering F(1)-H(2)···O(3)-O(4), and with the unpaired electrons on O_2 being of α spin, might be specified as

```
$CHOOSE
  ALPHA
    LONE  1  3
```

```
          3  3
          4  3     END
    BOND  S  1  2
          S  3  4  END
  END
  BETA
    LONE  1  3
          3  1
          4  1     END
    BOND  S  1  2
          T  3  4  END
  END
$END
```

Note that this example incorporates the idea of "different Lewis structures for different spins," with a distinct pattern of localized 1-c ('lone') and 2-c ('bond') functions for α and β spin.

(3) The closed-shell diborane molecule, with boron atoms B(1) and B(2) and bridging hydrogens H(3) and H(4) might be specified as:

```
$CHOOSE
   BOND S 1 5 S 1 6 S 2 7 S 2 8 END
   3C S 1 2 3 S 1 2 4 END
$END
```

As with other keylists, the $CHOOSE keylist can be condensed to a smaller number of lines, as long as no line is shared with another keylist. The order of keywords within the $CHOOSE keylist should be as listed in the table above (i.e., ALPHA before BETA, LONE before BOND, etc.), but the order of entries within a LONE or BOND list is immaterial.

The NBO program writes to the output file a $CHOOSE keylist that reflects the pattern of bonds and lone pairs identified by the NBO search. This keylist can be copied into the ESS input file and modified, if desired, for subsequent analysis.

A $CORE keylist (Sec. B.3), if present, must precede the $CHOOSE list.

Also, see the MOLUNIT keyword (Sec. B.2.2) that allows the user to specify molecular units for the NBO search without fully specifying the $CHOOSE details of the Lewis structure.

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

B.5.1 Introduction to NBO Energetic Analysis

The fourth and final type of keylist is a deletions ($DEL) keylist, to activate NBO energetic analysis. (NEDA input for GAMESS is also handled by the $DEL keylist, and is described in Sec. B.11.2.2) Standard NBO energetic analysis is performed by (1) deleting specified elements (or blocks of elements) from the NBO Fock matrix, (2) diagonalizing this new Fock matrix to obtain a new density matrix, and (3) passing this density matrix to the SCF routines for a single pass through the SCF energy evaluator. The difference between this `deletion' energy and the original SCF energy provides a useful measure of the energy contribution of the deleted terms. Since a Fock (or Kohn-Sham) matrix is required, the energetic analysis is performed only for RHF, UHF, and corresponding DFT levels. For deletion type (2), element deletions can optionally be performed on the NAO or NHO Fock matrix.

Input for the NBO energetic analysis is through the $DEL keylist, which specifies the deletions to be performed. Multiple analyses (deletions) can be performed during a single job, with each deletion included in the overall $DEL keylist. The nine distinct types of deletions input are described in Section B.5.2 below.

The deletions keylist begins with the “$DEL” keyword. For the analysis of UHF wavefunctions, the deletions for the α and β spin manifolds must be separately specified (see Section B.5.3). Otherwise, the input for closed shells RHF and UHF is identical. The input is free format and the input for a single deletion can be spread over as many lines as desired. The desired deletions should be listed one after the other. After the last deletion, the word “$END” signals the end of the keylist.

WARNING
If symmetry is used, one must be careful to only do deletions that will preserve the symmetry of the electronic wavefunction!! Otherwise, the energy of the deletion will be incorrect and the variational principle may be violated. (For example, if symmetry is used for ethane, it is permissible to do a “LEWIS” (a.k.a. “NOSTAR”) deletion, but not the deletion of a single C-H antibond.) The remedy is not to use symmetry in the SCF calculation.

In describing the deletion types, use is made of the terms “molecular unit” and “chemical fragment.” The NBO program looks at the chemical bonding pattern

produced by the bonding NBOs and identifies the groups of atoms that are linked together in distinct “molecular units” (usually synonymous with “molecules” in the chemical sense). The first atom that is not in molecular unit 1 will be in molecular unit 2, and so forth. For example, if the list of atoms is C(1), H(2), F(3), O(4), and bonding NBOs are found between C(1)-O(4) and H(2)-F(3), then molecular unit 1 will be CO and molecular unit 2 will be HF. A “chemical fragment” is taken to be any subset of the atoms, usually (but not necessarily) in the same molecular unit, and usually (but not necessarily) connected by bond NBOs. Typically, a chemical fragment might be specified to be a single atom, the four atoms of a methyl group, or any other `radical' of a molecular unit, identified by giving the atom numbers of which the fragment consists.

B.5.2 The Nine Deletion Types

The keywords and format to specify each of the nine allowed deletion types are described below. Except for type (2), deletions refer to NBOs only.

(1) Deletion of entire orbitals.

This is called for by typing "DELETE", then the number of orbitals to be deleted, then the keyword "ORBITAL" (or "ORBITALS"), then the list of the orbitals to be deleted; for example:

```
DELETE  3  ORBITALS  15  18  29
```

[See also deletion types (4) and (7) for deleting sets of orbitals.]

WARNING
The "single-pass" method of evaluating deletion energies is appropriate only for deletions of *low*-occupancy (non-Lewis) orbitals, for which the loss of self-consistency in the Coulomb and exchange potentials (due to redistribution of the electron density of deleted orbitals) is small compared to the net energy change of deletion. It is fundamentally erroneous to delete *high*-occupancy (Lewis) orbitals by this procedure.

(2) Deletion of specific Fock matrix elements.

This is requested by typing "DELETE", then the number of elements to be deleted, then the keyword "ELEMENT" (or "ELEMENTS"), then the list of the elements to be deleted (each as a pair of integers); for example:

```
DELETE  3  ELEMENTS  1 15  3 19  23 2
```

This example would result in the zeroing of the following NBO Fock matrix elements: (1,15), (15,1), (3,19), (19,3), (23,2), (2,23).

For this deletion type (only), one can also specify deletion of elements from the NAO or NHO Fock matrix by merely including the desired basis preceding "DELETE." Thus, the command "NHO DELETE 3 ELEMENTS..." would perform the deletions on the NHO Fock matrix.

(3) Deletion of off-diagonal blocks of the Fock matrix.

Each block is specified by two sets of orbitals, and all Fock matrix elements in common between these two sets are set to zero. This is called for by typing

"ZERO", then the number of off-diagonal blocks to be zeroed, and then, for each block, the following:

(1) the dimensions of the block, separated by the word "BY" (e.g., "6 BY 3" if the first set has 6 orbitals and the second set has 3 orbitals);

(2) the list of orbitals in the first set;

(3) the list of orbitals in the second set.

An example is shown below:

```
ZERO  2  BLOCKS  2  BY  5
                         3  4
                         9  10  11  14  19
                  3  BY  2
                         1  2  7
                        20  24
```

This will set the following Fock matrix elements to zero:

(3,9), (3,10), (3,11), (3,14), (3,19), (9,3), (10,3), (11,3), (14,3), (19,3), (4,9), (4,10), (4,11), (4,14), (4,19), (9,4), (10,4), (11,4), (14,4), (19,4), (1,20), (1,24), (2,20), (2,24), (7,20), (7,24) (20,1), (24,1), (20,2), (24,2), (20,7), (24,7)

[Usually, in studying the total delocalization from one molecular unit to another, it is much easier to use deletion type (8) below. Similarly, in studying the total delocalization from one chemical fragment to another, it is easier to use deletion type (9).]

(4) Deletion of all non-Lewis orbitals.

The non-Lewis NBO orbitals correspond to the "unfilled" (acceptor) orbitals of NBO analysis output, unused in the idealized Lewis structure picture. To delete all these orbitals, simply enter "LEWIS". The result of this deletion is the energy of the idealized NBO natural Lewis structure (NLS), with all Lewis NBOs doubly occupied. Unlike other deletions, in which there is a slight loss of variational self-consistency due to the redistributed occupancy of the deleted orbitals, the result of a "LEWIS" deletion corresponds rigorously to the variational expectation value of the determinant of doubly occupied Lewis NBOs. (For compatibility with previous NBO versions, "NOSTAR" is accepted as a synonym for "LEWIS".)

(5) Deletion of all vicinal delocalizations.

To delete all Fock matrix elements between Lewis NBOs and the vicinal non-Lewis NBOs, simply enter "NOVIC".

(6) Deletion of all geminal delocalizations.

To delete all Fock matrix elements between Lewis NBOs and the geminal non-Lewis NBOs, simply enter "NOGEM".

(7) Deletion of all non-Lewis orbitals on a particular molecular unit.

Unit-based deletions of non-Lewis orbitals are requested by typing "ULEWIS", then the number of molecular units to be described in idealized Lewis structure limit, then the keyword "UNIT" (or "UNITS"), then the list of units; for example:

```
ULEWIS  2  UNITS  3  4
```

(For compatibility with previous NBO versions, "DESTAR" is also accepted as a synonym for "ULEWIS".)

(8) Zeroing all delocalizations from one molecular unit to another.

This is requested by typing "ZERO", then the number of delocalizations to zero, then the keyword "DELOCALIZATION" (can be abbreviated to "DELOC"), and then, for each delocalization, the word "FROM", the number of the donor unit, the word "TO", and the number of the acceptor unit; for example:

```
ZERO  2  DELOC  FROM 1 TO 2   FROM 2 TO 1
```

The above example would zero *all* intermolecular delocalizations between units 1 and 2 (i.e., both 1 → 2 and 2 → 1). The effect is to remove all Fock matrix elements between high-occupancy (core/lone pair/bond) NBOs of the donor unit to the low-occupancy (antibond/Rydberg) NBOs of the acceptor unit. The donor and acceptor units may be the same.

(9) Zeroing all delocalization from one chemical fragment to another.

This is called for by typing "ZERO", then the number of inter-fragment delocalizations to be zeroed, then the words "ATOM BLOCKS", and then, for each delocalization, the following:

(1) the number of atoms in the two fragments, separated by the word "BY" (e.g., "6 BY 3" if the first fragment has 6 atoms and the second has 3 atoms);

(2) the list of atoms in the first fragment;

(3) the list of atoms in the second fragment.

For example, to zero all delocalizations between the fragments defined by atoms (1,2) and by atoms (3,4,5), the $DEL entries would be

```
ZERO  2  ATOM BLOCKS
         2  BY  3
                   1  2
                   3  4  5
         3  BY  2
                   3  4  5
                   1  2
```

In this example, the first block removes the (1,2) → (3,4,5) delocalizations, while the second removes the (3,4,5) → (1,2) delocalizations.

For additional examples of $DEL input, see Section B.6.10.

B.5.3 Input for UHF Analysis

Deletions of the alpha and beta Fock matrices can be done independently. The deletions are input as above (Section B.5.2) for RHF closed shell, but they must be specified separately for alpha and beta in the UHF case.

The deletion to be done on the alpha Fock matrix must be preceded by the keyword "ALPHA", and the deletion of the beta Fock matrix must be preceded by the keyword "BETA". (Actually, only the first letter "A" or "B" is searched for by the program.) The ALPHA deletion must precede the BETA deletion. The BETA deletion may be the same as the ALPHA deletion, or different.

NOTE: The types of the α NBOs often differ from those of the β NBOs, so that distinct α, β deletions lists are generally required. For example, O_2 (triplet) has one bond in the α system and three in the β system, if the unpaired electrons are in the α system.

Here are three examples to illustrate UHF open-shell deletions:

Example 1:

```
ALPHA  ZERO  1  DELOC  FROM  1  TO  2
BETA   NOSTAR
```

Example 2:

```
ALPHA  ZERO  1  DELOC  FROM  1  TO  2
BETA   ZERO  0  DELOC
```

Example 3:

```
ALPHA  DELETE  0  ORBITALS
BETA   DELETE  1  ORBITAL  8
```

If no deletion is done, this must be specified using zero (0) with one of the deletion input formats, as shown in Examples 2,3 above.

UHF deletions can also be done with MSPNBOs (Sec. B.2.2) by using the following two-step procedure: (i) compute and store the MSPNBOs in a non-$DEL job; (ii) read in the stored MSPNBOs and use them for the $DEL job. The initial job should include the $NBO keywords "MSPNBO NAONBO=W44" to write the MSPNBO NAO→NBO transformation matrix to an external file LFN 44 (cf. Sec. B.2.4), while the second job should include the $NBO keyword "NAONBO=R44" (but *not* MSPNBO) to read in the stored MSPNBOs from LFN 44 for the deletions.

B.5 THE $DEL KEYLIST (NBO ENERGETIC ANALYSIS)

Caveat for DFT Deletions

Density functional methods are often poorly parameterized to evaluate the energetics of $DEL densities, which by nature differ significantly from "usual" densities. The $DEL-based methods may therefore lead to unrealistic DFT energetics. Extreme caution should be exercised in employing $DEL options with DFT methods.

B.6 NBO ILLUSTRATIONS

B.6.1 Introduction

This section illustrates the output produced by several important keyword options of the NBO keylists ($NBO, $CHOOSE, $DEL, $CORE lists), supplementing the illustrations of Section A.3. Excerpts are provided rather than full output, since, e.g., NPA analysis is unaffected by keywords that modify the NBO search. Keywords of general applicability are illustrated with the methylamine example (RHF/3-21G, Pople-Gordon geometry) of Section A.3, which should be consulted for further information. More specialized keywords and options are illustrated with prototype molecules (benzene, diborane, methyl radical).

Sections B.6.2-B.6.8 illustrate representative examples from the $NBO keyword groups, including NLMO, DIPOLE, BNDIDX, NOBOND, 3CBOND, and matrix output keywords. Section B.6.9 and B.6.10 similarly illustrate the use of the $CHOOSE and $DEL keylists. Section B.6.11 illustrates the output for open-shell UHF cases, emphasizing features associated with the "different Lewis structures for different spins" representation of α and β spin manifolds. Section B.6.12 shows the effect of using effective core potentials for Cu_2, also illustrating aspects of the inclusion of *d* functions.

B.6.2 NLMO Keyword

When the NLMO keyword is activated, the program computes the NLMOs and prints out three tables summarizing their form. For RHF/3-21G methylamine (cf. Section A.3), the principal NLMO table is shown below:

```
 NATURAL LOCALIZED MOLECULAR ORBITAL (NLMO) ANALYSIS:

 1 pass over DM reduced the maximum off-diagonal element to 0.00000009

 Hybridization/Polarization Analysis of NLMOs in NAO Basis:
 NLMO / Occupancy / Percent from Parent NBO / Atomic Hybrid Contributions
 ---------------------------------------------------------------------------
   1. (2.00000)  99.9504% CR ( 1) C  1
                         99.951%  C  1 s(100.00%)p 0.00(  0.00%)
                          0.013%  H  3 s(100.00%)
                          0.013%  H  4 s(100.00%)
                          0.013%  H  5 s(100.00%)
   2. (2.00000)  99.9763% CR ( 1) N  2
                          0.010%  C  1 s( 22.45%)p 3.45( 77.55%)
                         99.980%  N  2 s(100.00%)p 0.00(  0.00%)
   3. (2.00000)  98.9222% LP ( 1) N  2
                          0.430%  C  1 s(  1.05%)p93.85( 98.95%)
                         98.922%  N  2 s( 18.13%)p 4.51( 81.87%)
                          0.477%  H  3 s(100.00%)
                          0.083%  H  4 s(100.00%)
                          0.083%  H  5 s(100.00%)
   4. (2.00000)  99.9247% BD ( 1) C  1- N  2
                         40.035%  C  1 s( 21.38%)p 3.68( 78.62%)
                         59.891%  N  2 s( 30.79%)p 2.25( 69.21%)
                          0.016%  H  3 s(100.00%)
                          0.022%  H  6 s(100.00%)
                          0.022%  H  7 s(100.00%)
   5. (2.00000)  99.9313% BD ( 1) C  1- H  3
                         59.681%  C  1 s( 25.55%)p 2.91( 74.45%)
                          0.039%  N  2 s(  2.19%)p44.61( 97.81%)
                         40.253%  H  3 s(100.00%)
   6. (2.00000)  99.7012% BD ( 1) C  1- H  4
                         60.854%  C  1 s( 25.29%)p 2.95( 74.71%)
                          0.092%  N  2 s( 14.19%)p 6.05( 85.81%)
                          0.013%  H  3 s(100.00%)
                         38.856%  H  4 s(100.00%)
                          0.016%  H  5 s(100.00%)
                          0.159%  H  6 s(100.00%)
   7. (2.00000)  99.7012% BD ( 1) C  1- H  5
                         60.854%  C  1 s( 25.29%)p 2.95( 74.71%)
                          0.092%  N  2 s( 14.19%)p 6.05( 85.81%)
                          0.013%  H  3 s(100.00%)
                          0.016%  H  4 s(100.00%)
                         38.856%  H  5 s(100.00%)
                          0.159%  H  7 s(100.00%)
   8. (2.00000)  99.7213% BD ( 1) N  2- H  6
                          0.113%  C  1 s(  5.20%)p18.23( 94.80%)
                         67.905%  N  2 s( 25.76%)p 2.88( 74.24%)
                          0.138%  H  4 s(100.00%)
                          0.014%  H  5 s(100.00%)
                         31.817%  H  6 s(100.00%)
   9. (2.00000)  99.7213% BD ( 1) N  2- H  7
                          0.113%  C  1 s(  5.20%)p18.23( 94.80%)
                         67.905%  N  2 s( 25.76%)p 2.88( 74.24%)
                          0.014%  H  4 s(100.00%)
                          0.138%  H  5 s(100.00%)
                         31.817%  H  7 s(100.00%)
```

For each of the nine occuplied NLMOs, the table shows first the NLMO occupancy (necessarily 2.0000 at SCF level, as in the present example), the percentage of the total NLMO composition represented by this parent NBO (usually > 99%), and the label of the `parent' NBO. Below this, there follows an NAO decomposition of the NLMO, showing the percentage of the NLMO on each atom and the hybrid composition ratios (effective sp^{λ} character and percentage *s*- and *p*-character) of the NAOs. For example, NLMO 3 is the most delocalized NLMO of the table, having only about a 98.9% contribution from the localized N(2) parent lone pair NBO, with “delocalization tails” composed primarily of contributions (~0.4% each) from C(1) and H(3), and smaller contributions (~0.09%) from H(4) and H(5). This corresponds to what might have been anticipated from the NBO summary table (Section A.3.6) or perturbation theory energy analysis table (Section A.3.5), which showed that the N(2) lone pair, NBO 3, is principally delocalized onto NBO 11, the vicinal C(1)-H(3) antibond [with lesser delocalizations onto NBOs 12, 13, the C(1)-H(4) and C(1)-H(5) antibonds].

B.6.3 DIPOLE Keyword

The DIPOLE keyword activates the NBO/NLMO analysis of the molecular dipole moment, as shown below for the example of RHF/3-21G methylamine (cf. Section A.3):

```
 DIPOLE MOMENT ANALYSIS:

 [Print threshold: Net dipole > 0.02 Debye]

                             NLMO bond dipole            NBO bond dipole
                           -------------------------  ------------------------
          Orbital            x     y     z   Total      x     y     z   Total
 ============================================================================
   1. CR ( 1) C 1           0.00  0.00  0.00  0.00     0.00  0.00  0.00  0.00

   2. CR ( 1) N 2           0.00 -0.01  0.00  0.01     0.00  0.00  0.00  0.00

   3. LP ( 1) N 2           0.76  2.84  0.00  2.94     1.00  2.91  0.00  3.08
                                          deloc  11: -0.16 -0.08  0.00  0.18
                                          deloc  12: -0.03 -0.01  0.01  0.03
                                          deloc  13: -0.03 -0.01 -0.01  0.03
                                          deloc  16: -0.01  0.02  0.00  0.03

   4. BD ( 1) C 1- N 2      0.76  0.06  0.00  0.76     0.76  0.08  0.00  0.76

   5. BD ( 1) C 1- H 3     -0.57 -1.88  0.00  1.96    -0.57 -1.88  0.00  1.97
                                          deloc  20: -0.03  0.01  0.00  0.03
                                          deloc  12:  0.01  0.00  0.02  0.02
                                          deloc  13:  0.01  0.00 -0.02  0.02

   6. BD ( 1) C 1- H 4     -0.65  0.79 -1.50  1.81    -0.69  0.81 -1.49  1.83
                                          deloc  14:  0.05  0.00  0.00  0.05
                                          deloc  13:  0.02 -0.03 -0.03  0.04
                                          deloc  11:  0.01  0.02  0.00  0.02

   7. BD ( 1) C 1- H 5     -0.65  0.79  1.50  1.81    -0.69  0.81  1.49  1.83
                                          deloc  15:  0.05  0.00  0.00  0.05
                                          deloc  12:  0.02 -0.03  0.03  0.04
                                          deloc  11:  0.01  0.02  0.00  0.02

   8. BD ( 1) N 2- H 6      0.44 -0.46  0.86  1.07     0.49 -0.47  0.89  1.11
                                          deloc  12: -0.06  0.01 -0.02  0.06

   9. BD ( 1) N 2- H 7      0.44 -0.46 -0.86  1.07     0.49 -0.47 -0.89  1.11
                                          deloc  13: -0.06  0.01  0.02  0.06
                           ---------------------------------------------------
        Net dipole moment   0.52  1.66  0.00  1.74     0.79  1.79  0.00  1.96
 Delocalization correction                             -0.26 -0.13  0.00  0.29
                           ---------------------------------------------------
       Total dipole moment   0.52  1.66  0.00  1.74     0.52  1.66  0.00  1.74
```

The bottom line of the table shows the individual (x,y,z) vector components (0.52,1.66,0.00) and length (1.74 D) of the total molecular dipole moment, in the coordinate system of the ESS program. This is decomposed in the main body of the table into the individual contributions of “NLMO bond dipoles” (which strictly add to give the net molecule dipole at the SCF level) and “NBO bond dipoles” (which must be added with their off-diagonal `deloc'

contributions to give the net molecular moment). Each NLMO or NBO bond dipole vector $\boldsymbol{\mu}_{AB}$ is evaluated as

$$\boldsymbol{\mu}_{AB} = \boldsymbol{\mu}_{AB}^{(elec)} + \boldsymbol{\mu}_{AB}^{(nuc)}$$

where $\boldsymbol{\mu}_{AB}^{(elec)} = 2e\langle\sigma_{AB}|\mathbf{r}|\sigma_{AB}\rangle$ is the electronic dipole expectation value for an electron pair in the σ_{AB} NLMO or NBO, and $\boldsymbol{\mu}_{AB}^{(nuc)}$ is the nuclear contribution of compensating unit positive charges at the positions of nuclei A and B (or both on A for a 1-center NBO). The `deloc' contributions below each NBO bond dipole show the off-diagonal corrections to an additive bond dipole approximation (i.e., the corrections to localized NBO bond dipoles to get the NLMO bond dipoles) to account for the delocalization from parent NBO *i* onto other (primarily, non-Lewis) NBOs *j*; in terms of the expansion of an NLMO in the set $\{\sigma_j\}$ of NBOs,

$$\sigma_u^{(NLMO)} = c_{ii}\sigma_i + \sum_j c_{ji}\sigma_j$$

this correction is (for each electron, α or β spin)

$$c_{ji}^2[\,\langle\sigma_j|\boldsymbol{\mu}|\sigma_j\rangle - \langle\sigma_i|\boldsymbol{\mu}|\sigma_i\rangle\,] + 2\,c_{ii}\,c_{ji}\langle\sigma_i|\boldsymbol{\mu}|\sigma_j\rangle + \sum_k{}'' c_{ji}\,c_{ki}\langle\sigma_j|\boldsymbol{\mu}|\sigma_k\rangle$$

where the primes on the summation denote omission of terms *k* equal to *i* or *j*. For example, in the above table the largest individual contribution to $\boldsymbol{\mu}$ is from the nitrogen lone pair, table entry 3, which has an NLMO dipole of 2.94 D or NBO dipole of 3.08 D. The latter has also the largest off-diagonal delocalization correction in the table, a 0.18 D correction due to the $n_N \rightarrow \sigma^*_{CH}$ delocalization into the vicinal C(1)-H(3) antibond, NBO 11. For a post-SCF (correlated) calculation, the dipole table would also include an additional line for the correction due to non-additivity of the NLMO bond dipoles. For an ionic species, there would also be an additional line for the "residual nuclear charge" contribution; here, one must be aware that the dipole moment is calculated with respect to the origin of the Cartesian coordinate system chosen by the ESS program (since the dipole moment is origin-dependent in this case).

Note that the amount of detail in the dipole table can be altered by using the "DIPOLE=thr" form of the keyword to alter the threshold dipole (`thr') for printing [default: 0.02 D].

B.6.4 Matrix Output Keywords

Three simple examples will be given to illustrate the formatting of output for operators or basis set transformation matrices using the matrix output keywords of Section B.2.4. For the RHF/3-21G methylamine example of Section A.3, the keyword "FNHO" would cause the Fock matrix in the NHO basis to be printed out. Shown below is a reproduction of the first eight columns (out of 28) of this output:

```
 NHO Fock matrix:

        NHO         1        2        3        4        5        6        7        8
     ---------- -------- -------- -------- -------- -------- -------- -------- -------
  1.  C 1(cr)  -11.0415   0.0481   0.0445 -0.3909 -0.4170 -0.4404 -0.3894 -0.4448
  2.  N 2(cr)    0.0481-15.2590 -0.6352 -0.6146 -0.7039 -0.0060 -0.0248 -0.0133
  3.  N 2(lp)    0.0445 -0.6352 -0.4475 -0.0771 -0.0961  0.1036 -0.0244 -0.0383
  4.  C 1( N 2) -0.3909 -0.6146 -0.0771 -0.0201 -0.7196 -0.0565 -0.0672 -0.0433
  5.  N 2( C 1) -0.4170 -0.7039 -0.0961 -0.7196 -0.3072 -0.0794 -0.0620 -0.0836
  6.  C 1( H 3) -0.4404 -0.0060  0.1036 -0.0565 -0.0794 -0.1401 -0.6760 -0.0642
  7.  H 3( C 1) -0.3894 -0.0248 -0.0244 -0.0672 -0.0620 -0.6760  0.1345 -0.0726
  8.  C 1( H 4) -0.4448 -0.0133 -0.0383 -0.0433 -0.0836 -0.0642 -0.0726 -0.1470
  9.  H 4( C 1) -0.3870 -0.0251  0.0159 -0.0697 -0.0639 -0.0735 -0.0680 -0.6761
 10.  C 1( H 5) -0.4448 -0.0133 -0.0383 -0.0433 -0.0836 -0.0642 -0.0726 -0.0550
 11.  H 5( C 1) -0.3870 -0.0251  0.0159 -0.0697 -0.0639 -0.0735 -0.0680 -0.0746
 12.  N 2( H 6)  0.0387 -0.6791 -0.0981 -0.0935 -0.1495 -0.0247  0.0112  0.0908
 13.  H 6( N 2) -0.0395 -0.4402 -0.0693 -0.1077 -0.0835  0.0006 -0.0233 -0.0108
 14.  N 2( H 7)  0.0387 -0.6791 -0.0981 -0.0935 -0.1495 -0.0247  0.0112 -0.0348
 15.  H 7( N 2) -0.0395 -0.4402 -0.0693 -0.1077 -0.0835  0.0006 -0.0233  0.0016
 16.  C 1(ry)    0.0045  0.1399  0.0217  0.1323 -0.0929 -0.0707  0.0818  0.0014
 17.  C 1(ry)    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0721
 18.  C 1(ry)   -0.0025  0.1049  0.0203  0.1014 -0.0760  0.0644 -0.0796 -0.0067
 19.  C 1(ry)    0.0030 -0.0297 -0.0025 -0.0276  0.0224 -0.0028  0.0069  0.0673
 20.  N 2(ry)    0.0040  0.0692  0.0026 -0.0160  0.0184  0.0351  0.0167 -0.0179
 21.  N 2(ry)    0.0000  0.0000  0.0000  0.0000  0.0000  0.0000  0.0000 -0.0158
 22.  N 2(ry)    0.0799 -0.0572 -0.0015 -0.1798  0.1437  0.0054 -0.0295  0.0035
 23.  N 2(ry)   -0.0257  0.0314  0.0026 -0.0176  0.0131  0.0049 -0.0211  0.0032
 24.  H 3(ry)    0.1157  0.0135 -0.0111 -0.0262  0.0042 -0.2834  0.3498 -0.0237
 25.  H 4(ry)    0.1217  0.0131  0.0106 -0.0240  0.0075 -0.0201  0.0063 -0.2788
 26.  H 5(ry)    0.1217  0.0131  0.0106 -0.0240  0.0075 -0.0201  0.0063 -0.0216
 27.  H 6(ry)    0.0161  0.0889 -0.0026 -0.0119 -0.0182  0.0066 -0.0221 -0.0077
 28.  H 7(ry)    0.0161  0.0889 -0.0026 -0.0119 -0.0182  0.0066 -0.0221  0.0058
```

The NHO labels on each row identify the atom to which the NHO belongs, and (in parentheses) the atom toward which the hybrid is pointed, if a bond hybrid, or a 1-center label (cr, lp, lp*, or ry), if a non-bonded hybrid. Thus, "C 1 (N 2)" (NHO 4) is the bonding hybrid on C(1) directed toward N(2), "N 2(lp)" (NBO 3) is a non-bonded (lone pair) hybrid on N(2), etc. This label allows one to find the precise form of the NHO in the main listing of NBOs. The FNHO matrix shows, for example, that the (4,5) Fock matrix element between the directly interacting NHOs forming the C-N bond NBO is -0.7196 a.u., whereas the (4,12) matrix element, between the C(1) hybrid pointing toward N(2) and the N(2) hybrid pointing toward H(6), is –0.0935 a.u.

As a second example, the keyword “NBOMO=PVAL” would print out the core + valence columns of the NBO → MO transformation, as reproduced below:

MOs in the NBO basis:

	NBO	1	2	3	4	5	6	7	8
1.	C 1(cr)	0.0021	0.9931	0.0692	0.0919	0.0000	0.0008	0.0015	0.0000
2.	N 2(cr)	-0.9935	-0.0019	0.1047	-0.0351	0.0000	-0.0130	0.0023	0.0000
3.	N 2(lp)	-0.0436	-0.0037	-0.1691	0.1245	0.0000	0.3341	0.1440	0.0000
4.	C 1- N 2	-0.0658	0.0571	-0.6291	-0.1241	0.0000	0.3063	-0.6894	0.0000
5.	C 1- H 3	-0.0019	0.0579	-0.2078	-0.4709	0.0000	-0.7782	-0.1175	0.0000
6.	C 1- H 4	-0.0023	0.0579	-0.1840	-0.4901	-0.3822	0.2409	0.3866	-0.5934
7.	C 1- H 5	-0.0023	0.0579	-0.1840	-0.4901	0.3822	0.2409	0.3866	0.5934
8.	N 2- H 6	-0.0570	0.0001	-0.4731	0.3577	0.5931	-0.1873	0.3083	-0.3823
9.	N 2- H 7	-0.0570	0.0001	-0.4731	0.3577	-0.5931	-0.1873	0.3083	0.3823
10.	C 1- N 2*	-0.0021	0.0031	0.0022	0.0017	0.0000	-0.0034	-0.0038	0.0000
11.	C 1- H 3*	-0.0012	0.0023	-0.0054	-0.0018	0.0000	0.0347	0.0131	0.0000
12.	C 1- H 4*	-0.0009	0.0028	-0.0143	-0.0035	0.0407	-0.0184	0.0063	-0.0148
13.	C 1- H 5*	-0.0009	0.0028	-0.0143	-0.0035	-0.0407	-0.0184	0.0063	0.0148
14.	N 2- H 6*	0.0011	0.0050	-0.0048	-0.0181	-0.0179	0.0129	0.0153	-0.0321
15.	N 2- H 7*	0.0011	0.0050	-0.0048	-0.0181	0.0179	0.0129	0.0153	0.0321
16.	C 1(ry)	0.0088	-0.0003	0.0112	-0.0088	0.0000	-0.0019	-0.0084	0.0000
17.	C 1(ry)	0.0000	0.0000	0.0000	0.0000	-0.0106	0.0000	0.0000	0.0069
18.	C 1(ry)	0.0062	0.0002	-0.0050	0.0035	0.0000	-0.0029	0.0027	0.0000
19.	C 1(ry)	-0.0020	-0.0003	-0.0003	0.0003	0.0000	-0.0009	0.0002	0.0000
20.	N 2(ry)	0.0041	-0.0003	-0.0007	-0.0017	0.0000	0.0194	0.0102	0.0000
21.	N 2(ry)	0.0000	0.0000	0.0000	0.0000	-0.0079	0.0000	0.0000	-0.0122
22.	N 2(ry)	-0.0035	-0.0060	-0.0040	-0.0104	0.0000	-0.0023	0.0042	0.0000
23.	N 2(ry)	0.0018	0.0023	-0.0007	-0.0013	0.0000	-0.0006	0.0005	0.0000
24.	H 3(ry)	0.0008	-0.0094	-0.0104	-0.0143	0.0000	0.0017	-0.0025	0.0000
25.	H 4(ry)	0.0008	-0.0100	-0.0061	-0.0117	-0.0064	0.0005	-0.0057	0.0097
26.	H 5(ry)	0.0008	-0.0100	-0.0061	-0.0117	0.0064	0.0005	-0.0057	-0.0097
27.	H 6(ry)	0.0052	-0.0013	-0.0147	0.0016	0.0030	-0.0018	-0.0100	0.0158
28.	H 7(ry)	0.0052	-0.0013	-0.0147	0.0016	-0.0030	-0.0018	-0.0100	-0.0158

	NBO	9	10	11	12	13	14	15
1.	C 1(cr)	0.0037	-0.0133	0.0082	0.0000	-0.0009	0.0000	0.0014
2.	N 2(cr)	-0.0191	-0.0054	-0.0031	0.0000	0.0026	0.0000	-0.0036
3.	N 2(lp)	0.9005	-0.0148	-0.0063	0.0000	-0.0913	0.0000	-0.0126
4.	C 1- N 2	-0.1066	0.0145	0.0009	0.0000	0.0056	0.0000	-0.0063
5.	C 1- H 3	0.3341	0.0044	0.0020	0.0000	0.0009	0.0000	-0.0077
6.	C 1- H 4	-0.1178	-0.0191	-0.0106	-0.0257	0.0049	0.0274	0.0094
7.	C 1- H 5	-0.1178	-0.0191	-0.0106	0.0257	0.0049	-0.0274	0.0094
8.	N 2- H 6	-0.1188	-0.0026	0.0146	0.0295	0.0164	0.0250	-0.0039
9.	N 2- H 7	-0.1188	-0.0026	0.0146	-0.0295	0.0164	-0.0250	-0.0039
10.	C 1- N 2*	0.0028	0.2347	0.2571	0.0000	-0.1089	0.0000	0.8057
11.	C 1- H 3*	0.0791	0.3240	-0.2615	0.0000	0.6693	0.0000	0.1125
12.	C 1- H 4*	-0.0367	0.2601	-0.3883	-0.4713	-0.2952	-0.3162	0.0485
13.	C 1- H 5*	-0.0367	0.2601	-0.3883	0.4713	-0.2952	0.3162	0.0485
14.	N 2- H 6*	-0.0025	0.4317	0.3150	0.3239	-0.0493	-0.4545	-0.2169
15.	N 2- H 7*	-0.0025	0.4317	0.3150	-0.3239	-0.0493	0.4545	-0.2169
16.	C 1(ry)	-0.0128	-0.0992	-0.0563	0.0000	-0.0538	0.0000	-0.3304
17.	C 1(ry)	0.0000	0.0000	0.0000	-0.0851	0.0000	-0.1849	0.0000
18.	C 1(ry)	-0.0039	-0.0588	-0.0751	0.0000	0.1152	0.0000	-0.1180
19.	C 1(ry)	-0.0018	0.0942	-0.0177	0.0000	-0.1045	0.0000	0.1524
20.	N 2(ry)	-0.0085	-0.0229	-0.0068	0.0000	0.0465	0.0000	0.0183
21.	N 2(ry)	0.0000	0.0000	0.0000	-0.0167	0.0000	0.0867	0.0000
22.	N 2(ry)	0.0007	0.0393	0.0844	0.0000	-0.0224	0.0000	0.1563
23.	N 2(ry)	0.0003	0.0611	0.0224	0.0000	-0.0119	0.0000	-0.0588
24.	H 3(ry)	-0.0217	-0.2491	0.2188	0.0000	-0.4844	0.0000	0.0041
25.	H 4(ry)	0.0058	-0.1984	0.3215	0.3399	0.2058	0.2121	0.0522
26.	H 5(ry)	0.0058	-0.1984	0.3215	-0.3399	0.2058	-0.2121	0.0522
27.	H 6(ry)	0.0026	-0.2845	-0.2161	-0.2283	0.0374	0.3552	0.1716
28.	H 7(ry)	0.0026	-0.2845	-0.2161	0.2283	0.0374	-0.3552	0.1716

In this transformation matrix, rows correspond to NBOs and columns to MOs (in the ordering used elesewhere in the program), and each basis NBO is further identified with a row label. The print parameter "PVAL" specified that only 15 MOs (the number of core + valence orbitals) should be printed, corresponding to the nine occupied MOs 1-9 and the lowest six virtual MOs 10-15. The matrix allows one to see the composition of each canonical MO in terms of localized bond NBOs. For example, MOs 5 and 8 can be approximately described as

$$\varphi_5 \cong -0.593(\sigma_{N2H6} - \sigma_{N2H7}) + 0.382(\sigma_{C1H4} - \sigma_{C1H5})$$

$$\varphi_8 \cong 0.382(\sigma_{N2H6} - \sigma_{N2H7}) + 0.593(\sigma_{C1H4} - \sigma_{C1H5})$$

whereas φ_6 is primarily the C-H(3) NBO and φ_9 the N lone pair NBO. Note that the CMO keyword (Sec. B.13) presents a more convenient summary of MO composition and bonding character.

As a final example, the keyword "SPNBO <3 11/9 13>" will print out the values of the $S_{3,11} = \langle n_N|\sigma^*_{CH3}\rangle$ and $S_{9,13} = \langle\sigma_{NH7}|\sigma^*_{CH5}\rangle$ PNBO overlap integrals as shown below:

```
 PNBO overlap matrix:

       2 user-requested elements:
     ------------------------------------------------------
        i     j       matrix(i,j)    label(i)   label(j)
     ------------------------------------------------------
        3    11    0.1658146514E+00  N 2(lp)    C 1- H 3*
        9    13    0.1707604944E+00  N 2- H 7   C 1- H 5*
     ------------------------------------------------------
```

Note that descriptive basis labels are provided for all basis sets except canonical MOs.

B.6.5 BNDIDX Keyword

The BNDIDX keyword activates the printing of several types of non-NRT bond order and valency indices. (For the NRT "natural bond order" and "natural atomic valency," see Sec. B.8.) These alternative indices are based on varying assumptions and formulas. We illustrate these bond order tables for the example of RHF/3-21G methylamine (Section A.3).

The first segment of BNDIDX output shows the Wiberg bond index [the sum of squares of off-diagonal density matrix elements between atoms; K. B. Wiberg, *Tetrahedron* **24**, 1083 (1968)], as formulated in terms of the NAO basis set:

```
Wiberg bond index matrix in the NAO basis:

    Atom    1       2       3       4       5       6       7
    ---- ------  ------  ------  ------  ------  ------  ------
  1.  C  0.0000  0.9959  0.9475  0.9394  0.9394  0.0020  0.0020
  2.  N  0.9959  0.0000  0.0203  0.0052  0.0052  0.8615  0.8615
  3.  H  0.9475  0.0203  0.0000  0.0004  0.0004  0.0002  0.0002
  4.  H  0.9394  0.0052  0.0004  0.0000  0.0009  0.0079  0.0005
  5.  H  0.9394  0.0052  0.0004  0.0009  0.0000  0.0005  0.0079
  6.  H  0.0020  0.8615  0.0002  0.0079  0.0005  0.0000  0.0002
  7.  H  0.0020  0.8615  0.0002  0.0005  0.0079  0.0002  0.0000


Wiberg bond index, Totals by atom:

    Atom    1
    ---- ------
  1.  C  3.8263
  2.  N  2.7496
  3.  H  0.9690
  4.  H  0.9543
  5.  H  0.9543
  6.  H  0.8723
  7.  H  0.8723
```

This index is intrinsically a positive quantity, making no distinction between net bonding or antibonding character of the density matrix elements.

The second segment reports that "natural binding indices" of the natural cluster unit (NCU) analysis. The values reported are the $\tau_{NCU}(A,B)$ interaction parameters described in Sec. B.19.

```
 NBI: Natural Binding Index (NCU strength parameters)

    Atom    1       2       3       4       5       6       7
    ---- ------  ------  ------  ------  ------  ------  ------
  1.  C  0.0000  0.9979  0.9734  0.9692  0.9692  0.0451  0.0451
  2.  N  0.9979  0.0000  0.1424  0.0720  0.0720  0.9281  0.9281
  3.  H  0.9734  0.1424  0.0000  0.0202  0.0202  0.0134  0.0134
  4.  H  0.9692  0.0720  0.0202  0.0000  0.0300  0.0889  0.0221
  5.  H  0.9692  0.0720  0.0202  0.0300  0.0000  0.0221  0.0889
  6.  H  0.0451  0.9281  0.0134  0.0889  0.0221  0.0000  0.0158
  7.  H  0.0451  0.9281  0.0134  0.0221  0.0889  0.0158  0.0000
```

Another type of BNDIDX output appears if the NLMO keyword is included, summarizing a formal "NLMO/NPA bond order" that can be associated with each NLMO:

```
 Individual LMO bond orders greater than 0.002 in magnitude,
 with the overlap between the hybrids in the NLMO given:

 Atom I / Atom J / NLMO / Bond Order / Hybrid Overlap /
    1       2       3     0.0086031       0.3051867
    1       2       4     0.8007093       0.7305290
    1       2       8     0.0022555       0.1809076
    1       2       9     0.0022555       0.1809076
    1       3       3    -0.0086031      -0.5768504
    1       3       5     0.8050682       0.7865538
    1       4       6     0.7771169       0.7875814
    1       4       8    -0.0022555      -0.5428010
    1       5       7     0.7771169       0.7875814
    1       5       9    -0.0022555      -0.5428010
    1       6       6    -0.0031742      -0.0925060
    1       6       8     0.0022555       0.0866524
    1       7       7    -0.0031742      -0.0925060
    1       7       9     0.0022555       0.0866524
    2       3       3    -0.0095444      -0.0937818
    2       4       8    -0.0027542      -0.0706654
    2       5       9    -0.0027542      -0.0706654
    2       6       8     0.6363467       0.7283871
    2       7       9     0.6363467       0.7283871
    4       6       6     0.0031742       0.0437116
    4       6       8     0.0027542       0.0407558
    5       7       7     0.0031742       0.0437116
    5       7       9     0.0027542       0.0407558
```

This NLMO bond order is calculated by the method described by A. E. Reed and P. v. R. Schleyer [*Inorg. Chem.* 27, 3969-3987 (1988); *J. Am. Chem. Soc.* **112**, 1434 (1990)], based on the shared occupancies and hybrid overlaps (last column) of NAOs composing the NLMO. In the above table, for example, NLMO 4 occurs only in the second line, contributing a bond of formal order 0.8007 between C(1) and N(2), whereas NLMO 3 (the nitrogen lone pair) contributes a slight strengthening (+0.0086) of the C(1)-N(2) bond, a

weakening (-0.0086) of the vicinal C(1)-H(3) bond, and a slight negative bond order (-0.0095) between atoms N(2), H(3).

The NLMO bond order contributions are then summed for each atom pair to give the net NLMO/NPA bond orders shown below:

Atom-Atom Net Linear NLMO/NPA Bond Orders:

	Atom	1	2	3	4	5	6	7
1.	C	0.0000	0.8171	0.7961	0.7732	0.7732	-0.0013	-0.0013
2.	N	0.8171	0.0000	-0.0102	-0.0067	-0.0067	0.6342	0.6342
3.	H	0.7961	-0.0102	0.0000	-0.0020	-0.0020	0.0001	0.0001
4.	H	0.7732	-0.0067	-0.0020	0.0000	0.0020	0.0062	0.0000
5.	H	0.7732	-0.0067	-0.0020	0.0020	0.0000	0.0000	0.0062
6.	H	-0.0013	0.6342	0.0001	0.0062	0.0000	0.0000	-0.0001
7.	H	-0.0013	0.6342	0.0001	0.0000	0.0062	-0.0001	0.0000

For example, the table attributes a formal bond order of 0.8171 to the C(1)-N(2) bond of methylamine, the highest bond order in this molecule. (The higher value for C(1)-H(3) than for the other two CH bonds reflects an unsatisfactory aspect of this method of assessing bond order.)

These non-NRT bond indices are based on different assumptions, with certain advantages and disadvantages. ***Caveat emptor!***

B.6.6 Strong Delocalization: Benzene

When NBO analysis is performed on a wavefunction that cannot be satisfactorily localized [i.e., in which one or more NBOs of the natural Lewis structure fail to achieve the default threshold occupancy (1.90) for a satisfactory "pair"], the NBO program successively lowers the occupancy threshold and repeats the search. (This formerly involved a coarse grid of 0.1*e* decrements, but the search now corresponds to an infinitely fine grid, with the search summary reporting only the discrete occupancies corresponding to changes of bonding pattern. For example, when benzene (RHF/STO-3G level, idealized Pople-Gordon geometry) is treated by the NBO program in default mode, one obtains the summary of NBO search cycles shown below.

```
 NATURAL BOND ORBITAL ANALYSIS:

                          Occupancies       Lewis Structure    Low   High
        Max    Occ     -------------------  -----------------   occ   occ
  Cycle  Ctr   Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
 ================================================================================
    1     2     1.90    38.87478   3.12522      6  12   0   3     3      3
    2     2     1.66    40.87478   1.12522      6  15   0   0     0      3
 --------------------------------------------------------------------------------
```

The NBO search considers "pair" occupancy thresholds throughout the range from 1.90e to 1.50e. In this case, the best Lewis structure (of lowest overall non-Lewis occupancy, 1.125e) was found at occupancy threshold 1.66e. The NBO program therefore resets the threshold to this value and calculates the set of NBOs corresponding to this "best" Lewis structure, as shown below:

```
    (Occupancy)   Bond orbital / Coefficients / Hybrids
 ----------------- Lewis ------------------------------------------------------
   1. (1.99995) CR ( 1) C  1            s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
   2. (1.99995) CR ( 1) C  2            s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
   3. (1.99995) CR ( 1) C  3            s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
   4. (1.99995) CR ( 1) C  4            s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
   5. (1.99995) CR ( 1) C  5            s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
   6. (1.99995) CR ( 1) C  6            s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
   7. (1.98935) BD ( 1) C  1- C  2
              ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847  0.7071 -0.3977  0.0000
              ( 50.00%)   0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.6979  0.4135  0.0000
   8. (1.66667) BD ( 2) C  1- C  2
              ( 50.00%)   0.7071* C  1 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  1.0000
              ( 50.00%)   0.7071* C  2 s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  1.0000
   9. (1.98935) BD ( 1) C  1- C  6
              ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                         0.0000  0.5847 -0.7071 -0.3977  0.0000
              ( 50.00%)   0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
```

```
                                        0.0000  0.5847  0.6979  0.4135  0.0000
 10. (1.98983) BD ( 1) C  1- H  7
              ( 51.74%)   0.7193* C  1 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.0000  0.8269  0.0000
              ( 48.26%)   0.6947* H  7 s(100.00%)
                                        1.0000
 11. (1.98935) BD ( 1) C  2- C  3
              ( 50.00%)   0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847 -0.0092  0.8112  0.0000
              ( 50.00%)   0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847 -0.0092 -0.8112  0.0000
 12. (1.98983) BD ( 1) C  2- H  8
              ( 51.74%)   0.7193* C  2 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.7161  0.4134  0.0000
              ( 48.26%)   0.6947* H  8 s(100.00%)
                                        1.0000
 13. (1.98935) BD ( 1) C  3- C  4
              ( 50.00%)   0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.6979 -0.4135  0.0000
              ( 50.00%)   0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.7071  0.3977  0.0000
 14. (1.66667) BD ( 2) C  3- C  4
              ( 50.00%)   0.7071* C  3 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
              ( 50.00%)   0.7071* C  4 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
 15. (1.98983) BD ( 1) C  3- H  9
              ( 51.74%)   0.7193* C  3 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.7161 -0.4134  0.0000
              ( 48.26%)   0.6947* H  9 s(100.00%)
                                        1.0000
 16. (1.98935) BD ( 1) C  4- C  5
              ( 50.00%)   0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.7071  0.3977  0.0000
              ( 50.00%)   0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.6979 -0.4135  0.0000
 17. (1.98983) BD ( 1) C  4- H 10
              ( 51.74%)   0.7193* C  4 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624  0.0000 -0.8269  0.0000
              ( 48.26%)   0.6947* H 10 s(100.00%)
                                        1.0000
 18. (1.98935) BD ( 1) C  5- C  6
              ( 50.00%)   0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.0092  0.8112  0.0000
              ( 50.00%)   0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.0092 -0.8112  0.0000
 19. (1.66667) BD ( 2) C  5- C  6
              ( 50.00%)   0.7071* C  5 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
              ( 50.00%)   0.7071* C  6 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
 20. (1.98983) BD ( 1) C  5- H 11
              ( 51.74%)   0.7193* C  5 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624 -0.7161 -0.4134  0.0000
              ( 48.26%)   0.6947* H 11 s(100.00%)
                                        1.0000
 21. (1.98983) BD ( 1) C  6- H 12
              ( 51.74%)   0.7193* C  6 s( 31.63%)p 2.16( 68.37%)
                                        0.0000  0.5624 -0.7161  0.4134  0.0000
              ( 48.26%)   0.6947* H 12 s(100.00%)
                                        1.0000
---------------- non-Lewis ----------------------------------------------------
 22. (0.01071) BD*( 1) C  1- C  2
              ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.7071 -0.3977  0.0000
              ( 50.00%)  -0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.6979  0.4135  0.0000
 23. (0.33333) BD*( 2) C  1- C  2
              ( 50.00%)   0.7071* C  1 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
              ( 50.00%)  -0.7071* C  2 s(  0.00%)p 1.00(100.00%)
```

```
                                        0.0000  0.0000  0.0000  0.0000  1.0000
24. (0.01071) BD*( 1) C  1- C  6
              ( 50.00%)   0.7071* C  1 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.7071 -0.3977  0.0000
              ( 50.00%)  -0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.6979  0.4135  0.0000
25. (0.01016) BD*( 1) C  1- H  7
              ( 48.26%)   0.6947* C  1 s( 31.63%)p 2.16( 68.37%)
                                        0.0000 -0.5624  0.0000 -0.8269  0.0000
              ( 51.74%)  -0.7193* H  7 s(100.00%)
                                       -1.0000
26. (0.01071) BD*( 1) C  2- C  3
              ( 50.00%)   0.7071* C  2 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847 -0.0092  0.8112  0.0000
              ( 50.00%)  -0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847 -0.0092 -0.8112  0.0000
27. (0.01016) BD*( 1) C  2- H  8
              ( 48.26%)   0.6947* C  2 s( 31.63%)p 2.16( 68.37%)
                                        0.0000 -0.5624 -0.7161 -0.4134  0.0000
              ( 51.74%)  -0.7193* H  8 s(100.00%)
                                       -1.0000
28. (0.01071) BD*( 1) C  3- C  4
              ( 50.00%)   0.7071* C  3 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847  0.6979  0.4135  0.0000
              ( 50.00%)  -0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                        0.0000 -0.5847 -0.7071 -0.3977  0.0000
29. (0.33333) BD*( 2) C  3- C  4
              ( 50.00%)   0.7071* C  3 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000 -1.0000
              ( 50.00%)  -0.7071* C  4 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000 -1.0000
30. (0.01016) BD*( 1) C  3- H  9
              ( 48.26%)   0.6947* C  3 s( 31.63%)p 2.16( 68.37%)
                                        0.0000 -0.5624 -0.7161  0.4134  0.0000
              ( 51.74%)  -0.7193* H  9 s(100.00%)
                                       -1.0000
31. (0.01071) BD*( 1) C  4- C  5
              ( 50.00%)   0.7071* C  4 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.7071  0.3977  0.0000
              ( 50.00%)  -0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847  0.6979 -0.4135  0.0000
32. (0.01016) BD*( 1) C  4- H 10
              ( 48.26%)   0.6947* C  4 s( 31.63%)p 2.16( 68.37%)
                                        0.0000 -0.5624  0.0000  0.8269  0.0000
              ( 51.74%)  -0.7193* H 10 s(100.00%)
                                       -1.0000
33. (0.01071) BD*( 1) C  5- C  6
              ( 50.00%)   0.7071* C  5 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.0092  0.8112  0.0000
              ( 50.00%)  -0.7071* C  6 s( 34.19%)p 1.93( 65.81%)
                                        0.0000  0.5847 -0.0092 -0.8112  0.0000
34. (0.33333) BD*( 2) C  5- C  6
              ( 50.00%)   0.7071* C  5 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
              ( 50.00%)  -0.7071* C  6 s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  1.0000
35. (0.01016) BD*( 1) C  5- H 11
              ( 48.26%)   0.6947* C  5 s( 31.63%)p 2.16( 68.37%)
                                        0.0000 -0.5624  0.7161  0.4134  0.0000
              ( 51.74%)  -0.7193* H 11 s(100.00%)
                                       -1.0000
36. (0.01016) BD*( 1) C  6- H 12
              ( 48.26%)   0.6947* C  6 s( 31.63%)p 2.16( 68.37%)
                                        0.0000 -0.5624  0.7161 -0.4134  0.0000
              ( 51.74%)  -0.7193* H 12 s(100.00%)
                                       -1.0000
```

As one can see from this table, the set of NBOs obtained by the program corresponds to one of the two equivalent Kekulé structures, with reasonably well localized σ_{CC} and σ_{CH} NBOs (1.9894 and 1.9898 electrons, respectively), but three severely depleted π_{CC} bonds (1.6667e) and corresponding high occupancy π^*_{CC} antibonds (0.3333e). Other sections of the NBO output (not shown) will similarly exhibit the sharp distinctions between benzene and more typical (non-aromatic) compounds.

In the case of the completely symmetric (D_{6h}) structure, the NBO program "arbitrarily" chooses one of the two equivalent localized Kekulé structures (in this case, the one with pi bonds between carbon atoms 1-2, 3-4, and 5-6), dependent on atom numbering. However, if slight distortions are introduced, the program will recognize that the two Kekulé structures are no longer exactly degenerate, and will return the unique "best" structure (of lowest ρ^*). More subtle aspects of the near-equivalency of aromatic Kekulé structures may be studied by the NRT method of Sec. B.8, avoiding the apparent "discontinuity" of bonding pattern in the main NBO structure that may occur when two closely related aromatic systems are compared.

B.6.7 NOBOND Keyword

The NOBOND keyword forces the NBO program to analyze the wavefunction in terms of 1-center functions only, thus forcing a description of the bonding in terms of atomic or ionic hybrids. The modifications of NBO output that result from activating this keyword can be illustrated for the HF molecule (RHF/3-21G level). This molecule might be described in terms of a polar covalent H-F bond or in terms of ionic H^+ F^- interactions.

The default NBO analysis of this example is shown below:

```
NATURAL BOND ORBITAL ANALYSIS:

                          Occupancies       Lewis Structure    Low   High
        Max    Occ     -------------------  -----------------   occ   occ
 Cycle  Ctr   Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
================================================================================
   1     2     1.90     9.99942   0.00058      1   1   0   3     0      0
--------------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

-------------------------------------------------------
  Core                     1.99993 ( 99.997% of   2)
  Valence Lewis            7.99948 ( 99.994% of   8)
 ==================      ============================
  Total Lewis              9.99942 ( 99.994% of  10)
 -------------------------------------------------------
  Valence non-Lewis        0.00000 (  0.000% of  10)
  Rydberg non-Lewis        0.00058 (  0.006% of  10)
 ==================      ============================
  Total non-Lewis          0.00058 (  0.006% of  10)
-------------------------------------------------------


    (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ----------------------------------------------------
  1. (1.99993) CR ( 1) F  1            s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000
  2. (2.00000) LP ( 1) F  1            s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  1.0000 -0.0013
                                        0.0000  0.0000  0.0000  0.0000
  3. (2.00000) LP ( 2) F  1            s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        1.0000 -0.0013  0.0000  0.0000
  4. (1.99948) LP ( 3) F  1            s( 83.71%)p 0.19( 16.29%)
                                        0.0000  0.9149 -0.0052  0.0000  0.0000
                                        0.0000  0.0000  0.4036  0.0062
  5. (2.00000) BD ( 1) F  1- H  2
             ( 75.22%)   0.8673* F  1 s( 16.31%)p 5.13( 83.69%)
                                        0.0000 -0.4036 -0.0158  0.0000  0.0000
                                        0.0000  0.0000  0.9148  0.0001
             ( 24.78%)   0.4978* H  2 s(100.00%)
                                       -1.0000  0.0000
---------------- non-Lewis ------------------------------------------------
  6. (0.00000) BD*( 1) F  1- H  2
             ( 24.78%)   0.4978* F  1 s( 16.31%)p 5.13( 83.69%)
             ( 75.22%)  -0.8673* H  2 s(100.00%)
  7. (0.00002) RY ( 1) F  1            s(  0.00%)p 1.00(100.00%)
  8. (0.00000) RY ( 2) F  1            s( 99.97%)p 0.00(  0.03%)
  9. (0.00000) RY ( 3) F  1            s(  0.00%)p 1.00(100.00%)
```

```
  10. (0.00000) RY ( 4) F  1            s(  0.00%)p 1.00(100.00%)
  11. (0.00056) RY ( 1) H  2            s(100.00%)
                                         0.0000  1.0000
```

As the output shows, default NBO analysis leads to a polar covalent description of HF. The σ_{HF} bond, NBO 1, is formed from a *p*-rich ($sp^{5.13}$, 83.69% *p*-character) hybrid on F and the 1*s* AO on H, strongly polarized (about 75.22%) toward F. This provides a satisfactory Lewis structure, describing 99.994% of the total electron density.

When the NOBOND keyword is activated to bypass the search for 2-center bonds, the NBO output is modified as shown below:

```
      /NOBOND / : No two-center NBO search

NATURAL BOND ORBITAL ANALYSIS:

                            Occupancies       Lewis Structure    Low   High
         Max    Occ     -------------------  -----------------   occ   occ
  Cycle  Ctr   Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
 ========================================================================
    1     1     1.00     9.50379   0.49621      1   0   0   4     0      1
 ------------------------------------------------------------------------

 Structure accepted: Search for bonds prevented by NOBOND keyword

 ---------------------------------------------------
   Core                    1.99993 ( 99.997% of   2)
   Valence Lewis           7.50386 ( 93.798% of   8)
  ==================      ============================
   Total Lewis             9.50379 ( 95.038% of  10)
  ---------------------------------------------------
   Valence non-Lewis       0.49563 (  4.956% of  10)
   Rydberg non-Lewis       0.00058 (  0.006% of  10)
  ==================      ============================
   Total non-Lewis         0.49621 (  4.962% of  10)
 ---------------------------------------------------

     (Occupancy)   Bond orbital / Coefficients / Hybrids
 ------------------ Lewis ------------------------------------------------------
   1. (1.99993) CR ( 1) F  1            s(100.00%)
                                         1.0000  0.0000  0.0000  0.0000  0.0000
                                         0.0000  0.0000  0.0000  0.0000
   2. (2.00000) LP ( 1) F  1            s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  1.0000 -0.0013
                                         0.0000  0.0000  0.0000  0.0000
   3. (2.00000) LP ( 2) F  1            s(  0.00%)p 1.00(100.00%)
                                         0.0000  0.0000  0.0000  0.0000  0.0000
                                         1.0000 -0.0013  0.0000  0.0000
   4. (1.99948) LP ( 3) F  1            s( 83.71%)p 0.19( 16.29%)
                                         0.0000  0.9149 -0.0052  0.0000  0.0000
                                         0.0000  0.0000  0.4036  0.0062
   5. (1.50437) LP ( 4) F  1            s( 16.31%)p 5.13( 83.69%)
                                         0.0000  0.4036  0.0158  0.0000  0.0000
                                         0.0000  0.0000 -0.9148 -0.0001
 ---------------- non-Lewis ----------------------------------------------------
   6. (0.49563) LP ( 1) H  2            s(100.00%)
                                         1.0000  0.0000
   7. (0.00002) RY ( 1) F  1            s(  0.00%)p 1.00(100.00%)
   8. (0.00000) RY ( 2) F  1            s( 99.97%)p 0.00(  0.03%)
```

```
  9. (0.00000) RY ( 3) F  1           s(  0.00%)p 1.00(100.00%)
 10. (0.00000) RY ( 4) F  1           s(  0.00%)p 1.00(100.00%)
 11. (0.00056) RY ( 1) H  2           s(100.00%)
                                       0.0000  1.0000
```

In this case, the NBO output indicates a rather poor Lewis structure (4.962% non-Lewis density), with a severely depleted F^- lone pair (NBO 5, the $sp^{5.13}$ hybrid) and significant occupancy (about 0.496e) in the 'empty' H^+ 1*s* orbital (NBO 6) of the cation. The NOBOND comparison would therefore indicate the superiority of a polar covalent description in this case.

B.6.8 Hypovalent Bonding: Diborane

When the standard NBO search of previous NBO program versions is applied to diborane or related electron-deficient compounds, one finds a dramatic failure to represent the electronic distribution in terms of 1- and 2-center (1c/2c) functions only. For example, for B_2H_6 (RHF/3-21G level), the default NBO search of *NBO 5.0* returns a fractured set of 4 units (two BH_2^+ and two H^- fragments), with about 2.14 electrons unaccounted for (13.4% non-Lewis occupancy), symptomatic of severe breakdown of the conventional Lewis structure representation. Only with inclusion of the "3CBOND" keyword was the NBO search extended to 3-center bridge-bonding NBOs that are generally required to describe such species accurately.

In *NBO 7.0*, however, no special 3CBOND keyword is required. Instead, the NBO search is *always* widened to include possible 3-center electron-pair (3c/2e) bonds if the conventional 1c/2c search fails to yield a satisfactory Lewis structure. For diborane, one obtains the NBO output shown below:

```
NATURAL BOND ORBITAL ANALYSIS:

                           Occupancies       Lewis Structure    Low   High
        Max    Occ     -------------------  -----------------   occ   occ
 Cycle  Ctr   Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
 ============================================================================
   1     2     1.90    13.86001   2.13999      2   4   0   2     2      4
   2     3     1.90    15.94323   0.05677      2   4   2   0     0      0
 ----------------------------------------------------------------------------

 Structure accepted: No low occupancy Lewis orbitals

          1 low occupancy (<1.9990e) core orbital  found on  B 1
          1 low occupancy (<1.9990e) core orbital  found on  B 2

 ------------------------------------------------------
  Core                     3.99702 ( 99.925% of   4)
  Valence Lewis           11.94621 ( 99.552% of  12)
 ==================      ============================
  Total Lewis             15.94323 ( 99.645% of  16)
 ------------------------------------------------------
  Valence non-Lewis        0.04574 (  0.286% of  16)
  Rydberg non-Lewis        0.01103 (  0.069% of  16)
 ==================      ============================
  Total non-Lewis          0.05677 (  0.355% of  16)
 ------------------------------------------------------


    (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ---------------------------------------------------
  1. (1.99851) CR ( 1) B  1           s(100.00%)
                                       1.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0000  0.0000  0.0000  0.0000
  2. (1.99851) CR ( 1) B  2           s(100.00%)
                                       1.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0000  0.0000  0.0000  0.0000
  3. (1.99425) BD ( 1) B  1- H  6
```

```
              ( 48.80%)   0.6986* B  1 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062  0.4274  0.0221
                                      -0.7067  0.0244  0.0000  0.0000
              ( 51.20%)   0.7155* H  6 s(100.00%)
                                       1.0000  0.0004
   4. (1.99425) BD ( 1) B  1- H  7
              ( 48.80%)   0.6986* B  1 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062  0.4274  0.0221
                                       0.7067 -0.0244  0.0000  0.0000
              ( 51.20%)   0.7155* H  7 s(100.00%)
                                       1.0000  0.0004
   5. (1.99425) BD ( 1) B  2- H  5
              ( 48.80%)   0.6986* B  2 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                       0.7067 -0.0244  0.0000  0.0000
              ( 51.20%)   0.7155* H  5 s(100.00%)
                                       1.0000  0.0004
   6. (1.99425) BD ( 1) B  2- H  8
              ( 48.80%)   0.6986* B  2 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                      -0.7067  0.0244  0.0000  0.0000
              ( 51.20%)   0.7155* H  8 s(100.00%)
                                       1.0000  0.0004
   7. (1.98461) 3C ( 1) B  1- B  2- H  3
              ( 26.44%)   0.5142* B  1 s( 18.30%)p 4.46( 81.70%)
                                       0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                       0.0000  0.0000 -0.7067 -0.0246
              ( 26.44%)   0.5142* B  2 s( 18.30%)p 4.46( 81.70%)
                                       0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                       0.0000  0.0000 -0.7067 -0.0246
              ( 47.13%)   0.6865* H  3 s(100.00%)
                                      -1.0000 -0.0066
   8. (1.98461) 3C ( 1) B  1- B  2- H  4
              ( 26.44%)   0.5142* B  1 s( 18.30%)p 4.46( 81.70%)
                                       0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                       0.0000  0.0000  0.7067  0.0246
              ( 26.44%)   0.5142* B  2 s( 18.30%)p 4.46( 81.70%)
                                       0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                       0.0000  0.0000  0.7067  0.0246
              ( 47.13%)   0.6865* H  4 s(100.00%)
                                      -1.0000 -0.0066
---------------- non-Lewis ----------------------------------------------------
   9. (0.00400) BD*( 1) B  1- H  6
              ( 51.20%)   0.7155* B  1 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062  0.4274  0.0221
                                      -0.7067  0.0244  0.0000  0.0000
              ( 48.80%)  -0.6986* H  6 s(100.00%)
                                       1.0000  0.0004
  10. (0.00400) BD*( 1) B  1- H  7
              ( 51.20%)   0.7155* B  1 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062  0.4274  0.0221
                                       0.7067 -0.0244  0.0000  0.0000
              ( 48.80%)  -0.6986* H  7 s(100.00%)
                                       1.0000  0.0004
  11. (0.00400) BD*( 1) B  2- H  5
              ( 51.20%)   0.7155* B  2 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                       0.7067 -0.0244  0.0000  0.0000
              ( 48.80%)  -0.6986* H  5 s(100.00%)
                                       1.0000  0.0004
  12. (0.00400) BD*( 1) B  2- H  8
              ( 51.20%)   0.7155* B  2 s( 31.69%)p 2.16( 68.31%)
                                       0.0000  0.5629 -0.0062 -0.4274 -0.0221
                                      -0.7067  0.0244  0.0000  0.0000
              ( 48.80%)  -0.6986* H  8 s(100.00%)
                                       1.0000  0.0004
  13. (0.01445) 3C*( 1) B  1- B  2- H  3
              ( 23.56%)   0.4854* B  1 s( 18.30%)p 4.46( 81.70%)
                                       0.0000  0.4276  0.0124 -0.5630  0.0008
                                       0.0000  0.0000  0.7067  0.0246
              ( 23.56%)   0.4854* B  2 s( 18.30%)p 4.46( 81.70%)
```

```
                                      0.0000  0.4276  0.0124  0.5630 -0.0008
                                      0.0000  0.0000  0.7067  0.0246
             ( 52.87%)   0.7271* H  3 s(100.00%)
                                     -1.0000 -0.0066
 14. (0.01445) 3C*( 1) B  1- B  2- H  4
             ( 23.56%)   0.4854* B  1 s( 18.30%)p 4.46( 81.70%)
                                      0.0000  0.4276  0.0124 -0.5630  0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
             ( 23.56%)   0.4854* B  2 s( 18.30%)p 4.46( 81.70%)
                                      0.0000  0.4276  0.0124  0.5630 -0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
             ( 52.87%)   0.7271* H  4 s(100.00%)
                                     -1.0000 -0.0066
 15. (0.00041) 3Cn( 1) B  1- B  2- H  3
             ( 50.00%)   0.7071* B  1 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
             ( 50.00%)  -0.7071* B  2 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                      0.0000  0.0000 -0.7067 -0.0246
             (  0.00%)   0.0000* H  3 s(  0.00%)p 0.00(  0.00%)
                                      0.0000  0.0000
 16. (0.00041) 3Cn( 1) B  1- B  2- H  4
             ( 50.00%)   0.7071* B  1 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124  0.5630 -0.0008
                                      0.0000  0.0000  0.7067  0.0246
             ( 50.00%)  -0.7071* B  2 s( 18.30%)p 4.46( 81.70%)
                                      0.0000 -0.4276 -0.0124 -0.5630  0.0008
                                      0.0000  0.0000  0.7067  0.0246
             (  0.00%)   0.0000* H  4 s(  0.00%)p 0.00(  0.00%)
                                      0.0000  0.0000
 17. (0.00148) RY ( 1) B  1           s(  0.00%)p 1.00(100.00%)
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0345  0.9994  0.0000  0.0000
 18. (0.00081) RY ( 2) B  1           s(  4.04%)p23.76( 95.96%)
                                      0.0000  0.0244  0.1995  0.0215 -0.9794
                                      0.0000  0.0000  0.0000  0.0000
 19. (0.00002) RY ( 3) B  1           s( 95.99%)p 0.04(  4.01%)
 20. (0.00000) RY ( 4) B  1           s(  0.00%)p 1.00(100.00%)
 21. (0.00148) RY ( 1) B  2           s(  0.00%)p 1.00(100.00%)
                                      0.0000  0.0000  0.0000  0.0000  0.0000
                                      0.0345  0.9994  0.0000  0.0000
 22. (0.00081) RY ( 2) B  2           s(  4.04%)p23.76( 95.96%)
                                      0.0000  0.0244  0.1995 -0.0215  0.9794
                                      0.0000  0.0000  0.0000  0.0000
 23. (0.00002) RY ( 3) B  2           s( 95.99%)p 0.04(  4.01%)
 24. (0.00000) RY ( 4) B  2           s(  0.00%)p 1.00(100.00%)
 25. (0.00181) RY ( 1) H  3           s(100.00%)
                                     -0.0066  1.0000
 26. (0.00181) RY ( 1) H  4           s(100.00%)
                                     -0.0066  1.0000
 27. (0.00070) RY ( 1) H  5           s(100.00%)
                                     -0.0004  1.0000
 28. (0.00070) RY ( 1) H  6           s(100.00%)
                                     -0.0004  1.0000
 29. (0.00070) RY ( 1) H  7           s(100.00%)
                                     -0.0004  1.0000
 30. (0.00070) RY ( 1) H  8           s(100.00%)
                                     -0.0004  1.0000
```

The resulting NBO Lewis structure has improved significantly [only 0.057e (0.36%) non-Lewis occupancy]. The structure includes the expected 3-center B-H-B bonds (NBOs 7, 8), each with reasonably high occupancy (1.9846e). Each 3-c bond is composed of *p*-rich ($sp^{4.46}$) boron hybrids and the hydrogen 1*s* NAO, with about 47.13% of the orbital density on the central hydrogen. Note

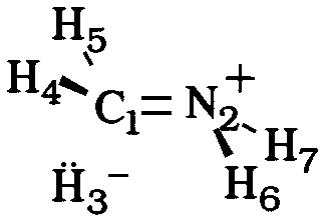
that each 3-center bond NBO is associated with *two* 3-c non-Lewis NBOs [viz., NBOs 13 ("3C*") and 15 ("3Cn") for the first 3-c bond], which contribute in distinct ways to delocalization interactions. The "3C*" and "3Cn" labels are assigned to the orbital with "greater" and "lesser" 3-center character, respectively, i.e.. "n" has the smaller ("non-bonding") contribution from its least important atomic component).

Of course, the accuracy of *any* standard Lewis structure might be improved slightly by extending the NBO search from 2-center to 3-center bonds, thus allowing greater variational flexibility to maximize occupancy. However, this example illustrates the kind of *qualitative* improvement that signals the need for a truly new type of 3-center "connector" to augment the zeroth-order 1c/2c picture of Lewis structural bonding.

Note that the NBO 3c label may appear to have the wrong connectivity (as in the present case, e.g., where "B 1- B 2- H 3" is written instead of the more reasonable "B 1- H 3- B 2"). This is a consequence of the fact that the NBO algorithms have no inkling of the positions of the atoms in space, and thus of which label is more "reasonable."

B.6.9 NBO Directed Search ($CHOOSE Keylist)

To illustrate the $CHOOSE keylist for a directed NBO search, we again make use of the methylamine example (Section A.3). The vicinal $n_N \rightarrow \sigma^*_{CH}$ delocalization, to which attention has been repeatedly called in the examples, may be associated, in resonance theory terms, with the "double-bond, no-bond" resonance structure shown below:



To investigate the suitability of this resonance structure for describing the methylamine wavefunction, we would specify the $CHOOSE keylist (Section B.4) as follows:

```
$CHOOSE             !double-bond, no-bond resonance
   LONE  3  1  END
   BOND  S 1 4  S 1 5  D 1 2  S 2 6  S 2 7  END
$END
```

When this is included in the input file, the NBO program produces the output shown below:

```
NATURAL BOND ORBITAL ANALYSIS:
Reading $CHOOSE keylist

                          Occupancies       Lewis Structure    Low   High
       Max    Occ      -------------------  -----------------   occ   occ
 Cycle  Ctr   Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
================================================================================
   1     2     0.71    16.67241   1.32759      2   6   0   1     0      2
--------------------------------------------------------------------------------

Structure accepted: NBOs selected via the $CHOOSE keylist

-----------------------------------------------------
  Core                     3.99853 ( 99.963% of   4)
  Valence Lewis           12.67387 ( 90.528% of  14)
 ==================      ============================
  Total Lewis             16.67241 ( 92.624% of  18)
 -----------------------------------------------------
  Valence non-Lewis        1.29951 (  7.220% of  18)
  Rydberg non-Lewis        0.02808 (  0.156% of  18)
 ==================      ============================
  Total non-Lewis          1.32759 (  7.376% of  18)
-----------------------------------------------------

    (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ----------------------------------------------------
  1. (1.99901) CR ( 1) C  1            s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
```

```
                                     0.0000  0.0000  0.0000  0.0000
   2. (1.99953) CR ( 1) N  2        s(100.00%)
                                     1.0000  0.0000  0.0000  0.0000  0.0000
                                     0.0000  0.0000  0.0000  0.0000
   3. (0.81422) LP ( 1) H  3        s(100.00%)
                                     1.0000  0.0000
   4. (1.96987) BD ( 1) C  1- N  2
              (  6.75%)   0.2598* C  1 s(  0.71%)p99.99( 99.29%)
                                     0.0000  0.0822  0.0182  0.5683 -0.0569
                                     0.8142 -0.0612  0.0000  0.0000
              ( 93.25%)   0.9657* N  2 s( 19.87%)p 4.03( 80.13%)
                                     0.0000 -0.4458  0.0000 -0.0427 -0.0067
                                     0.8940 -0.0111  0.0000  0.0000
   5. (1.92744) BD ( 2) C  1- N  2
              ( 39.65%)   0.6297* C  1 s( 39.10%)p 1.56( 60.90%)
                                     0.0000  0.6241  0.0374 -0.6684 -0.0667
                                     0.3945 -0.0469  0.0000  0.0000
              ( 60.35%)   0.7769* N  2 s( 20.55%)p 3.87( 79.45%)
                                     0.0000  0.4534 -0.0012  0.8504 -0.0020
                                     0.2665 -0.0135  0.0000  0.0000
   6. (1.98627) BD ( 1) C  1- H  4
              ( 61.01%)   0.7811* C  1 s( 29.91%)p 2.34( 70.09%)
                                     0.0000  0.5469 -0.0001  0.3391 -0.0075
                                    -0.2929 -0.0075  0.7070 -0.0104
              ( 38.99%)   0.6244* H  4 s(100.00%)
                                     1.0000  0.0008
   7. (1.98627) BD ( 1) C  1- H  5
              ( 61.01%)   0.7811* C  1 s( 29.91%)p 2.34( 70.09%)
                                     0.0000  0.5469 -0.0001  0.3391 -0.0075
                                    -0.2929 -0.0075 -0.7070  0.0104
              ( 38.99%)   0.6244* H  5 s(100.00%)
                                     1.0000  0.0008
   8. (1.99490) BD ( 1) N  2- H  6
              ( 68.36%)   0.8268* N  2 s( 29.77%)p 2.36( 70.23%)
                                     0.0000  0.5456  0.0005 -0.3706 -0.0171
                                     0.2542 -0.0038 -0.7070 -0.0093
              ( 31.64%)   0.5625* H  6 s(100.00%)
                                     1.0000  0.0031
   9. (1.99490) BD ( 1) N  2- H  7
              ( 68.36%)   0.8268* N  2 s( 29.77%)p 2.36( 70.23%)
                                     0.0000  0.5456  0.0005 -0.3706 -0.0171
                                     0.2542 -0.0038  0.7070  0.0093
              ( 31.64%)   0.5625* H  7 s(100.00%)
                                     1.0000  0.0031
---------------- non-Lewis ----------------------------------------------------
  10. (1.02153) BD*( 1) C  1- N  2
              ( 93.25%)   0.9657* C  1 s(  0.71%)p99.99( 99.29%)
                                     0.0000  0.0822  0.0182  0.5683 -0.0569
                                     0.8142 -0.0612  0.0000  0.0000
              (  6.75%)  -0.2598* N  2 s( 19.87%)p 4.03( 80.13%)
                                     0.0000 -0.4458  0.0000 -0.0427 -0.0067
                                     0.8940 -0.0111  0.0000  0.0000
  11. (0.23037) BD*( 2) C  1- N  2
              ( 60.35%)   0.7769* C  1 s( 39.10%)p 1.56( 60.90%)
                                     0.0000  0.6241  0.0374 -0.6684 -0.0667
                                     0.3945 -0.0469  0.0000  0.0000
              ( 39.65%)  -0.6297* N  2 s( 20.55%)p 3.87( 79.45%)
                                     0.0000  0.4534 -0.0012  0.8504 -0.0020
                                     0.2665 -0.0135  0.0000  0.0000
  12. (0.01206) BD*( 1) C  1- H  4
              ( 38.99%)   0.6244* C  1 s( 29.91%)p 2.34( 70.09%)
                                     0.0000 -0.5469  0.0001 -0.3391  0.0075
                                     0.2929  0.0075 -0.7070  0.0104
              ( 61.01%)  -0.7811* H  4 s(100.00%)
                                    -1.0000 -0.0008
  13. (0.01206) BD*( 1) C  1- H  5
              ( 38.99%)   0.6244* C  1 s( 29.91%)p 2.34( 70.09%)
                                     0.0000 -0.5469  0.0001 -0.3391  0.0075
                                     0.2929  0.0075  0.7070 -0.0104
              ( 61.01%)  -0.7811* H  5 s(100.00%)
                                    -1.0000 -0.0008
```

```
 14. (0.01174) BD*( 1) N  2- H  6
              ( 31.64%)   0.5625* N  2 s( 29.77%)p 2.36( 70.23%)
                                        0.0000 -0.5456 -0.0005  0.3706  0.0171
                                       -0.2542  0.0038  0.7070  0.0093
              ( 68.36%)  -0.8268* H  6 s(100.00%)
                                       -1.0000 -0.0031
 15. (0.01174) BD*( 1) N  2- H  7
              ( 31.64%)   0.5625* N  2 s( 29.77%)p 2.36( 70.23%)
                                        0.0000 -0.5456 -0.0005  0.3706  0.0171
                                       -0.2542  0.0038 -0.7070 -0.0093
              ( 68.36%)  -0.8268* H  7 s(100.00%)
                                       -1.0000 -0.0031
 16. (0.01936) RY ( 1) C  1            s( 10.51%)p 8.51( 89.49%)
                                        0.0000 -0.0740  0.3157  0.0052 -0.7444
                                       -0.0985 -0.5753  0.0000  0.0000
 17. (0.00032) RY ( 2) C  1            s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0147  0.9999
 18. (0.00024) RY ( 3) C  1            s( 58.63%)p 0.71( 41.37%)
                                        0.0000 -0.0010  0.7657  0.0177 -0.1576
                                        0.0064  0.6233  0.0000  0.0000
 19. (0.00003) RY ( 4) C  1            s( 31.23%)p 2.20( 68.77%)
 20. (0.00116) RY ( 1) N  2            s(  1.59%)p62.07( 98.41%)
                                        0.0000 -0.0066  0.1257 -0.0071 -0.0764
                                       -0.0164 -0.9889  0.0000  0.0000
 21. (0.00042) RY ( 2) N  2            s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000 -0.0131  0.9999
 22. (0.00039) RY ( 3) N  2            s( 33.56%)p 1.98( 66.44%)
                                        0.0000  0.0135  0.5791 -0.0082  0.8149
                                        0.0126  0.0104  0.0000  0.0000
 23. (0.00002) RY ( 4) N  2            s( 64.89%)p 0.54( 35.11%)
 24. (0.00175) RY ( 1) H  3            s(100.00%)
                                        0.0000  1.0000
 25. (0.00096) RY ( 1) H  4            s(100.00%)
                                       -0.0008  1.0000
 26. (0.00096) RY ( 1) H  5            s(100.00%)
                                       -0.0008  1.0000
 27. (0.00124) RY ( 1) H  6            s(100.00%)
                                       -0.0031  1.0000
 28. (0.00124) RY ( 1) H  7            s(100.00%)
```

One can see that the $CHOOSE resonance structure is significantly inferior to the principal resonance structure found by the default NBO search in Section A.3. About 1.33e, or 7.4% of the electron density, is found in non-Lewis NBOs of the $CHOOSE structure (compared to 0.05e, or 0.3%, for the principal structure). Particularly defective is the hydride `lone pair' (NBO 3), which has less than half the expected occupancy (0.814e). The C-N π bond (NBO 4) is seen to be more than 93% polarized toward N, indicative of essential lone pair character.

Note that structural elements shared by the two resonance structures (e.g., the two N-H bonds, which are common to both structures) need not have identical forms, since each detail of the NBOs is optimized with respect to the overall structure.

B.6.10 NBO Energetic Analysis ($DEL Keylist)

The NBO energetic analysis with deletions ($DEL keylist) will be illustrated with two simple examples for RHF/3-21G methylamine (Section A.3).

The first example is the "LEWIS" option (type 4, Section B.5), requesting deletion of all non-Lewis orbitals, and hence leading to the energy of the idealized Natural Lewis Structure (NLS). (In former NBO versions, this option was known as the "NOSTAR" deletion, an alias that is retained for compatibility.) The $DEL keylist in this case is

```
    $DEL   LEWIS   $END
```

which leads to the output shown below:

```
LEWIS: Delete all non-Lewis NBOs
Deletion of the following orbitals from the NBO Fock matrix:
  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28

Orbital occupancies:

      Orbital                          No deletions  This deletion    Change
-------------------------------------------------------------------------------
   1. CR ( 1) C  1                       1.99900        2.00000       0.00100
   2. CR ( 1) N  2                       1.99953        2.00000       0.00047
   3. LP ( 1) N  2                       1.97795        2.00000       0.02205
   4. BD ( 1) C  1- N  2                 1.99856        2.00000       0.00144
   5. BD ( 1) C  1- H  3                 1.99861        2.00000       0.00139
   6. BD ( 1) C  1- H  4                 1.99401        2.00000       0.00599
   7. BD ( 1) C  1- H  5                 1.99401        2.00000       0.00599
   8. BD ( 1) N  2- H  6                 1.99441        2.00000       0.00559
   9. BD ( 1) N  2- H  7                 1.99441        2.00000       0.00559
  10. BD*( 1) C  1- N  2                 0.00012        0.00000      -0.00012
  11. BD*( 1) C  1- H  3                 0.01569        0.00000      -0.01569
  12. BD*( 1) C  1- H  4                 0.00770        0.00000      -0.00770
  13. BD*( 1) C  1- H  5                 0.00770        0.00000      -0.00770
  14. BD*( 1) N  2- H  6                 0.00427        0.00000      -0.00427
  15. BD*( 1) N  2- H  7                 0.00427        0.00000      -0.00427
  16. RY ( 1) C  1                       0.00105        0.00000      -0.00105
  17. RY ( 2) C  1                       0.00034        0.00000      -0.00034
  18. RY ( 3) C  1                       0.00022        0.00000      -0.00022
  19. RY ( 4) C  1                       0.00002        0.00000      -0.00002
  20. RY ( 1) N  2                       0.00116        0.00000      -0.00116
  21. RY ( 2) N  2                       0.00044        0.00000      -0.00044
  22. RY ( 3) N  2                       0.00038        0.00000      -0.00038
  23. RY ( 4) N  2                       0.00002        0.00000      -0.00002
  24. RY ( 1) H  3                       0.00178        0.00000      -0.00178
  25. RY ( 1) H  4                       0.00096        0.00000      -0.00096
  26. RY ( 1) H  5                       0.00096        0.00000      -0.00096
  27. RY ( 1) H  6                       0.00122        0.00000      -0.00122
  28. RY ( 1) H  7                       0.00122        0.00000      -0.00122

NEXT STEP:  Evaluate the energy of the new density matrix
            that has been constructed from the deleted NBO
            Fock matrix by doing one SCF cycle.

-------------------------------------------------------------------------------

  Energy of deletion :        -94.618078245
    Total SCF energy :        -94.679444938
                       --------------------
       Energy change :          0.061367 a.u.,          38.508 kcal/mol
```

In the output above, the NBO program first enumerates the 19 NBOs to be deleted by the “LEWIS” request, then gives the complete list of NBOs with their occupancies before (“no deletions”) and after (“this deletion”) deletions, with the net change for each. For this LEWIS deletion, each of the nine Lewis NBOs (1-9) necessarily gets 2.0000 electrons, and each of the non-Lewis NBOs (10-28) gets occupancy 0.0000. The program than reports the energy (−94.618078 a.u.) obtained from a single pass through the SCF evaluator with the modified density matrix. In this case, deletion of the 19 non-Lewis orbitals led to an energy change of only 0.061367 a.u. (38.5 kcal/mol), less than 0.07% of the total energy.

The next example is a more selective set of deletions between `chemical fragments' (type 9), selected by the $DEL keylist input shown below:

```
    $DEL
       ZERO  2  ATOM BLOCKS
                 4  BY  3
                    1  3  4  5
                    2  6  7
                 3  BY  4
                    2  6  7
                    1  3  4  5
    $END
```

This specifies removal of all delocalizing interactions from Lewis NBOs of the methyl fragment (atoms 1,3,4,5) into non-Lewis NBOs of the amine fragment (atoms 2,6,7), or vice versa. The NBO output for this example is shown below:

```
Zero delocalization from NBOs localized on atoms:
    1   3   4   5
 to NBOs localized on atoms:
    2   6   7
     (NBOs in common to the two groups of atoms left out)
 Zero delocalization from NBOs localized on atoms:
    2   6   7
 to NBOs localized on atoms:
    1   3   4   5
     (NBOs in common to the two groups of atoms left out)
 Deletion of the NBO Fock matrix elements between orbitals:
    1   5   6   7
 and orbitals:
   14  15  20  21  22  23  27  28
 Deletion of the NBO Fock matrix elements between orbitals:
    2   3   8   9
 and orbitals:
   11  12  13  16  17  18  19  24  25  26

 Orbital occupancies:

       Orbital                        No deletions  This deletion    Change
 ------------------------------------------------------------------------------
```

```
   1. CR ( 1) C  1                    1.99900        1.99919       0.00019
   2. CR ( 1) N  2                    1.99953        1.99974       0.00021
   3. LP ( 1) N  2                    1.97795        1.99996       0.02201
   4. BD ( 1) C  1- N  2              1.99856        1.99857       0.00001
   5. BD ( 1) C  1- H  3              1.99861        1.99938       0.00077
   6. BD ( 1) C  1- H  4              1.99401        1.99915       0.00513
   7. BD ( 1) C  1- H  5              1.99401        1.99915       0.00513
   8. BD ( 1) N  2- H  6              1.99441        1.99979       0.00538
   9. BD ( 1) N  2- H  7              1.99441        1.99979       0.00538
  10. BD*( 1) C  1- N  2              0.00012        0.00027       0.00016
  11. BD*( 1) C  1- H  3              0.01569        0.00026      -0.01543
  12. BD*( 1) C  1- H  4              0.00770        0.00057      -0.00713
  13. BD*( 1) C  1- H  5              0.00770        0.00057      -0.00713
  14. BD*( 1) N  2- H  6              0.00427        0.00009      -0.00418
  15. BD*( 1) N  2- H  7              0.00427        0.00009      -0.00418
  16. RY ( 1) C  1                    0.00105        0.00016      -0.00090
  17. RY ( 2) C  1                    0.00034        0.00000      -0.00033
  18. RY ( 3) C  1                    0.00022        0.00002      -0.00020
  19. RY ( 4) C  1                    0.00002        0.00002       0.00000
  20. RY ( 1) N  2                    0.00116        0.00004      -0.00112
  21. RY ( 2) N  2                    0.00044        0.00000      -0.00044
  22. RY ( 3) N  2                    0.00038        0.00003      -0.00035
  23. RY ( 4) N  2                    0.00002        0.00001      -0.00001
  24. RY ( 1) H  3                    0.00178        0.00088      -0.00090
  25. RY ( 1) H  4                    0.00096        0.00057      -0.00039
  26. RY ( 1) H  5                    0.00096        0.00057      -0.00039
  27. RY ( 1) H  6                    0.00122        0.00057      -0.00065
  28. RY ( 1) H  7                    0.00122        0.00057      -0.00065

NEXT STEP:  Evaluate the energy of the new density matrix
            that has been constructed from the deleted NBO
            Fock matrix by doing one SCF cycle.

-------------------------------------------------------------------------------

  Energy of deletion :        -94.635054298
    Total SCF energy :        -94.679444938
                           --------------------
       Energy change :          0.044391 a.u.,          27.856 kcal/mol
-------------------------------------------------------------------------------
```

The output first lists the various orbitals and Fock matrix elements affected by this deletion, then the "before" and "after'" occupancies and net changes for each NBO. In this case, one can see that the principal effect of the deletion was increased occupancy (+0.022) of the nitrogen lone pair, NBO 3, and depleted occupancy (−0.015) of the antiperiplanar σ^*_{C1H3} antibond, NBO 11, with somewhat lesser depletion (−0.007) of the other two C-H antibonds. The total energy change (loss of delocalization energy) associated with this deletion was 27.9 kcal/mol.

To further pinpoint the source of this delocalization, one could do more selective deletions of individual orbitals or Fock matrix elements. For example, if one uses deletion type 2 (deletion of a single Fock matrix element, Section B.5.2) to delete the (3,11) element associated with the $n_N \rightarrow \sigma^*_{C1H3}$ interaction, one finds a deletion energy of 7.06 kcal/mol associated with this interaction alone. [This value may be compared with the simple second-order perturbative estimate (7.92 kcal/mol) of the $n_N \rightarrow \sigma^*_{C1H3}$ (3→11) interaction that was noted in Section A.3.5.]

B.6.11 Open-Shell UHF Output: Methyl Radical

Open-shell NBO output will be illustrated with the simple example of the planar methyl radical (CH_3), treated at the UHF/6-31G* level (R_{CH} = 1.0736 Å). In the open-shell case, one obtains two separate NPA and NBO listings, one for the α and one for the β spin set, corresponding to the "different Lewis structures for different spins" description. A portion of the NBO output for the α spin manifold is reproduced below:

```
NATURAL BOND ORBITAL ANALYSIS, alpha spin orbitals:

                          Occupancies       Lewis Structure    Low   High
        Max    Occ     ------------------  -----------------   occ   occ
 Cycle  Ctr   Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
=============================================================================
   1     2     0.95     4.99906   0.00094      1   3   0   1     0      0
-----------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

-----------------------------------------------------
  Core                     0.99984 ( 99.984% of   1)
  Valence Lewis            3.99923 ( 99.981% of   4)
 ==================      ============================
  Total Lewis              4.99906 ( 99.981% of   5)
 -----------------------------------------------------
  Valence non-Lewis        0.00070 (  0.014% of   5)
  Rydberg non-Lewis        0.00024 (  0.005% of   5)
 ==================      ============================
  Total non-Lewis          0.00094 (  0.019% of   5)
-----------------------------------------------------


    (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ----------------------------------------------------
  1. (0.99984) CR ( 1) C  1            s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
  2. (1.00000) LP ( 1) C  1            s(  0.00%)p 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.9975 -0.0708
                                        0.0000  0.0000  0.0000  0.0000  0.0000
  3. (0.99974) BD ( 1) C  1- H  2
             ( 60.49%)   0.7778* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                        0.0000  0.5773 -0.0030  0.0000 -0.4078
                                       -0.0120  0.7064  0.0208  0.0000  0.0000
                                       -0.0244  0.0000  0.0000 -0.0141 -0.0090
             ( 39.51%)   0.6286* H  2 s(100.00%)
                                        1.0000  0.0049
  4. (0.99974) BD ( 1) C  1- H  3
             ( 60.49%)   0.7778* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                        0.0000  0.5773 -0.0030  0.0000 -0.4078
                                       -0.0120 -0.7064 -0.0208  0.0000  0.0000
                                        0.0244  0.0000  0.0000 -0.0141 -0.0090
             ( 39.51%)   0.6286* H  3 s(100.00%)
                                        1.0000  0.0049
  5. (0.99974) BD ( 1) C  1- H  4
             ( 60.49%)   0.7778* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                        0.0000  0.5773 -0.0030  0.0000  0.8157
                                        0.0241  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0282 -0.0090
             ( 39.51%)   0.6286* H  4 s(100.00%)
```

```
                                        1.0000  0.0049
---------------- non-Lewis ----------------------------------------------------
  6. (0.00023) BD*( 1) C  1- H  2
               ( 39.51%)   0.6286* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                        0.0000 -0.5773  0.0030  0.0000  0.4078
                                        0.0120 -0.7064 -0.0208  0.0000  0.0000
                                        0.0244  0.0000  0.0000  0.0141  0.0090
               ( 60.49%)  -0.7778* H  2 s(100.00%)
                                       -1.0000 -0.0049
  7. (0.00023) BD*( 1) C  1- H  3
               ( 39.51%)   0.6286* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                        0.0000 -0.5773  0.0030  0.0000  0.4078
                                        0.0120  0.7064  0.0208  0.0000  0.0000
                                       -0.0244  0.0000  0.0000  0.0141  0.0090
               ( 60.49%)  -0.7778* H  3 s(100.00%)
                                       -1.0000 -0.0049
  8. (0.00023) BD*( 1) C  1- H  4
               ( 39.51%)   0.6286* C  1 s( 33.33%)p 2.00( 66.59%)d 0.00(  0.09%)
                                        0.0000 -0.5773  0.0030  0.0000 -0.8157
                                       -0.0241  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000 -0.0282  0.0090
               ( 60.49%)  -0.7778* H  4 s(100.00%)
                                       -1.0000 -0.0049
  9. (0.00000) RY ( 1) C  1            s( 17.19%)p 0.00(  0.00%)d 4.82( 82.81%)
 10. (0.00000) RY ( 2) C  1            s( 85.66%)p 0.01(  0.58%)d 0.16( 13.76%)
 11. (0.00000) RY ( 3) C  1            s(  0.00%)p 1.00( 97.18%)d 0.03(  2.82%)
 12. (0.00000) RY ( 4) C  1            s(  0.62%)p99.99( 94.94%)d 7.17(  4.44%)
 13. (0.00000) RY ( 5) C  1            s(  4.96%)p 0.80(  3.95%)d18.36( 91.09%)
 14. (0.00000) RY ( 6) C  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 15. (0.00000) RY ( 7) C  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 16. (0.00000) RY ( 8) C  1            s( 91.59%)p 0.01(  0.65%)d 0.08(  7.76%)
 17. (0.00000) RY ( 9) C  1            s(  0.00%)p 1.00(  2.94%)d33.04( 97.06%)
 18. (0.00000) RY (10) C  1            s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
 19. (0.00008) RY ( 1) H  2            s(100.00%)
 20. (0.00008) RY ( 1) H  3            s(100.00%)
 21. (0.00008) RY ( 1) H  4            s(100.00%)
```

As can be seen in the output, the initial NBO spin-orbital occupancy threshold was set at 0.95 (rather than 1.90). The occupancies of L-type spin-NBOs 1-5 are about 1.0000, but other aspects of the output are familiar. Note the slight admixture of *d*-character (0.09%) in the σ_{CH} bond hybrids (NBOs 4-6), whereas the out-of-plane radical LP ("lone particle") orbital (NBO 2) has pure *p*-character.

The NBO output for the β ('ionized') spin set then follows:

```
NATURAL BOND ORBITAL ANALYSIS, beta spin orbitals:

                          Occupancies       Lewis Structure    Low   High
        Max    Occ     -------------------  -----------------   occ   occ
 Cycle  Ctr   Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
================================================================================
   1     2     0.95     3.99969   0.00031      1   3   0   0     0      0
--------------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

-------------------------------------------------------
  Core                      0.99985 ( 99.985% of   1)
  Valence Lewis             2.99984 ( 99.995% of   3)
 ==================      ============================
  Total Lewis               3.99969 ( 99.992% of   4)
```

```
 ------------------------------------------------------
  Valence non-Lewis          0.00008 (  0.002% of   4)
  Rydberg non-Lewis          0.00023 (  0.006% of   4)
 ==================      ============================
  Total non-Lewis            0.00031 (  0.008% of   4)
------------------------------------------------------


    (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ---------------------------------------------------
  1. (0.99985) CR ( 1) C  1            s(100.00%)
                                        1.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
  2. (0.99995) BD ( 1) C  1- H  2
               ( 57.47%)   0.7581* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
                                        0.0000  0.5768  0.0033  0.0000 -0.4078
                                       -0.0127  0.7063  0.0221  0.0000  0.0000
                                       -0.0244  0.0000  0.0000 -0.0141 -0.0256
               ( 42.53%)   0.6521* H  2 s(100.00%)
                                        1.0000 -0.0041
  3. (0.99995) BD ( 1) C  1- H  3
               ( 57.47%)   0.7581* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
                                        0.0000  0.5768  0.0033  0.0000 -0.4078
                                       -0.0127 -0.7063 -0.0221  0.0000  0.0000
                                        0.0244  0.0000  0.0000 -0.0141 -0.0256
               ( 42.53%)   0.6521* H  3 s(100.00%)
                                        1.0000 -0.0041
  4. (0.99995) BD ( 1) C  1- H  4
               ( 57.47%)   0.7581* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
                                        0.0000  0.5768  0.0033  0.0000  0.8156
                                        0.0255  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0282 -0.0256
               ( 42.53%)   0.6521* H  4 s(100.00%)
                                        1.0000 -0.0041
---------------- non-Lewis -----------------------------------------------
  5. (0.00000) LV ( 1) C  1            s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
  6. (0.00003) BD*( 1) C  1- H  2
               ( 42.53%)   0.6521* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
               ( 57.47%)  -0.7581* H  2 s(100.00%)
  7. (0.00003) BD*( 1) C  1- H  3
               ( 42.53%)   0.6521* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
               ( 57.47%)  -0.7581* H  3 s(100.00%)
  8. (0.00003) BD*( 1) C  1- H  4
               ( 42.53%)   0.6521* C  1 s( 33.27%)p 2.00( 66.59%)d 0.00(  0.14%)
               ( 57.47%)  -0.7581* H  4 s(100.00%)
  9. (0.00001) RY ( 1) C  1            s(  5.35%)p 0.00(  0.00%)d17.69( 94.65%)
 10. (0.00000) RY ( 2) C  1            s( 90.24%)p 0.06(  5.72%)d 0.04(  4.05%)
 11. (0.00000) RY ( 3) C  1            s(  0.00%)p 1.00( 91.42%)d 0.09(  8.58%)
 12. (0.00000) RY ( 4) C  1            s(  6.64%)p12.61( 83.70%)d 1.46(  9.66%)
 13. (0.00000) RY ( 5) C  1            s( 72.52%)p 0.00(  0.34%)d 0.37( 27.14%)
 14. (0.00000) RY ( 6) C  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 15. (0.00000) RY ( 7) C  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 16. (0.00000) RY ( 8) C  1            s(  0.00%)p 1.00(100.00%)d 0.00(  0.00%)
 17. (0.00000) RY ( 9) C  1            s(  0.00%)p 1.00(  8.70%)d10.50( 91.30%)
 18. (0.00000) RY (10) C  1            s( 25.46%)p 0.41( 10.37%)d 2.52( 64.18%)
 19. (0.00008) RY ( 1) H  2            s(100.00%)
 20. (0.00008) RY ( 1) H  3            s(100.00%)
 21. (0.00008) RY ( 1) H  4            s(100.00%)
```

The principal difference to be seen is that the radical orbital (NBO 5) is essentially empty in this spin set, and the polarization of the σ_{CH} bonds is somewhat altered (about 57.5% on the C atom in the β set set, *vs.* 60.5% in the α set). [In other cases, the α and β NBO Lewis structures might differ even in the number and location of 1-c (non-bonding) and 2-c (bond) structural

elements.] Note that the overall quality of the open-shell natural Lewis structure description (> 99.9%) is comparable to that of ordinary closed-shell molecules, and the interpretation of the NBO output follows familiar lines.

B.6.12 Effective Core Potential: Cu_2 Dimer

To illustrate the variations of NBO output associated with use of effective core potentials (ECP) and inclusion of *d* orbitals, we use the example of the copper dimer Cu_2 (R = 2.2195 Å, RHF/LANL1DZ level). Because the NBO program communicates directly with the ESS program for details of the ECP, no special keywords are necessary.

Use of an ECP shows up most directly in the NPA portion of the output, shown below:

```
 NATURAL POPULATIONS:  Natural atomic orbital occupancies

  NAO Atom No lang   Type(AO)    Occupancy      Energy
 --------------------------------------------------------
    1   Cu  1  s      Val( 4s)     0.99541      -0.03232
    2   Cu  1  s      Ryd( 5s)     0.00034       1.55373
    3   Cu  1  px     Ryd( 4p)     0.00130       0.16919
    4   Cu  1  px     Ryd( 5p)     0.00000       0.10809
    5   Cu  1  py     Ryd( 4p)     0.00130       0.16919
    6   Cu  1  py     Ryd( 5p)     0.00000       0.10809
    7   Cu  1  pz     Ryd( 4p)     0.00760       1.01137
    8   Cu  1  pz     Ryd( 5p)     0.00020       0.29342
    9   Cu  1  dxy    Val( 3d)     1.99997      -0.46633
   10   Cu  1  dxy    Ryd( 4d)     0.00003       1.04801
   11   Cu  1  dxz    Val( 3d)     1.99870      -0.46849
   12   Cu  1  dxz    Ryd( 4d)     0.00000       1.13602
   13   Cu  1  dyz    Val( 3d)     1.99870      -0.46849
   14   Cu  1  dyz    Ryd( 4d)     0.00000       1.13602
   15   Cu  1  dx2y2  Val( 3d)     1.99997      -0.46633
   16   Cu  1  dx2y2  Ryd( 4d)     0.00003       1.04801
   17   Cu  1  dz2    Val( 3d)     1.99626      -0.46858
   18   Cu  1  dz2    Ryd( 4d)     0.00018       1.65132

   19   Cu  2  s      Val( 4s)     0.99541      -0.03232
   20   Cu  2  s      Ryd( 5s)     0.00034       1.55373
   21   Cu  2  px     Ryd( 4p)     0.00130       0.16919
   22   Cu  2  px     Ryd( 5p)     0.00000       0.10809
   23   Cu  2  py     Ryd( 4p)     0.00130       0.16919
   24   Cu  2  py     Ryd( 5p)     0.00000       0.10809
   25   Cu  2  pz     Ryd( 4p)     0.00760       1.01137
   26   Cu  2  pz     Ryd( 5p)     0.00020       0.29342
   27   Cu  2  dxy    Val( 3d)     1.99997      -0.46633
   28   Cu  2  dxy    Ryd( 4d)     0.00003       1.04801
   29   Cu  2  dxz    Val( 3d)     1.99870      -0.46849
   30   Cu  2  dxz    Ryd( 4d)     0.00000       1.13602
   31   Cu  2  dyz    Val( 3d)     1.99870      -0.46849
   32   Cu  2  dyz    Ryd( 4d)     0.00000       1.13602
   33   Cu  2  dx2y2  Val( 3d)     1.99997      -0.46633
   34   Cu  2  dx2y2  Ryd( 4d)     0.00003       1.04801
   35   Cu  2  dz2    Val( 3d)     1.99626      -0.46858
   36   Cu  2  dz2    Ryd( 4d)     0.00018       1.65132

 [36 electrons found in the effective core potential]
     Population inversion found on atom Cu  1
     Population inversion found on atom Cu  2


 Summary of Natural Population Analysis:
```

```
                                    Natural Population
            Natural    -----------------------------------------------
 Atom No    Charge        Core      Valence    Rydberg      Total
-------------------------------------------------------------------
  Cu  1    0.00000     18.00000    10.98901    0.01099    29.00000
  Cu  2    0.00000     18.00000    10.98901    0.01099    29.00000
===================================================================
* Total *  0.00000     36.00000    21.97802    0.02198    58.00000

                                 Natural Population
-----------------------------------------------------------
  Effective Core            36.00000
  Valence                   21.97802 ( 99.9001% of   22)
  Natural Minimal Basis     57.97802 ( 99.9621% of   58)
  Natural Rydberg Basis      0.02198 (  0.0379% of   58)
-----------------------------------------------------------

   Atom No         Natural Electron Configuration
--------------------------------------------------------------------------------
    Cu  1      [core]4s( 1.00)3d( 9.99)4p( 0.01)
    Cu  2      [core]4s( 1.00)3d( 9.99)4p( 0.01)
```

As noted below the first NPA table, 36 electrons were found in the ECP, so the labels for NAOs in the table begin with the designations 4*s*, 5*s*, etc. of the presumed extra-core electrons. The ECP electrons are duly entered in the NPA tables (labelled as “effective core” in the NPA summary table) as part of the total Lewis occupancy, and are taken into proper account in assigning atomic charges. The NPA output in this case includes a “population inversion” message to indicate that one or more NAO occupancies are not ordered in accordance with the energy order [e.g., NBO 34 has lower energy than NBO 36 (1.04801 a.u. vs. 1.65132 a.u.), but NBO 36 has the higher occupancy (0.00018e vs. 0.00003e), a “population inversion” of negligible physical significance].

The main ECP effect in the NBO portion of the output is the omission of core NBOs, as illustrated below:

```
NATURAL BOND ORBITAL ANALYSIS:

                          Occupancies       Lewis Structure    Low   High
        Max    Occ     -------------------  -----------------   occ   occ
 Cycle  Ctr    Thresh    Lewis   non-Lewis     CR  BD  nC  LP    (L)   (NL)
================================================================================
   1     2     1.90    57.99424   0.00576      0   1   0  10     0      0
--------------------------------------------------------------------------------

Structure accepted: No low occupancy Lewis orbitals

-----------------------------------------------------
  Effective core           36.00000
  Valence Lewis            21.99424 ( 99.974% of  22)
 ==================      ============================
  Total Lewis              57.99424 ( 99.990% of  58)
 -----------------------------------------------------
  Valence non-Lewis         0.00000 (  0.000% of  58)
  Rydberg non-Lewis         0.00576 (  0.010% of  58)
 ==================      ============================
```

```
  Total non-Lewis           0.00576 (  0.010% of  58)
-------------------------------------------------------


    (Occupancy)   Bond orbital / Coefficients / Hybrids
------------------ Lewis ----------------------------------------------------
  1. (1.99999) LP ( 1)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  1.0000 -0.0036
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000
  2. (1.99999) LP ( 2)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  1.0000
                                       -0.0036  0.0000  0.0000
  3. (1.99966) LP ( 3)Cu  1            s(  0.30%)p 0.05(  0.02%)d99.99( 99.68%)
                                        0.0545 -0.0063  0.0000  0.0000  0.0000
                                        0.0000 -0.0074 -0.0098  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000 -0.9984 -0.0063
  4. (1.99874) LP ( 4)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000  0.0042  0.0011  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        1.0000  0.0004  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000
  5. (1.99874) LP ( 5)Cu  1            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0042
                                        0.0011  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  1.0000  0.0004  0.0000
                                        0.0000  0.0000  0.0000
  6. (1.99999) LP ( 1)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  1.0000 -0.0036
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000
  7. (1.99999) LP ( 2)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  1.0000
                                       -0.0036  0.0000  0.0000
  8. (1.99966) LP ( 3)Cu  2            s(  0.30%)p 0.05(  0.02%)d99.99( 99.68%)
                                        0.0545 -0.0063  0.0000  0.0000  0.0000
                                        0.0000  0.0074  0.0098  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000 -0.9984 -0.0063
  9. (1.99874) LP ( 4)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000 -0.0042 -0.0011  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        1.0000  0.0004  0.0000  0.0000  0.0000
                                        0.0000  0.0000  0.0000
 10. (1.99874) LP ( 5)Cu  2            s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
                                        0.0000  0.0000  0.0000  0.0000 -0.0042
                                       -0.0011  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0000  1.0000  0.0004  0.0000
                                        0.0000  0.0000  0.0000
 11. (2.00000) BD ( 1)Cu  1-Cu  2
              ( 50.00%)   0.7071*Cu  1 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
                                        0.9947  0.0007  0.0000  0.0000  0.0000
                                        0.0000 -0.0865  0.0026  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0549  0.0051
              ( 50.00%)   0.7071*Cu  2 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
                                        0.9947  0.0007  0.0000  0.0000  0.0000
                                        0.0000  0.0865 -0.0026  0.0000  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                        0.0000  0.0549  0.0051
---------------- non-Lewis ------------------------------------------------
 12. (0.00000) BD*( 1)Cu  1-Cu  2
              ( 50.00%)   0.7071*Cu  1 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
              ( 50.00%)  -0.7071*Cu  2 s( 98.95%)p 0.01(  0.75%)d 0.00(  0.30%)
```

```
 13. (0.00126) RY ( 1)Cu  1           s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                       0.0000  0.0000  0.9996  0.0258  0.0000
                                       0.0000  0.0000  0.0000  0.0000  0.0000
                                      -0.0042 -0.0093  0.0000  0.0000  0.0000
                                       0.0000  0.0000  0.0000
 14. (0.00126) RY ( 2)Cu  1           s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                       0.0000  0.0000  0.0000  0.0000  0.9996
                                       0.0258  0.0000  0.0000  0.0000  0.0000
                                       0.0000  0.0000 -0.0042 -0.0093  0.0000
                                       0.0000  0.0000  0.0000
 15. (0.00034) RY ( 3)Cu  1           s( 75.24%)p 0.03(  2.18%)d 0.30( 22.59%)
                                      -0.0102  0.8673  0.0000  0.0000  0.0000
                                       0.0000 -0.1383  0.0515  0.0000  0.0000
                                       0.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0000 -0.0026 -0.4753
 16. (0.00001) RY ( 4)Cu  1           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 17. (0.00001) RY ( 5)Cu  1           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 18. (0.00000) RY ( 6)Cu  1           s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 19. (0.00000) RY ( 7)Cu  1           s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 20. (0.00000) RY ( 8)Cu  1           s(  0.35%)p99.99( 97.55%)d 6.06(  2.10%)
 21. (0.00000) RY ( 9)Cu  1           s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 22. (0.00000) RY (10)Cu  1           s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 23. (0.00000) RY (11)Cu  1           s(  1.45%)p67.18( 97.47%)d 0.74(  1.07%)
 24. (0.00000) RY (12)Cu  1           s( 23.72%)p 0.09(  2.03%)d 3.13( 74.25%)
 25. (0.00126) RY ( 1)Cu  2           s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                       0.0000  0.0000  0.9996  0.0258  0.0000
                                       0.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0042  0.0093  0.0000  0.0000  0.0000
                                       0.0000  0.0000  0.0000
 26. (0.00126) RY ( 2)Cu  2           s(  0.00%)p 1.00( 99.99%)d 0.00(  0.01%)
                                       0.0000  0.0000  0.0000  0.0000  0.9996
                                       0.0258  0.0000  0.0000  0.0000  0.0000
                                       0.0000  0.0000  0.0042  0.0093  0.0000
                                       0.0000  0.0000  0.0000
 27. (0.00034) RY ( 3)Cu  2           s( 75.24%)p 0.03(  2.18%)d 0.30( 22.59%)
                                      -0.0102  0.8673  0.0000  0.0000  0.0000
                                       0.0000  0.1383 -0.0515  0.0000  0.0000
                                       0.0000  0.0000  0.0000  0.0000  0.0000
                                       0.0000 -0.0026 -0.4753
 28. (0.00001) RY ( 4)Cu  2           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 29. (0.00001) RY ( 5)Cu  2           s(  0.00%)p 0.00(  0.00%)d 1.00(100.00%)
 30. (0.00000) RY ( 6)Cu  2           s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 31. (0.00000) RY ( 7)Cu  2           s(  0.00%)p 1.00(  0.09%)d99.99( 99.91%)
 32. (0.00000) RY ( 8)Cu  2           s(  0.35%)p99.99( 97.55%)d 6.06(  2.10%)
 33. (0.00000) RY ( 9)Cu  2           s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 34. (0.00000) RY (10)Cu  2           s(  0.00%)p 1.00( 99.92%)d 0.00(  0.08%)
 35. (0.00000) RY (11)Cu  2           s(  1.45%)p67.18( 97.47%)d 0.74(  1.07%)
 36. (0.00000) RY (12)Cu  2           s( 23.72%)p 0.09(  2.03%)d 3.13( 74.25%)
```

As the output shows, the NBO tables include reference to only 11 occupied NBOs, rather than the 29 that would appear in a full calculation. Semi-empirical methods that neglect core electrons (AMPAC, etc.) are handled similarly.

The output for the Cu_2 example also illustrates some aspects of the inclusion of *d* orbitals in the basis set. NBOs 1-5 and 6-10 represent the $3d^8$ subshells on each atom, essentially of pure atomic *d* character (except for a small admixture of *p* character in NBOs 3, 8 oriented along the internuclear axis). The σ_{CuCu} bond (NBO 11) contains a very slight admixture (0.3%) of *d* character, but remaining orbitals of predominant *d* character (e.g., NBOs 16-19 and 28-31) are of negligible occupancy. Note that the abbreviated "$sp^{\lambda}d^{\mu}$" designations can

lead to strange variations among hybrids of essentially similar character. For example, NBO 3 ("$sp^{0.05}d^{99.99}$") , NBO 17 ("$d^{1.00}$"), and NBO 18 ("$p^{1.00}d^{99.99}$") are all of essentially pure (>99%) *d* character, but with strikingly different labels depending on whether there is sufficient *s* or *p* character (in numerical terms) to express the hybrid ratios in $sp^{\lambda}d^{\mu}$ form. Consult the percentages of *s*-. *p*-, and *d*-character whenever there is doubt about how to interpret a particular $sp^{\lambda}d^{\mu}$ designation.

B.7 FILE47: INPUT FOR THE GenNBO STAND-ALONE NBO PROGRAM

B.7.1 Introduction

The general NBO program, GenNBO, is a stand-alone program that is not directly attached to an ESS program. Rather, information about the wavefunction is provided to the NBO routines by the text file, FILE47, described in this section.

Some knowledge of FILE47 is useful even if your NBO program is attached to an ESS package. If requested (see the ARCHIVE keyword, Section B.2.5), the NBO program writes FILE47, a file that summarizes all information pertaining to the computed electronic wavefunction. This file can be subsequently used as standard input to the GenNBO program to repeat the analysis of the wavefunction; simply include the $NBO keylist, and, if desired, the $CORE, $CHOOSE, and $NRTSTR keylists in FILE47 and execute GenNBO. You need never recompute the wavefunction to vary its NBO analysis! In fact, generating FILE47 is a useful way to archive a wavefunction for future use or reference.

If you intend to use the NBO program in conjunction with an ESS package that is not supported (i.e. for which no NBO interface is available), you might consider attaching a routine to the ESS program that writes a FILE47 for subsequent use with the GenNBO program. Thus, a two-step process would be required to obtain the NBO analysis of a wavefunction: (i) the initial calculation of the wavefunction with the ESS package, writing FILE47, and (ii) the NBO analysis using the GenNBO program with FILE47 as input.

Note that the GenNBO program *cannot* perform the NBO energetic analysis (described in Section B.5) or other options that require energy evaluation or access to the two-electron integrals of the parent ESS package.

Section B.7.2 describes and illustrates the format of FILE47. Sections B.7.3-B.7.8 detail the entries of the keylists and datalists that compose this file.

B.7.2 Format of FILE47

FILE47 is composed of a set of keylists and datalists, each list beginning with a "$" identifier (e.g. "$BASIS") and ending with "$END",

```
     $BASIS  entries  $END
```

Individual lists are used to specify basis set information ($BASIS), density matrix elements ($DENSITY), and so forth. The $GENNBO keylist and the $COORD, $BASIS, $DENSITY, and $OVERLAP datalists are required. All other datalists ($WF, $FOCK, $KINETIC, $NUCLEAR, $LCAOMO, $CONTRACT, $DIPOLE, $C10, $H01, $H11) and the standard NBO keylists ($NBO, $CORE, $CHOOSE, $NRTSTR, $NPEPA) are optional, depending on the requested application. If the $NBO keylist is not present in FILE47, default NBO analysis is performed.

The order of the keylists and datalists within FILE47 is immaterial. Entries within each list are generally free format, and may be continued on as many lines as desired. Each line is limited to 4096 characters. Entries can be formatted to facilitate the parsing of FILE47 (see FORMAT in B.7.3). An exclamation point (!) on any line terminates input for the line, and may be followed by arbitrary comments. Equal (=) and comma (,) characters are ignored as FILE47 is parsed.

The entries of each keylist or datalist may be keywords, numerical matrix elements, or other parameters of prescribed form. A sample FILE47 input file for the RHF/3-21G methylamine example of Section A.3 is shown below (with only the first three elements of each datalist):

```
$GENNBO  NATOMS=7  NBAS=28  UPPER  BODM  FORMAT=PRECISE  $END
$NBO  $END
$COORD
Methylamine
    6    6       0.745914       0.011106       0.000000
    7    7      -0.721743      -0.071848       0.000000
    1    1       1.042059       1.060105       0.000000
    1    1       1.129298      -0.483355       0.892539
    1    1       1.129298      -0.483355      -0.892539
    1    1      -1.076988       0.386322      -0.827032
    1    1      -1.076988       0.386322       0.827032
$END
$BASIS
 CENTER =    1    1    1    1    1    1    1    1    1    2    2    2    2
             2    2    2    2    2    3    3    4    4    5    5    6    6
             7    7
  LABEL =    1    1  101  102  103    1  101  102  103    1    1  101  102
           103    1  101  102  103    1    1    1    1    1    1    1    1
             1    1
$END
$CONTRACT
```

```
 NSHELL =   16
   NEXP =   27
  NCOMP =    1    4    4    1    4    4    1    1    1    1    1    1    1
             1    1    1
  NPRIM =    3    2    1    3    2    1    2    1    2    1    2    1    2
             1    2    1
   NPTR =    1    4    6    7   10   12   13   15   16   18   19   21   22
            24   25   27
    EXP =  0.172256000000E+03  0.259109000000E+02  0.553335000000E+01
           0.366498000000E+01  0.770545000000E+00  0.195857000000E+00
           0.242766000000E+03  0.364851000000E+02  0.781449000000E+01
           0.542522000000E+01  0.114915000000E+01  0.283205000000E+00
           0.544717800000E+01  0.824547240000E+00  0.183191580000E+00
           0.544717800000E+01  0.824547240000E+00  0.183191580000E+00
           0.544717800000E+01  0.824547240000E+00  0.183191580000E+00
           0.544717800000E+01  0.824547240000E+00  0.183191580000E+00
           0.544717800000E+01  0.824547240000E+00  0.183191580000E+00
     CS =  0.617669074000E-01  0.358794043000E+00  0.700713084000E+00
          -0.395895162000E+00  0.121583436000E+01  0.100000000000E+01
           0.598657005000E-01  0.352955003000E+00  0.706513006000E+00
          -0.413300077000E+00  0.122441727000E+01  0.100000000000E+01
           0.156284979000E+00  0.904690877000E+00  0.100000000000E+01
           0.156284979000E+00  0.904690877000E+00  0.100000000000E+01
           0.156284979000E+00  0.904690877000E+00  0.100000000000E+01
           0.156284979000E+00  0.904690877000E+00  0.100000000000E+01
           0.156284979000E+00  0.904690877000E+00  0.100000000000E+01
     CP =  0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
           0.236459947000E+00  0.860618806000E+00  0.100000000000E+01
           0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
           0.237972016000E+00  0.858953059000E+00  0.100000000000E+01
           0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
           0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
           0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
           0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
           0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
$END
$WF  BASIS=MO  NDET=1  NELE=0  NACT=0
 1.0000000
$END
$OVERLAP
 0.100000000000E+01  0.191447444408E+00  0.100000000000E+01
$END
$DENSITY
 0.203642496554E+01  0.110916720865E+00  0.103889621321E+00
$END
$FOCK
-0.111276104122E+02 -0.285894568529E+01 -0.895997224316E+00
$END
$LCAOMO
-0.581395484288E-03 -0.241638924924E-02 -0.179639931958E-02
$END
$KINETIC
 0.165789737789E+02 -0.143502704294E+01  0.135736735277E+01
$END
$NUCLEAR
-0.389337728279E+02 -0.316983323746E+01 -0.107384085178E+02
$END
$DIPOLE
 0.745914056961E+00  0.142803339953E+00  0.745914056961E+00
$END
```

The various datalists of FILE47 are described in turn in the following sections, making use of this example for illustration.

B.7.3 $GENNBO Keylist

The $GENNBO keylist (required) contains keywords essential for the proper execution of the NBO program. The following keywords are recognized:

KEYWORD	*OPTION DESCRIPTION*
REUSE	Instructs GenNBO to reuse an old NBO direct access file, FILE48, rather than create a new FILE48 from the wavefunction information contained in the FILE47 datalists. Therefore, if the REUSE keyword is specified, all datalists in FILE47 will be ignored, but the $NBO, $CORE, $CHOOSE, and $NRTSTR keylists are still recognized. The REUSE keyword preempts all other keywords of the $GENNBO keylist.
SAVE	Instructs GenNBO to save the NBO direct access file, FILE48, on program termination. By default, FILE48 is deleted.
NATOMS	Number of atoms (required, unless REUSE).
NBAS	Number of basis functions (required, unless REUSE).
OPEN	Designates an open-shell wavefunction. GenNBO will subsequently read alpha and beta density, Fock, and MO coefficient matrices. Do not specify OPEN (even for open-shell wavefunctions) when only spin-averaged matrices are available.
ORTHO	Indicates that the AO basis set is orthogonal (basis functions are always assumed normalized). If this keyword is specified, GenNBO will not read the $OVERLAP datalist. This keyword is incompatible with $NBO keywords that require the "pre-orthogonal" basis sets (e.g. SPNAO, SPNHO, SPNBO, SPNLMO, AOPNAO, AOPNHO, AOPNBO, AOPNLMO, FPNHO, FPNBO, STERIC, etc.).
UPPER	Indicates that only the upper triangular portions of the overlap, density, Fock, dipole, MO derivative, and Hamiltonian derivative matrices are listed in their respective datalists. By default, GenNBO assumes that the full matrices are given.
BODM	Indicates that the $DENSITY datalist contains the bond-order matrix ("Fock-Dirac density matrix") rather than the density matrix (i.e., matrix elements of the density operator). In orthogonal AO basis sets, the bond-order matrix and density matrix are identical, but in nonorthogonal basis sets they must be distinguished. By default, GenNBO assumes this datalist contains the density matrix elements. If BODM is specified, the $DENSITY datalist elements are transformed with the AO overlap matrix to produce the true density matrix.

BOHR	Indicates that the atomic coordinates ($COORD) and the dipole integrals ($DIPOLE) are in atomic units, rather than the default angstroms.
EV	Indicates that the Fock matrix elements ($FOCK) have units of electron volts (eV), rather than the default atomic units (Hartrees).
CUBICF	Instructs GenNBO to use the set of seven cubic *f*-type functions rather than the seven spherical *f* functions (cf. Section B.7.5).
FORMAT	Read formatted (rather than free-formatted) matrix elements for the $OVERLAP, $DENSITY, $FOCK, $LCAOMO, $KINETIC, $NUCLEAR, $DIPOLE, $H01, and $H11 datalists. The format is (2x,5e15.7). Alternatively, use FORMAT=PRECISE for higher precision (4e20.12) formatted input.

The methylamine sample $GENNBO keylist specifies 7 atoms, 28 basis functions, upper triangular matrix input, a $DENSITY datalist containing the bond-order matrix, and high-precision formatted input.

B.7.4 $COORD Datalist

The $COORD datalist (required, unless REUSE is specified in $GENNBO) contains the job title and information indicating the identity and coordinates of each atom, including missing core electrons or effective core potentials.

The first line following the $COORD identifier is an arbitrary job title of up to 80 characters. The title is written to the NBO output immediately after the header and citation information. Providing a title is optional; if there is no job title, leave this line blank.

Subsequent lines are used to specify the atomic number, the nuclear charge, and the Cartesian coordinates of each atom. [For example, atom 1 in the methylamine sample input is a carbon atom (atomic number 6) with nuclear charge 6 and coordinates x = 0.745914, y = 0.011106, z = 0.00000, in angstroms.] Coordinates are in angstroms unless the BOHR keyword appears in the $GENNBO keylist, specifying atomic units. The atomic number and nuclear charge are generally identical. However, if core electrons are neglected (as in most semi-empirical treatments) or if effective core potentials (ECP) are employed, the nuclear charge will be less than the atomic number by the number of electrons neglected on that particular atom. Thus, for an AMPAC calculation, in which the two 1*s* core electron of a carbon atom are neglected, the line following the job title in the methylamine example would read

```
6    4       0.745914       0.011106       0.000000
```

where “4” is the effective (valence) nuclear charge of the atom.

B.7.5 $BASIS Datalist

The $BASIS datalist (required, unless REUSE is specified in $GENNBO) provides essential information about the AO basis functions, specifying the atomic center and the angular symmetry (*s*, p_x, p_y, p_z, etc.) of each AO. This information is listed in two arrays: CENTER and LABEL.

The atomic center for each AO is specified by entering "CENTER=" followed by the number of the atom for each AO, separated by commas or spaces. For example, the entry

```
CENTER = 1,1,1,1,1,1,1,1,1,2,2,2,2,2,2,2,2,2,3,3,4,4,5,5,6,6,7,7
```

of the methylamine sample file indicates that the first 9 AOs (1-9) are centered on atom 1 (the carbon atom), the next nine AOs (10-18) on center 2, and so forth.

The angular symmetry for each AO is specified by entering "LABEL=" followed by a symmetry label for each AO, separated by commas or spaces. The NBO program handles Cartesian *s*, *p*, *d*, *f*, *g*, and *h* functions and spherical *s*, *p*, *d*, *f*, *g*, *h*, and *i* functions (l = 0-6). The label for each AO is a 3-digit integer of the form l*100 + k + m, where k is 0 (Cartesian) or 50 (spherical), and m is a particular component of the l-type symmetry (see table below). For *s* or *p* AOs, the Cartesian and spherical l-symmetry sets are identical, so each AO can be labelled in two distinct ways (e.g. either 1 or 51 for an *s*-type function, either 101 or 151 for a p_x function, etc.), but the six Cartesian *d* functions can be transformed to the five spherical *d* functions plus an additional *s* function, and the ten Cartesian *f* functions can be transformed to the seven spherical *f* functions plus three additional *p* functions. Two distinct sets of spherical *f* functions are recognized, the "standard" [default] set and the "cubic" set, the latter being used whenever the "CUBICF" keyword is included in the $GENNBO keylist.

The labels associated with each allowed AO function type are tabulated below, where *x, y, z* refer to the specified Cartesian axis system:

Cartesian Sets	*Angular Symmetries*
s (1)	s
p (101-103)	x, y, z
d (201-206)	xx, xy, xz, yy, yz, zz
f (301-310)	xxx, xxy, xxz, xyy, xyz, xzz, yyy, yyz, yzz, zzz

g (401-415)	xxxx, xxxy, xxxz, xxyy, xxyz, xxzz, xyyy, xyyz, xyzz, xzzz, yyyy, yyyz, yyzz, yzzz, zzzz
h (501-521)	xxxxx, xxxxy, xxxxz, xxxyy, xxxyz, xxxzz, xxyyy, xxyyz, xxyzz, xxzzz, xyyyy, xyyyz, xyyzz, xyzzz, xzzzz, yyyyy, yyyyz, yyyzz, yyzzz, yzzzz, zzzzz

Spherical Sets

s (51)	s
p (151-153)	x, y, z
d (251-255)	s2=xy, s1=xz, c1=yz, c2=x2-y2, 0=z2
f (351-357) (standard)	0=z(5z2-3r2), c1=x(5z2-r2), s1=y(5z2-r2), c2=z(x2-y2), s2=xyz, c3=x(x2-3y2), s3=y(3x2-y2)
f (351-357) (cubic)	D1=x(5x2-3r2), D2=y(5y2-3r2), D3=z(5z2-3r2), B=xyz, E1=x(z2-y2), E2=y(z2-x2), E3=z(x2-y2)
g (451-459)	0, c1, s1, c2, s2, c3, s3, c4, s4
h (551-561)	0, c1, s1, c2, s2, c3, s3, c4, s4, c5, s5
i (651-663)	0, c1, s1, c2, s2, c3, s3, c4, s4, c5, s5, c6, s6

For example, in the methylamine sample input the first nine entries of the LABEL array,

```
LABEL = 1,1,101,102,103,1,101,102,103,. . .
```

identify the first 9 AOs (of carbon) as being of *s*, *s*, p_x, p_y, p_z, *s*, p_x, p_y, p_z type, respectively.

B.7.6 $CONTRACT Datalist

The $CONTRACT datalist (optional) contains information about contraction coefficients and orbital exponents of AO basis functions. This information is not used in basic NBO analysis of a wavefunction. However, if the AOINFO or PLOT keyword is specified in the $NBO keylist (See Section B.2.5), the GenNBO writes out this information to an external file (LFN 31) in the proper format for orbital plotting with the *NBOView* program. This information is also required for the NCS, NJC, NBCP, and hybrid directionality analyses.

Two integers must be initially given: NSHELL (the number of shells of basis functions) and NEXP (the number of orbital exponents). In the methylamine example, there are 16 shells of basis functions and 27 orbital exponents. These integers should precede the remainder of the basis set information of this datalist.

The number of components (basis functions) in each shell is specified in the NCOMP array. The sum of the components for each shell should equal the total number of basis functions. This list of components is a partitioning of the basis function centers and labels (in the $BASIS datalist) into shells. For example, in the methylamine sample, the NCOMP array

```
NCOMP = 1,4,4,. . .
```

indicates that the first three shells have a total of 9 (i.e. 1+4+4) basis functions. These are the 9 AOs (1-9) discussed previously in the $BASIS datalist.

The NPRIM array gives the number of primitive gaussian functions of each shell. For the methylamine example, the first three shells of the AO basis are contractions of

```
NPRIM = 3,2,1,. . .
```

three, two, and one primitives, respectively, corresponding to the conventional “3-21G” basis set designation.

Pointers for each shell are listed in the NPTR array. These pointers specify the location of the orbital exponents (EXP) and contraction coefficients (CS, CP, CD, CF, etc.) for each shell. In the sample input file,

```
 NPTR = 1,4,6,. . .
```

the orbital exponents and contraction coefficients for the first three shells begin at elements 1, 4, and 6, respectively.

EXP, CS, CP, CD, CF, CG, CH, and CI are free format, real arrays containing the orbital exponents, and the *s*, *p*, *d*, *f*, *g*, *h*, and *i* contraction coefficients of the AO basis set. NEXP elements should appear in each array, and the arrays of contraction coefficients need only be given in $CONTRACT if there are basis functions of that particular symmetry in the basis set. For example, the 3-21G basis of the sample methylamine input has *s* and *p* basis functions only. Therefore, the CD, CF, etc. arrays are not necessary.

The information in the $CONTRACT datalist along with that in the $BASIS datalist is enough to completely determine the AO basis set. For example, the second shell on the methylamine sample contains four basis functions (NCOMP). These are *s*, p_x, p_y, and p_z orbitals (LABEL), all centered on atom 1 (CENTER), and each basis function is a contraction of two primitive gaussians (NPRIM). From NPTR, EXP, CS, and CP, we find the explicit form of these functions:

$$\varphi_s(\mathbf{r}) = -0.396\, e^{-3.66\, r2} + 1.216\, e^{-0.77\, r2}$$

$$\varphi_{px}(\mathbf{r}) = 0.236\, x\, e^{-3.66\, r2} + 0.801\, x\, e^{-0.77\, r2}$$

$$\varphi_{py}(\mathbf{r}) = 0.236\, y\, e^{-3.66\, r2} + 0.801\, y\, e^{-0.77\, r2}$$

$$\varphi_{pz}(\mathbf{r}) = 0.236\, z\, e^{-3.66\, r2} + 0.801\, z\, e^{-0.77\, r2}$$

where $\mathbf{r} = (x,y,z)$ is measured in bohr units relative to the Cartesian coordinates of atom 1.

B.7.7 $WF Datalist

The $WF datalist (optional) contains information about the multi-configurational character of a correlated wavefunction that allows the NBO program to construct the 2-particle density matrix. The datalist includes information about the electrons and orbitals that comprise the active space, the determinants that thereby arise in the expansion of the wavefunction, and the expansion coefficients.

The following is an example of a $WF datalist for the CAS(2,3)/3-21G wavefunction for methylamine at the geometry given in Section B.7.2:

```
$WF  BASIS=MO  NDET=9  NELE=2  NORB=3
 0.9975877   2   1  -1                                    ! 200
-0.0693049  -2   1   2   2  -2                            ! 020
-0.0039400  -2   1   3   2  -3                            ! 002
-0.0000021  -2   1   3   2  -2                            ! 0ba
-0.0000021  -2   1   2   2  -3                            ! 0ab
-0.0000005  -1   1   2                                    ! ba0
-0.0000005  -1   2  -2                                    ! ab0
 0.0000004  -1   1   3                                    ! b0a
 0.0000004  -1   2  -3                                    ! a0b
$END
```

The first line indicates that the active space consists of two electrons (NELE) in three orbitals (NORB), yielding nine determinants (NDET) expressed in the MO basis. This line is followed by the specification of the expansion coefficients and MO occupations of the nine determinants. The keylist is terminated by $END.

The occupation patterns of the nine determinants are given by the integer lists that appear on each line of the datalist. These lists specify the determinants in one of two formats.

Reference format: If the first integer in the list is positive, the integer indicates the total number of electrons in the determinant (must equal NELE) and is followed by that number of integers, each describing the location of one of the electrons. Thus, "2 1 −1" describes a two-electron determinant with the first electron of alpha spin in MO 1 (+1) and the second electron of beta spin, also in MO 1 (−1). Because the first integer in the list is positive, this determinant may serve as a reference for subsequent specifications of determinants.

Excitation format: If the first integer in the list is instead negative, the determinant is specified by electron excitation from the preceding reference determinant. The integer list for the second determinant, "−2 1 2 2 −2",

serves as an example. The "−2" indicates that this determinant is obtained double excitation of the reference determinant. The first electron (1) moves to MO 2 with alpha spin (+2), and the second electron (2) moves to MO 2 with beta spin (−2). Because the reference determinant has two electrons in MO 1, this double excitation moves the two electrons into MO 2.

Of the nine determinants specified in the example, only the first one serves as the reference; determinants 2-5 result from double excitations (−2) of the reference, and determinants 6-9 result from single excitations (−1).

The first determinant specified in this datalist must be a reference determinant. The remaining determinants may be specified as either reference or by excitation.

The $WF datalist is entirely free-format. Determinants may be listed in any order, not necessarily sorted as shown in the example. The expansion coefficients will be normalized by the NBO program (assuming orthogonal determinants), if not already normalized. The occupation strings (e.g. 200, 020, etc.) in the example are optional comments that are shown here for clarity.

Note that the single determinant of an uncorrelated calculation may be specified as follows:

```
$WF  BASIS=MO  NDET=1  NELE=0  NORB=0
  1.0000000
$END
```

B.7.8 Matrix Datalists

The remaining datalists ($OVERLAP, $DENSITY, $FOCK, $LCAOMO, $KINETIC, $NUCLEAR, $DIPOLE, $C10, $H01, $H11) specify various matrix elements possibly used by NBO analysis. All entries in these datalists are free format, with entries separated by commas or spaces, unless the FORMAT keyword is specified in $GENNBO.

Only the upper triangular portions of each symmetric matrix should be provided if the UPPER keyword is specified in the $GENNBO keylist. The numbering of the matrix rows and columns must correspond to the ordering of the AOs in the $BASIS datalist.

The AO-MO transformation is a square matrix (NBAS×NBAS) that must be provided in full (both occupied and virtual MOs) in the $LCAOMO datalist. MOs should be listed consecutively in this datalist, all AO coefficients for the first MO before those of the second, then the third, and so forth. In the case of linear dependence, for which there are fewer MOs than AOs (i.e. the transformation is rectangular, NMO<NBAS), the datalist should be terminated by NBAS–NMO null vectors.

The alpha matrix should appear before the beta matrix in $DENSITY, $FOCK, and $LCAOMO if the OPEN keyword is specified in the $GENNBO keylist. All three matrices of dipole integrals should appear in the $DIPOLE datalist, with *x* integrals before *y* before *z*. Similarly, the *x* integrals should appear before *y* before *z* in the $C10 keylist. For $H01, order the integrals *x*, *y*, *z* for atom 1 before *x*, *y*, *z* for atom 2, etc. For $H11, order the integrals *xx*, *xy*, *xz*, *yx*, *yy*, *yz*, *zx*, *zy*, *zz* for atom 1 before those of atom 2, etc.

Of the matrix datalists, the $DENSITY datalist is always required, and the $OVERLAP datalist is required for all non-orthogonal AO basis sets, but all other datalists are optional (unless implicitly required by specified keyword options). The following table lists the leading $NBO keywords that require each datalist to be included in FILE47 (requirements for keywords of the supplementary modules, Sec. B.8 *et seq.*, can be determined by analogy):

Datalist	*$NBO Keywords Requiring the Datalist*
$OVERLAP	SAO, SPAO, SPNAO, SPNHO, SPNBO, SPNLMO, AOPNAO, AOPNHO, AOPNBO, AOPNLMO
$FOCK	E2PERT, FAO, FNAO, F(P)NHO, F(P)NBO, FNLMO, FNO, FMO

	STERIC
$KINETIC	KAO, KNAO, KNHO, KNBO, KNLMO, KNO, KMO
$NUCLEAR	VAO, VNAO, VNHO, VNBO, VNLMO, VNO, VMO
$LCAOMO	AOMO, NAOMO, NHOMO, NBOMO, NLMOMO, NOMO
$DIPOLE	DIAO, DINAO, DINHO, DINBO, DINLMO, DINO, DIMO, DIPOLE
$CONTRACT	AOINFO, BEND, NBCP, PLOT
$C10	NCS
$H01	NCS
$H11	NCS

For example, in the methylamine sample input, if the keywords STERIC and NCS were included in the $NBO keylist, the $FOCK (STERIC) and $C10, $H01, and $H11 (NCS) datalists would be required (in addition to the $OVERLAP and $DENSITY datalists) to successfully complete the requested analyzes, but the $DIPOLE datalist would not be used and might have been omitted from FILE47 in this case. Nevertheless, it is good practice to include as many of these datalists in FILE47 as possible for later use with the various keyword options that require them.

B.8 NATURAL RESONANCE THEORY (NRT)

References: E. D. Glendening and F. Weinhold, *J. Comput. Chem.* **19**, 593-609 (1998); E. D. Glendening and F. Weinhold, *J. Comput. Chem.* **19**, 610-627 (1998); E. D. Glendening, J. K. Badenhoop, and F. Weinhold, *J. Comput. Chem.* **19**, 628-646 (1998); E. D. Glendening, S. J. Wright, and F. Weinhold, "Efficient Optimization of Natural Resonance Theory Weights and Bond Orders by Gram-Based Convex Programming" *J. Comput. Chem.* **40**, 2234-2241 (2019); E. D. Glendening, C. R. Landis, and F. Weinhold, *J. Am. Chem. Soc.* **140**, 4156-4166 (2019).

B.8.1 Introduction

Natural resonance theory (NRT) provides an analysis of molecular electron density in terms of resonance structures and weights. It also calculates measures of bond order and valency that are closely related to classical resonance theory concepts.

The NRT algorithm represents the one-electron reduced density operator, $\mathbf{\Gamma}_{QC}$, obtained from a quantum chemical calculation, as an optimized "resonance hybrid" of density operators, $\{\mathbf{\Gamma}_\alpha\}$,

$$\mathbf{\Gamma}_{QC} \cong \mathbf{\Gamma}_{NRT} = \sum_\alpha w_\alpha \mathbf{\Gamma}_\alpha$$

where each $\mathbf{\Gamma}_\alpha$ is the reduced density operator corresponding to an idealized resonance structure wavefunction Ψ_α (the determinant of doubly occupied NBOs for structure α). The NRT resonance weights $\{w_\alpha\}$ are constrained to satisfy

$$w_\alpha \geq 0, \quad \sum_\alpha w_\alpha = 1$$

in order to preserve the normalization, hermiticity, and positivity of $\mathbf{\Gamma}_{QC}$. NRT analysis can be performed on any wavefunction or density functional method that yields a one-electron density matrix.

Resonance weights are variationally optimized to minimize the NRT objective function $D(w)$, the mean-square deviation of $\mathbf{\Gamma}_{NRT}$ from $\mathbf{\Gamma}_{QC}$, expressed in Frobenius norm notation as

$$D(w) = \min (1/n_b)^{1/2} \cdot \| \mathbf{\Gamma}_{QC} - \sum_\alpha w_\alpha \mathbf{\Gamma}_\alpha \| = \min (\mathbf{w^T G w}/n_b)^{1/2}$$

where the weights satisfying the above constraints, n_b is the number of basis functions, and **G** is the Gram matrix of elements

$$G_{\alpha\beta} = \mathrm{Trace}((\mathbf{\Gamma}_{QC} - \mathbf{\Gamma}_{\alpha})^{T}(\mathbf{\Gamma}_{QC} - \mathbf{\Gamma}_{\beta}))$$

The convex objective function $D(w)$ can be efficiently minimized for large numbers of candidate resonance structures using an active-set quadratic programming (QP) strategy, referred to as QPNRT in NRT program output. Regularization ensures that the Gram matrix has positive definite form that usually avoids numerical indeterminacy issues. QP minimization is considerably more efficient than the optimization methods used in the original NRT implementation of pre-NBO 7.0 versions.

Bond orders and valencies are evaluated from the final optimized resonance weights $\{w_\alpha\}$. The *natural bond order* is evaluated as

$$b_{AB} = \sum_\alpha w_\alpha \, b_{AB}^{(\alpha)}$$

where $b_{AB}^{(\alpha)}$ is the integer number of bonds connecting centers A,B in resonance structure Ψ_α. The program also calculates the ionic ($b_{AB}^{(ion)}$) and covalent ($b_{AB}^{(cov)}$) contributions to bond order

$$b_{AB}^{(ion)} = b_{AB}\, i_{AB}, \quad b_{AB}^{(cov)} = b_{AB}(1 - i_{AB})$$

in terms of the (average) ionic character i_{AB} of each A-B bond,

$$i_{AB} = \sum_\alpha w_\alpha \, i_{AB}^{(\alpha)} / b_{AB}$$

where $i_{AB}^{(\alpha)}$ is the ionicity of the A-B bond in the resonance structure Ψ_α, as determined from NBO polarization coefficients c_A, c_B

$$i_{AB}^{(\alpha)} = |(c_A^2 - c_B^2) / (c_A^2 + c_B^2)|$$

(averaged, if necessary, over multiple bonds).

Finally, the program evaluates the *natural atomic valency,*

$$V_A = \sum_{B \neq A} b_{AB}$$

its electrovalent ($V_A^{(ion)}$) and covalent ($V_A^{(cov)}$) contributions,

$$V_A^{(ion)} = \sum_{B \neq A} b_{AB}^{(ion)}, \quad V_A^{(cov)} = \sum_{B \neq A} b_{AB}^{(cov)}$$

and formal *electron count*

$$e_A = 2 \sum_B b_{AB}$$

The NRT program can automatically generate candidate resonance structures to be considered, including (i) the natural Lewis structure (NLS) of the NBO search, (ii) structures resulting from the leading orbital interactions of the perturbative E(2) delocalization lists, and (iii) any symmetry-equivalent structures of the above. Additional structures can be optionally generated through analysis of the natural binding indices (NRTNBI keyword), or by explicitly designating a selected set of resonance structures ($NRTSTR keylist, cf. Sec. B.8.3). For convenience, the program reports the leading structures of the resonance expansion in a sample $NRTSTR keylist at the end of the NRT output, for possible use in subsequent calculations. The NRTLST keyword can be used to set the level of detail written to $NRTSTR keylist output.

The NRT search/minimization procedure is an iterative process, summarized as follows:

1. Generate an initial set of candidate resonance structures. These are provided either by $NRTSTR keylist input or by the NLS of the NBO search. If "NRTNBI=on" (the default), augment the set with additional structures obtained from analyzing the natural binding indices. Perform symmetry operations on all structures to ensure that the set includes all symmetry-equivalent forms.

2. Perform CHOOSE directed searches of the current set of resonance structures to generate idealized density operators $\mathbf{\Gamma}_\alpha$.

3. Eliminate ionic structures for all covalent/ionic resonance structure pairs. These pairs differ only in the polarity of one NBO, the covalent structure generally exhibiting a polar covalent A-B bond whereas the ionic structure has an A-B bond that is fully polarized toward either atom A or B. (Ionic character in NRT is fully accounted for by the ionicity of polar covalent bonds, as described above. Ionic structures provide no new information and can therefore be reasonably discarded.)

4. Construct the Gram matrix, QP-minimize the objective function, and checkpoint the optimized NRT weights, bond orders, and valencies.

5. Potentially cull the current set of resonance structures, discarding all structures that have not contributed to the resonance hybrid in any of the

previous *n* cycles of this procedure, where *n* is set by the NRTCULL keyword.

6. Construct a list of "parent" resonance structures (those of highest weight as determined by the NRTPAR threshold keyword). For each parent structure, generate new "secondary" structures from the leading delocalizations of the perturbative E(2) analysis (cf. Sec. A.3.5). The E(2) energy threshold for adding new structures is set by the NRTE2 keyword. Apply symmetry operations again to ensure that the set of candidates includes all symmetry-equivalent forms.

7. Write to the output file a one-line report of the current state of the NRT search. Terminate the NRT search if step 6 generated no new structures or if the search has taken too many cycles (see the NRTCYC keyword). Otherwise, cycle back to step 2.

8. Report NRT results for the checkpointed weights of step 4. The output includes a summary of the resonance structures and weights, the bond orders and valencies, and a $NRTSTR keylist specification of the leading resonance structures.

If, while generating new structures in step 6, the total number of resonance structures in the candidate set exceeds the maximum possible number determined by the user (using the NRTRES keyword), the iterative search will cease (with warning), and NRT will report the most recently checkpointed results of step 4.

A principal concern of the user will be to select values for the NRTPAR and NRTE2 thresholds that yield a sufficient number of resonance structures to provide the desired level of detail without generating so many structures that completing the analysis becomes too computationally demanding. NRT uses the leading donor-acceptor interactions of the E(2) perturbative analysis (cf. Sec. A.3.5) to generate new structures, and NRTE2 allows the user to determine how deeply NRT should go into this list as it generates structures. The user should focus particular attention on NRTE2. The NRTPAR threshold determines which resonance structures have their delocalization lists examined. NRTPAR and NRTE2 are described in more detail in Sec. B.8.2.

The NRT program also supports "local" NRT options to deal with the numerical challenges of increasing numbers of resonating units. These options allow systematic divide/conquer strategies to deal with complex systems beyond the reach of default NRT search.

B.8.2 NRT Job Control Keywords

NRT analysis is requested by inserting NRT job control keywords in the $NBO keylist. Below, we list the NRT keywords and the effect that each has on NRT program execution:

KEYWORD	*OPTION DESCRIPTION*
NRT	Perform NRT analysis.
NRTPAR=*val(%)*	Select the weight threshold that triggers searches for additional resonance structures. NRTPAR=*val* forces NRT to search delocalization lists for all "parent" resonance structures of weight ≥ *val*%. NRTPAR=*val%* searches the delocalization lists for all parent structures having weight ≥ *val*% of the weight for the leading structure. For example, if the weight of the leading structure in the current expansion is 80% and NRTPAR=50%, the program will search the delocalization lists of all structures in the expansion having weight ≥ 40% (i.e. 50% of 80). NRTPAR should be used in conjunction with the NRTE2 keyword to control the level of detail desired in the NRT expansion. NRTPAR determines which resonance structures have sufficiently high weight to have their delocalization lists examined, and NRTE2 determines the depth of interactions in the delocalization list that will be considered. The default is NRTPAR=50%.
NRTE2=*val(%)*	Select the delocalization list energy threshold (*val*, in kcal/mol, or *val%*). Increasing the NRT threshold shortens the expansion and speeds execution but also sacrifices detail of the delocalization list (see Sec. A.3.5). NRTE2=*val* generates structures for each valence delocalizing interaction of the delocalization list ≥ *val* kcal/mol. Alternatively, NRTE2=*val%* sets the threshold to a percentage of the strongest individual interaction of the delocalization list. For example, NRTE2=10% for a delocalization list having a strongest *E*(2) interaction of 14 kcal/mol sets the threshold to 1.4 kcal/mol (i.e., to 10% of 14 kcal/mol). NRTE2=off prevents NRT from generating any structures from the delocalization list. The default is NRTE2=1 (kcal/mol).
NRTLONG	Include long-bonded resonance forms when generating new secondary structures from the leading E(2) interactions.
NRTRES=*val*	Set the maximum number of resonance structures in the NRT expansion. By default, NRTRES=10000.

NRTCULL=*val*	Eliminate resonance structures that apparently do not contribute to the NRT expansion. NRTCULL=*val* sets the "cull level" to *val*, eliminating all structures that have not contributed to the expansion for the last *val* invocations of the QP optimizer. Lower cull levels conserve memory and shorten executation times, but potentially compromise NRT bond orders and valencies. Cull levels less than 5-6 are not recommended unless the user has carefully examined the influence of culling in their resonance expansions. NRTCULL=0 (the default) disables culling of resonance structures.
NRTOUT	Write intermediate results at the end of each NRT cycle to external file (with extension .nrt).
NRTCYC=*val*	Terminate the NRT search for resonance structures after *val* cycles. By default, NRTCYC=3, limiting the NRT search to three cycles only. Setting NRTCYC=0 allows NRT to take as many cycles as needed to achieve convergence.
NRTNBI=*on,off*	Generate an initial set of resonance structures for the NRT expansion by analysis of the natural binding indices. By default, NRTNBI=on.
NRTSYM=*on,off*	Control the application of symmetry in NRT. NRTSYM=off disables symmetry throughout the analysis, except for the determination of point group symmetry and warning if the optimal NRT expansion is symmetry-broken. NRTSYM=on, which is <u>not recommended</u>, enables symmetry, including the application of symmetry operators to generate equivalent resonance forms and the treatment of symmetry equivalent forms on the QP minimization. By default, symmetry is used to generate resonance structures but is disabled in the QP minimization.
NRTION=*on,off*	Retain ionic structures in the resonance expansion if NRTION=on, or discard ionic structures if NRTION=off. By default, NRTION=off.
NRTLST=*val*	Set the threshold for writing structures for $NRTSTR, NRTCML, and NRTMOL output. All structures with weight ≥ *val*% will be written. For example, NRTLST=0.1 writes $NRTSTR specifications for all structures with 0.1% or greater weight. The default is NRTLST=1.
NRTPR=*val(s)*	Print details of the NBOs for structure *val*. For example, NRTPR=2 prints the details for the second structure of the resonance hybrid (as listed in NRT output). NRTPR=1,3-5 prints the details of structures 1, 3, 4, and 5.

NRTSTR	Write the $NRTSTR keylist to external file (FILE.nrtstr). Also, see NRTLST.
NRTCML	Write CML-formatted resonance structures to external file (FILE-nrt.cml). See Sec. B.22 for more information.
NRTMOL=*form*	Write MOL-formatted resonance structures to external file (FILE-nrt.mol), in either *form*=v2000 or v3000 format. By default, NRTMOL writes v3000 format.
NRTBO	Write an external text file (FILE.bo) of natural bond orders, Wiberg bond indices, and distances for each atom-pair having bond order ≥ 0.0001.
NRTDTL	Print additional details of the NRT optimizations and the search for resonance structures. This keyword is primarily for debugging and development. Extra and excessive levels of detail can be requested with NRTDTL=EXTRA and NRTDTL=EXCESS.
NRTCHG=*val*	Set the maximum formal charges (with respect to net total charge) allowed in candidate structures generated from the natural binding indices. By default, NRTCHG=0. [For neutral species, the effect of setting NRTCHG=0 is to ignore candidate resonance structures with formal charge on any atom, whereas NRTCHG=1 allows one pair of charges (one positive charge and one negative) to appear in a candidate structure. Setting NRTCHG>1 is not recommended.)
NRTREG=*val*	Set the regularization value for the Gram matrix of the QP minimization. Higher values provide stronger regularization but can strongly perturb the optimal NRT expansion. Lower values make the QP minimization susceptible to singularities in the Gram matrix. Regularization is disabled by setting NRTREG=0.0 or NRTREG=off. By default, NRTREG=0.001, and users are encouraged to leave this value unchanged.

Note that inserting any one of these "NRT keywords" in the $NBO keylist automatically invokes the NRT keyword.

The main NRT keyword can also be followed by a bracket list to specify a "local" subset of atom numbers to which NRT averaging is restricted

NRT <atom-1 atom-2 ... atom-n>

For example, NRT <12 15 18 19> allows the NRT procedure to only consider resonance delocalizations involving atoms 12, 15, 18, 19.

B.8.3 Auxiliary $NRTSTR Keylist Input

The $NRTSTR keylist allows the user to specify candidate resonance structures for NRT analysis. This option is useful for ensuring that a consistent set of resonance structures will be used to compare two NRT expansions, or to specify a common set of structures to examine along a reaction pathway.

$NRTSTR keylist input is similar to $CHOOSE input (Sec. B.4). The format of the $NRTSTR keylist is:

first line:	The keylist identifier "$NRTSTR"
next line:	The keyword "STRUCTURE" (only "STR" is necessary) to begin the specification of the first resonance structure.
next lines:	"LONE" and "BOND" specifications of the resonance structure, for all electron pairs, identical to those of the $CHOOSE keylist. The NRT program determines whether an appropriate number of bonds and lone pairs have been listed in each STR entry of the $NRTSTR keylist, and rejects those resonance structures for which this is not the case.
next line:	The word "END" to terminate the specification of the first resonance structure. (Note that there must be a matching "END" for each "STR," "BOND," or "LONE" keyword.)
next lines:	Additional input for other resonance structures, each beginning with the word "STRUCTURE" and terminated by the word "END".
next line:	The keylist terminator "$END".

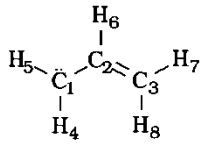
As with the other keylists of the NBO program, the $NRTSTR keylist can be condensed to a smaller number of lines, as long as no line of this keylist is shared with any other keylist.

For open-shell NRT, the user should specify separate $NRTSTR keylists for different spins. The alpha-spin keylist has the identifier, $NRTSTRA, and the beta, $NRTSTRB. A different number of resonance structures can be specified in the $NRTSTRA and $NRTSTRB keylists. Otherwise, the form of these keylists is identical to that described above.

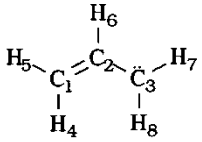
The order in which keylists appear in the input deck is important for some electronic structure packages. Therefore, we recommend that the $NRTSTR

keylist follow the $NBO, $CORE, and $CHOOSE keylists and precede the $DEL keylist.

An example serves to illustrate the $NRTSTR format. The $NRTSTR specification for the leading two resonance structures of allyl anion (**I**,**II**)



I



II

could be given as follows:

```
$NRTSTR
  STR1       ! C1 anion center
    LONE  1 1  END
    BOND  S 1 2  S 1 4  S 1 5  D 2 3  S 2 6  S 3 7  S 3 8  END
  END
  STR2       ! C3 anion center
    LONE  3 1  END
    BOND  D 1 2  S 1 4  S 1 5  S 2 3  S 2 6  S 3 7  S 3 8  END
  END
$END
```

Note that these two resonance forms for allyl anion are symmetry equivalent. The user is, in this case, only required to specify one of the above structures in the $NRTSTR keylist because the second structure will be automatically generated by the symmetry routines of the NRT program. Similarly, if a user were to provide a $NRTSTR keylist for a benzene calculation, only one Kekule structure would be required; the second would be generated by symmetry.

B.8.4 NRT Illustrations

We describe output of NRT analysis for two illustrative examples: (i) the closed-shell methylamine molecule (RHF/3-21G level) and (ii) the open-shell allyl radical (B3LYP/6-311++G** level)

B.8.4.1 Methylamine

We first consider the NRT output for RHF/3-21G methylamine (Pople-Gordon bond lengths, tetrahedral bond angles). The default-level output is obtained by simply including the "NRT" keyword in the $NBO keylist.

The first segment of NRT output is shown below:

```
NATURAL RESONANCE THEORY ANALYSIS:

   Parent structure threshold:  50% of leading weight
Delocalization list threshold:  1 kcal/mol
        Maximum search cycles:  3

Cs symmetry, 2 symmetry operator(s), 2 unique atom permutation(s)
1 initial TOPO matrices: NLS = 1; NBI = 0; SYM = 0

 cycle  structures    D(w)      kmax  CHOOSE   ION    E2    SYM   dbmax   dbrms
-------------------------------------------------------------------------------
   1       1/1     0.04181078     1       1     0     7     0   1.000   1.000
   2       6/6     0.04033466     6      16     0     0     0   0.084   0.043

QPNRT(6/6): D(0)=0.04181078; D(w)=0.04033466; dbmax=0.084; dbrms=0.043
Timing(sec): search=0.01; Gram matrix=0.00; minimize=0.00; other=0.28
```

NRT output begins by describing the molecular point group symmetry and the set of initial resonance structures. In this case, NRT starts with only one structure (in TOPO matrix form, described below). This structure is obtained from the NBO search (the NLS), and no additional structures are generated from analysis of the natural binding indices (NBI) or from symmetry transformations (SYM).

The NRT search/minimization converges in two cycles. The first cycle considers the single initial structure, yielding a $D(w)$ objective function value of 0.04181078 in one (kmax) QP iterations. This cycle requires only one CHOOSE search of a single TOPO matrix, and no ionic structures are identified. Analysis of the delocalization list (E2) for this resonance structure generates an additional seven TOPO matrices for subsequent analysis.

The second cycle yields a resonance hybrid of six structures from six candidates (6/6), requiring 16 CHOOSE searches of six TOPO matrices. $D(w)$ decreases to 0.04033466. No new TOPO matrices are generated by the delocalization lists, so the NRT search terminates.

The last two columns of the table show the convergence of the natural bond orders, include the maximum change in bond order, and the root-mean-square change (only for bond orders $b \geq 0.0001$).

QPNRT reports a single line summary of the search and timing information, including time taken (i) to search for resonance structures, (ii) to construct the Gram matrix, (ii) to QP minimize the resonance expansion, and (iv) for other operations.

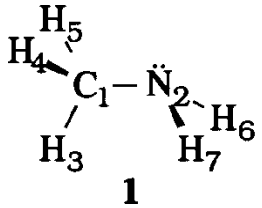
The next segment reports the optimized NRT weights and resonance structures:

```
TOPO matrix for the leading resonance structure:

    Atom  1   2   3   4   5   6   7
    ---- --- --- --- --- --- --- ---
  1.  C   0   1   1   1   1   0   0
  2.  N   1   1   0   0   0   1   1
  3.  H   1   0   0   0   0   0   0
  4.  H   1   0   0   0   0   0   0
  5.  H   1   0   0   0   0   0   0
  6.  H   0   1   0   0   0   0   0
  7.  H   0   1   0   0   0   0   0

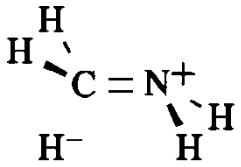
       Resonance
   RS  Weight(%)                  Added(Removed)
-------------------------------------------------------------------------------
    1     91.59
    2      2.92    C  1- N  2, ( C  1- H  3), ( N  2),  H  3
    3      1.49    C  1- N  2, ( C  1- H  5), ( N  2- H  7),  H  5
    4      1.49    C  1- N  2, ( C  1- H  4), ( N  2- H  6),  H  4
    5      1.25    C  1- N  2, ( C  1- H  4), ( N  2- H  6),  H  6
    6      1.25    C  1- N  2, ( C  1- H  5), ( N  2- H  7),  H  7
-------------------------------------------------------------------------------
         100.00   * Total *
```

The TOPO matrix shows the number of bonds and lone pairs (lone pairs as diagonal elements, bonds off-diagonal) for the leading resonance structure, corresponding to the expected methylamine structure diagram (having dominant 91.59% weight in this case),



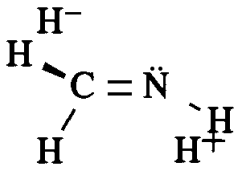
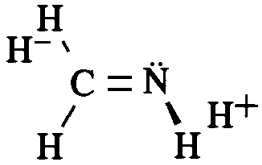
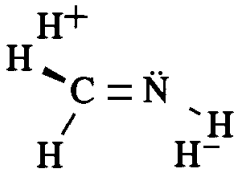
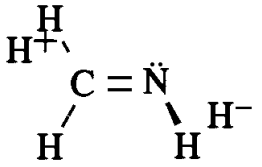
1

This search generated five distinct "secondary" resonance structures, **2**-**6**. Each secondary structure is specified by listing the bonds and lone pairs to be *added* to (or, in parentheses, those to be *removed* from) the leading structure. For example, structure **2** (with resonance weighting 2.92%) is formed from structure **1** by adding a bond C_1-N_2, removing a bond C_2-H_3, removing a lone pair on N_2, and adding a lone pair on H_3, to obtain the "double bond-no bond" structure shown below (associated with the $n_N \rightarrow \sigma^*_{CH}$ NBO interaction):



2

In a similar way, one can determine from the output table that the remaining entries **3**-**6** have the structures and weights shown below (with the associated NBO interaction also given for each entry):

	Structure	*Weight*	*Interaction*
3.		1.49%	$\sigma_{NH} \rightarrow \sigma_{CH}^*$
4.		1.49%	$\sigma_{NH} \rightarrow \sigma_{CH}^*$
5.		1.25%	$\sigma_{CH} \rightarrow \sigma_{NH}^*$
6.		1.25%	$\sigma_{CH} \rightarrow \sigma_{NH}^*$

The NRT output convention of specifying resonance structures by adding or deleting elements from the leading structure provides a compact general depiction of the bonding pattern for any molecular structure framework.

The next segment of the NRT output gives the table of "natural bond orders," showing the total (t), covalent (c), and ionic (i) bond order contributions for each atom pair:

```
 Natural Bond Order:  (total/covalent/ionic)

     Atom       1      2      3      4      5      6      7
     ----   ------ ------ ------ ------ ------ ------ ------
  1.  C  t 0.0000 1.0841 0.9708 0.9726 0.9726 0.0000 0.0000
         c   ---  0.8247 0.7805 0.7566 0.7566 0.0000 0.0000
         i   ---  0.2594 0.1903 0.2160 0.2160 0.0000 0.0000

  2.  N  t 1.0841 0.9708 0.0000 0.0000 0.0000 0.9726 0.9726
         c 0.8247   ---  0.0000 0.0000 0.0000 0.6197 0.6197
         i 0.2594   ---  0.0000 0.0000 0.0000 0.3528 0.3528

  3.  H  t 0.9708 0.0000 0.0292 0.0000 0.0000 0.0000 0.0000
         c 0.7805 0.0000   ---  0.0000 0.0000 0.0000 0.0000
         i 0.1903 0.0000   ---  0.0000 0.0000 0.0000 0.0000

  4.  H  t 0.9726 0.0000 0.0000 0.0149 0.0000 0.0000 0.0000
         c 0.7566 0.0000 0.0000   ---  0.0000 0.0000 0.0000
         i 0.2160 0.0000 0.0000   ---  0.0000 0.0000 0.0000

  5.  H  t 0.9726 0.0000 0.0000 0.0000 0.0149 0.0000 0.0000
         c 0.7566 0.0000 0.0000 0.0000   ---  0.0000 0.0000
         i 0.2160 0.0000 0.0000 0.0000   ---  0.0000 0.0000

  6.  H  t 0.0000 0.9726 0.0000 0.0000 0.0000 0.0125 0.0000
         c 0.0000 0.6197 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.3528 0.0000 0.0000 0.0000   ---  0.0000

  7.  H  t 0.0000 0.9726 0.0000 0.0000 0.0000 0.0000 0.0125
         c 0.0000 0.6197 0.0000 0.0000 0.0000 0.0000   ---
         i 0.0000 0.3528 0.0000 0.0000 0.0000 0.0000   ---
```

This shows, for example, that the total NRT bond order between C_1 and N_2 is 1.0841 (corresponding to the slight "partial double-bond character" associated with the contributions of structures **2**-**6**, all of which have formal double bonds), and its covalent (0.8247) and ionic (0.2594) components correspond to about 23.4% ionic character. In addition, one can see that the C_1-H_3 bond order (0.9708) is slightly less than those (0.9726) for C_1-H_4, C_1-H_5 (corresponding to the slightly higher weight of structure **2** among the secondary structures). The latter difference in $b_{CH}^{(N)}$ bond orders, despite the identical Pople-Gordon bond geometries, reflects the greater strength of hyperconjugative $n_N \rightarrow \sigma_{CH}^*$ NBO interactions in antiperiplanar arrangements.

The diagonal elements of the bond order table correspond to the "lone pair character" at the respective center. For example, the diagonal element for N2 (0.9708) shows that one (lone) pair of electrons is largely localized on that atom.

The next table shows the result of summing over bond orders on each atom to obtain the natural atomic valencies:

```
Natural Atomic Valencies and Electron Counts:

                    Co-    Electro- Electron
    Atom  Valency  Valency  Valency   Count
    ----  -------  -------  -------  -------
  1.  C    4.0000   3.1183   0.8817   8.0000
  2.  N    3.0292   2.0642   0.9650   8.0000
  3.  H    0.9708   0.7805   0.1903   2.0000
  4.  H    0.9726   0.7566   0.2160   1.9750
  5.  H    0.9726   0.7566   0.2160   1.9750
  6.  H    0.9726   0.6197   0.3528   1.9701
  7.  H    0.9726   0.6197   0.3528   1.9701
```

This table shows the near-integer total NRT atomic valencies (viz., 4.00 for C, 3.03 for N, etc.) and its decomposition into covalent and electrovalent (ionic) contributions. The formal electron counts reveal essentially complete valence shells at each atom (8*e* at C and N; ~2*e* at each H).

The final segment shows the $NRTSTR keylist specifications (cf. Sec. B.8.3) for the resonance structure of methylamine with weights exceeding the NRTLST threshold keyword:

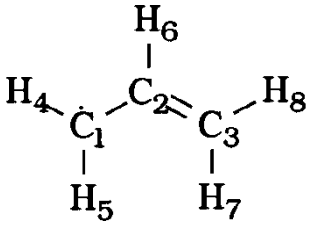
```
$NRTSTR
  STR        ! Wgt=91.59%; rhoNL=0.04795; D(0)=0.04181
    LONE 2 1 END
    BOND S 1 2 S 1 3 S 1 4 S 1 5 S 2 6 S 2 7 END
  END
  STR        ! Wgt=2.92%; rhoNL=1.31883; D(0)=0.21711
    LONE 3 1 END
    BOND D 1 2 S 1 4 S 1 5 S 2 6 S 2 7 END
  END
  STR        ! Wgt=1.49%; rhoNL=1.85471; D(0)=0.25744
    LONE 2 1 5 1 END
    BOND D 1 2 S 1 3 S 1 4 S 2 6 END
  END
  STR        ! Wgt=1.49%; rhoNL=1.85471; D(0)=0.25744
    LONE 2 1 4 1 END
    BOND D 1 2 S 1 3 S 1 5 S 2 7 END
  END
  STR        ! Wgt=1.25%; rhoNL=1.99643; D(0)=0.26709
    LONE 2 1 6 1 END
    BOND D 1 2 S 1 3 S 1 5 S 2 7 END
  END
  STR        ! Wgt=1.25%; rhoNL=1.99643; D(0)=0.26709
    LONE 2 1 7 1 END
    BOND D 1 2 S 1 3 S 1 4 S 2 6 END
```

```
  END
$END
```

Weights and non-Lewis densities are reported for each structure. (Note that all characters following "!" in NBO input are treated as comments and will not be processed if this keylist is used as input for a subsequent calculation.)

B.8.4.2 Allyl Radical

We next describe an open-shell example of the allyl radical (UB3LYP/6-311++G** optimized geometry).



In this case, the NRT analysis is applied separately to the alpha and beta spin manifolds, resulting in "different resonance structures for different spins." The alpha (majority) spin analysis closely resembles the NRT analysis of the closed-shell allyl anion, whereas the beta (minority) spin analysis is most similar to the allyl cation.

The following is the NRT output for the alpha spin system:

```
NATURAL RESONANCE THEORY ANALYSIS, alpha spin:

   Parent structure threshold:  50% of leading weight
Delocalization list threshold:  1 kcal/mol
        Maximum search cycles:  3

C2v symmetry, 4 symmetry operator(s), 2 unique atom permutation(s)
2 initial TOPO matrices: NLS = 1; NBI = 1; SYM = 0

 cycle  structures    D(w)      kmax  CHOOSE   ION    E2   SYM   dbmax   dbrms
-------------------------------------------------------------------------------
   1       2/2     0.05390968     2       2     0    20     0   0.750   0.582
   2      18/26    0.05304704    17      24     0     0     0   0.040   0.022

QPNRT(18/26): D(0)=0.07234643; D(w)=0.05304704; dbmax=0.040; dbrms=0.022
Timing(sec): search=0.26; Gram matrix=0.02; minimize=0.00; other=0.23


TOPO matrix for the leading resonance structure:

    Atom  1   2   3   4   5   6   7   8
    ---- --- --- --- --- --- --- --- ---
  1.  C   0   1   2   1   0   0   0   0
  2.  C   1   1   0   0   1   1   0   0
  3.  C   2   0   0   0   0   0   1   1
  4.  H   1   0   0   0   0   0   0   0
  5.  H   0   1   0   0   0   0   0   0
```

```
  6.  H   0   1   0   0   0   0   0   0
  7.  H   0   0   1   0   0   0   0   0
  8.  H   0   0   1   0   0   0   0   0

      Resonance
  RS  Weight(%)                  Added(Removed)
-------------------------------------------------------------------------------
   1     42.80
   2     42.80    C  1- C  2, ( C  1- C  3), ( C  2),  C  3
   3      1.52   ( C  1- C  2),  C  1- C  3, ( C  3- H  7),  C  2
   4      1.52    C  1- C  2,  C  1- C  2, ( C  1- C  3), ( C  1- C  3),
                 ( C  2- H  5), ( C  2),  C  3,  C  3
   5      1.05    C  1- C  2, ( C  1- H  4), ( C  2- H  6),  H  6
   6      1.05    C  1- C  3, ( C  1- H  4), ( C  3- H  8),  H  8
   7      1.05    C  1- C  2,  C  1- C  2, ( C  1- C  3), ( C  1- H  4),
                 ( C  2- H  6), ( C  2),  C  3,  H  6
   8      1.05    C  1- C  2, ( C  1- H  4), ( C  3- H  8), ( C  2),
                  C  3,  H  8
   9      0.97    C  1- C  3, ( C  1- H  4), ( C  3- H  8),  H  4
  10      0.97    C  1- C  2, ( C  1- H  4), ( C  3- H  8), ( C  2),
                  C  3,  H  4
  11      0.97    C  1- C  2, ( C  1- H  4), ( C  2- H  6),  H  4
  12      0.97    C  1- C  2,  C  1- C  2, ( C  1- C  3), ( C  1- H  4),
                 ( C  2- H  6), ( C  2),  C  3,  H  4
  13      0.61   ( C  1- C  2),  C  1- C  3, ( C  3- H  7),  H  7
  14      0.61    C  1- C  2,  C  1- C  2, ( C  1- C  3), ( C  1- C  3),
                 ( C  2- H  5), ( C  2),  C  3,  H  5
  15      0.61    C  1- C  2, ( C  1- C  3), ( C  2- H  5),  H  5
  16      0.61   ( C  3- H  7), ( C  2),  C  3,  H  7
  17      0.41   ( C  1- C  3), ( C  1- C  3),  C  1, ( C  2),  C  3,
                  C  3
  18      0.41   ( C  1- C  2), ( C  1- C  3),  C  1,  C  2
others    0.00
-------------------------------------------------------------------------------
         100.00   * Total *


Natural Bond Order:  (total/covalent/ionic)

    Atom       1      2      3      4      5      6      7      8
    ----   ------ ------ ------ ------ ------ ------ ------ ------
  1.  C  t 0.0041 0.7661 0.7661 0.4596 0.0000 0.0000 0.0000 0.0000
         c   ---  0.4989 0.4989 0.2810 0.0000 0.0000 0.0000 0.0000
         i   ---  0.2672 0.2672 0.1786 0.0000 0.0000 0.0000 0.0000

  2.  C  t 0.7661 0.2597 0.0000 0.0000 0.4863 0.4798 0.0000 0.0000
         c 0.x4989   ---  0.0000 0.0000 0.2911 0.2929 0.0000 0.0000
         i 0.2672   ---  0.0000 0.0000 0.1952 0.1868 0.0000 0.0000

  3.  C  t 0.7661 0.0000 0.2597 0.0000 0.0000 0.0000 0.4863 0.4798
         c 0.4989 0.0000   ---  0.0000 0.0000 0.0000 0.2911 0.2929
         i 0.2672 0.0000   ---  0.0000 0.0000 0.0000 0.1952 0.1868

  4.  H  t 0.4596 0.0000 0.0000 0.0194 0.0000 0.0000 0.0000 0.0000
         c 0.2810 0.0000 0.0000   ---  0.0000 0.0000 0.0000 0.0000
         i 0.1786 0.0000 0.0000   ---  0.0000 0.0000 0.0000 0.0000

  5.  H  t 0.0000 0.4863 0.0000 0.0000 0.0061 0.0000 0.0000 0.0000
         c 0.0000 0.2911 0.0000 0.0000   ---  0.0000 0.0000 0.0000
         i 0.0000 0.1952 0.0000 0.0000   ---  0.0000 0.0000 0.0000

  6.  H  t 0.0000 0.4798 0.0000 0.0000 0.0000 0.0105 0.0000 0.0000
         c 0.0000 0.2929 0.0000 0.0000 0.0000   ---  0.0000 0.0000
         i 0.0000 0.1868 0.0000 0.0000 0.0000   ---  0.0000 0.0000

  7.  H  t 0.0000 0.0000 0.4863 0.0000 0.0000 0.0000 0.0061 0.0000
         c 0.0000 0.0000 0.2911 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.0000 0.1952 0.0000 0.0000 0.0000   ---  0.0000

  8.  H  t 0.0000 0.0000 0.4798 0.0000 0.0000 0.0000 0.0000 0.0105
         c 0.0000 0.0000 0.2929 0.0000 0.0000 0.0000 0.0000   ---
```

```
         i 0.0000 0.0000 0.1868 0.0000 0.0000 0.0000 0.0000   ---

 Natural Atomic Valencies and Electron Counts:

                      Co-    Electro- Electron
    Atom  Valency  Valency  Valency   Count
    ----  -------  -------  -------  -------
  1.  C    1.9918   1.2788   0.7130   3.9918
  2.  C    1.7322   1.0830   0.6492   3.9837
  3.  C    1.7322   1.0830   0.6492   3.9837
  4.  H    0.4596   0.2810   0.1786   0.9579
  5.  H    0.4863   0.2911   0.1952   0.9848
  6.  H    0.4798   0.2929   0.1868   0.9806
  7.  H    0.4863   0.2911   0.1952   0.9848
  8.  H    0.4798   0.2929   0.1868   0.9806


 $NRTSTRA
   STR        ! Wgt=42.80%; rhoNL=0.26382; D(0)=0.07235
     LONE 2 1 END
     BOND S 1 2 D 1 3 S 1 4 S 2 5 S 2 6 S 3 7 S 3 8 END
   END
   STR        ! Wgt=42.80%; rhoNL=0.26382; D(0)=0.07235
     LONE 3 1 END
     BOND D 1 2 S 1 3 S 1 4 S 2 5 S 2 6 S 3 7 S 3 8 END
   END
   STR        ! Wgt=1.52%; rhoNL=1.14490; D(0)=0.15060
     LONE 2 2 END
     BOND T 1 3 S 1 4 S 2 5 S 2 6 S 3 8 END
   END
   STR        ! Wgt=1.52%; rhoNL=1.14490; D(0)=0.15060
     LONE 3 2 END
     BOND T 1 2 S 1 4 S 2 6 S 3 7 S 3 8 END
   END
   STR        ! Wgt=1.05%; rhoNL=1.18582; D(0)=0.15327
     LONE 2 1 6 1 END
     BOND D 1 2 D 1 3 S 2 5 S 3 7 S 3 8 END
   END
   STR        ! Wgt=1.05%; rhoNL=1.18582; D(0)=0.15327
     LONE 2 1 8 1 END
     BOND S 1 2 T 1 3 S 2 5 S 2 6 S 3 7 END
   END
   STR        ! Wgt=1.05%; rhoNL=1.18582; D(0)=0.15327
     LONE 3 1 6 1 END
     BOND T 1 2 S 1 3 S 2 5 S 3 7 S 3 8 END
   END
   STR        ! Wgt=1.05%; rhoNL=1.18582; D(0)=0.15327
     LONE 3 1 8 1 END
     BOND D 1 2 D 1 3 S 2 5 S 2 6 S 3 7 END
   END
 $END
```

Notice that the bond order and valency values are roughly half of the expected values, because only alpha spin resonance structures are considered here.

Following is the NRT output for the beta spin system:

```
 NATURAL RESONANCE THEORY ANALYSIS, beta spin:

    Parent structure threshold:  50% of leading weight
 Delocalization list threshold:  1 kcal/mol
         Maximum search cycles:  3

 C2v symmetry, 4 symmetry operator(s), 2 unique atom permutation(s)
 2 initial TOPO matrices: NLS = 1; NBI = 1; SYM = 0
```

B.8 NATURAL RESONANCE THEORY (NRT)

cycle	structures	D(w)	kmax	CHOOSE	ION	E2	SYM	dbmax	dbrms
1	2/2	0.05293408	2	2	0	20	0	0.750	0.582
2	12/16	0.05148879	11	20	-2	0	0	0.040	0.027

QPNRT(12/16): D(0)=0.07123551; D(w)=0.05148879; dbmax=0.040; dbrms=0.027
Timing(sec): search=0.17; Gram matrix=0.01; minimize=0.00; other=0.07

TOPO matrix for the leading resonance structure:

Atom	1	2	3	4	5	6	7	8
1. C	0	2	1	1	0	0	0	0
2. C	2	0	0	0	1	1	0	0
3. C	1	0	0	0	0	0	1	1
4. H	1	0	0	0	0	0	0	0
5. H	0	1	0	0	0	0	0	0
6. H	0	1	0	0	0	0	0	0
7. H	0	0	1	0	0	0	0	0
8. H	0	0	1	0	0	0	0	0

RS	Resonance Weight(%)	Added(Removed)
1	39.71	
2	39.71	(C 1- C 2), C 1- C 3
3	3.93	(C 1- C 2), C 1- C 3, (C 3- H 7), C 2
4	3.93	(C 2- H 5), C 3
5	2.11	C 1- C 2, (C 1- H 4), (C 2- H 6), H 6
6	2.11	(C 1- C 2), C 1- C 3, C 1- C 3, (C 1- H 4), (C 3- H 8), H 8
7	1.95	(C 1- C 2), (C 1- C 2), C 1- C 3, C 1- C 3, (C 3- H 7), H 7
8	1.95	C 1- C 2, (C 1- C 3), (C 2- H 5), H 5
9	1.88	(C 1- C 2), C 1- C 3, C 1- C 3, (C 1- H 4), (C 3- H 8), H 4
10	1.88	C 1- C 2, (C 1- H 4), (C 2- H 6), H 4
11	0.42	C 1- C 2, (C 1- C 3), (C 2- H 5), C 3
12	0.42	(C 1- C 2), (C 1- C 2), C 1- C 3, C 1- C 3, (C 3- H 7), C 2
others	0.00	
	100.00	* Total *

Natural Bond Order: (total/covalent/ionic)

Atom		1	2	3	4	5	6	7	8
1. C	t	0.0000	0.7699	0.7699	0.4601	0.0000	0.0000	0.0000	0.0000
	c	---	0.4635	0.4635	0.2709	0.0000	0.0000	0.0000	0.0000
	i	---	0.3065	0.3065	0.1892	0.0000	0.0000	0.0000	0.0000
2. C	t	0.7699	0.0218	0.0000	0.0000	0.4685	0.4801	0.0000	0.0000
	c	0.4635	---	0.0000	0.0000	0.3139	0.3262	0.0000	0.0000
	i	0.3065	---	0.0000	0.0000	0.1546	0.1538	0.0000	0.0000
3. C	t	0.7699	0.0000	0.0218	0.0000	0.0000	0.0000	0.4685	0.4801
	c	0.4635	0.0000	---	0.0000	0.0000	0.0000	0.3139	0.3262
	i	0.3065	0.0000	---	0.0000	0.0000	0.0000	0.1546	0.1538
4. H	t	0.4601	0.0000	0.0000	0.0188	0.0000	0.0000	0.0000	0.0000
	c	0.2709	0.0000	0.0000	---	0.0000	0.0000	0.0000	0.0000
	i	0.1892	0.0000	0.0000	---	0.0000	0.0000	0.0000	0.0000
5. H	t	0.0000	0.4685	0.0000	0.0000	0.0097	0.0000	0.0000	0.0000
	c	0.0000	0.3139	0.0000	0.0000	---	0.0000	0.0000	0.0000
	i	0.0000	0.1546	0.0000	0.0000	---	0.0000	0.0000	0.0000

```
  6.  H  t 0.0000 0.4801 0.0000 0.0000 0.0000 0.0105 0.0000 0.0000
         c 0.0000 0.3262 0.0000 0.0000 0.0000   ---  0.0000 0.0000
         i 0.0000 0.1538 0.0000 0.0000 0.0000   ---  0.0000 0.0000

  7.  H  t 0.0000 0.0000 0.4685 0.0000 0.0000 0.0000 0.0097 0.0000
         c 0.0000 0.0000 0.3139 0.0000 0.0000 0.0000   ---  0.0000
         i 0.0000 0.0000 0.1546 0.0000 0.0000 0.0000   ---  0.0000

  8.  H  t 0.0000 0.0000 0.4801 0.0000 0.0000 0.0000 0.0000 0.0105
         c 0.0000 0.0000 0.3262 0.0000 0.0000 0.0000 0.0000   ---
         i 0.0000 0.0000 0.1538 0.0000 0.0000 0.0000 0.0000   ---


 Natural Atomic Valencies and Electron Counts:

                      Co-    Electro- Electron
    Atom  Valency  Valency  Valency   Count
    ----  -------  -------  -------  -------
  1.  C    2.0000   1.1979   0.8021   4.0000
  2.  C    1.7185   1.1036   0.6149   3.4805
  3.  C    1.7185   1.1036   0.6149   3.4805
  4.  H    0.4601   0.2709   0.1892   0.9578
  5.  H    0.4685   0.3139   0.1546   0.9565
  6.  H    0.4801   0.3262   0.1538   0.9812
  7.  H    0.4685   0.3139   0.1546   0.9565
  8.  H    0.4801   0.3262   0.1538   0.9812
```

Finally, we show the composite bond orders and atomic valencies for the sum of alpha and beta spin structures (printed just after the beta valency table, before the $NRTSTRB list):

```
 Natural Bond Order (total):

    Atom    1       2       3       4       5       6       7       8
    ---- ------  ------  ------  ------  ------  ------  ------  ------
  1.  C  0.0041  1.5361  1.5361  0.9197  0.0000  0.0000  0.0000  0.0000
  2.  C  1.5361  0.2814  0.0000  0.0000  0.9548  0.9598  0.0000  0.0000
  3.  C  1.5361  0.0000  0.2814  0.0000  0.0000  0.0000  0.9548  0.9598
  4.  H  0.9197  0.0000  0.0000  0.0382  0.0000  0.0000  0.0000  0.0000
  5.  H  0.0000  0.9548  0.0000  0.0000  0.0159  0.0000  0.0000  0.0000
  6.  H  0.0000  0.9598  0.0000  0.0000  0.0000  0.0211  0.0000  0.0000
  7.  H  0.0000  0.0000  0.9548  0.0000  0.0000  0.0000  0.0159  0.0000
  8.  H  0.0000  0.0000  0.9598  0.0000  0.0000  0.0000  0.0000  0.0211


 Natural Atomic Valencies and Electron Counts (total):

                      Co-    Electro- Electron
    Atom  Valency  Valency  Valency   Count
    ----  -------  -------  -------  -------
  1.  C    3.9918   2.4767   1.5151   7.9918
  2.  C    3.4507   2.1866   1.2641   7.4642
  3.  C    3.4507   2.1866   1.2641   7.4642
  4.  H    0.9197   0.5519   0.3678   1.9157
  5.  H    0.9548   0.6050   0.3498   1.9413
  6.  H    0.9598   0.6192   0.3407   1.9618
  7.  H    0.9548   0.6050   0.3498   1.9413
  8.  H    0.9598   0.6192   0.3407   1.9618


 $NRTSTRB
  STR        ! Wgt=39.71%; rhoNL=0.25576; D(0)=0.07124
    BOND D 1 2 S 1 3 S 1 4 S 2 5 S 2 6 S 3 7 S 3 8 END
  END
  STR        ! Wgt=39.71%; rhoNL=0.25576; D(0)=0.07124
    BOND S 1 2 D 1 3 S 1 4 S 2 5 S 2 6 S 3 7 S 3 8 END
  END
```

```
  STR        ! Wgt=3.93%; rhoNL=1.04095; D(0)=0.14361
    LONE 2 1 END
    BOND S 1 2 D 1 3 S 1 4 S 2 5 S 2 6 S 3 8 END
  END
  STR        ! Wgt=3.93%; rhoNL=1.04095; D(0)=0.14361
    LONE 3 1 END
    BOND D 1 2 S 1 3 S 1 4 S 2 6 S 3 7 S 3 8 END
  END
  STR        ! Wgt=2.11%; rhoNL=1.16638; D(0)=0.15201
    LONE 6 1 END
    BOND T 1 2 S 1 3 S 2 5 S 3 7 S 3 8 END
  END
  STR        ! Wgt=2.11%; rhoNL=1.16638; D(0)=0.15201
    LONE 8 1 END
    BOND S 1 2 T 1 3 S 2 5 S 2 6 S 3 7 END
  END
  STR        ! Wgt=1.95%; rhoNL=1.22311; D(0)=0.15566
    LONE 7 1 END
    BOND T 1 3 S 1 4 S 2 5 S 2 6 S 3 8 END
  END
  STR        ! Wgt=1.95%; rhoNL=1.22311; D(0)=0.15566
    LONE 5 1 END
    BOND T 1 2 S 1 4 S 2 6 S 3 7 S 3 8 END
  END
  STR        ! Wgt=1.88%; rhoNL=1.18750; D(0)=0.15338
    LONE 4 1 END
    BOND S 1 2 T 1 3 S 2 5 S 2 6 S 3 7 END
  END
  STR        ! Wgt=1.88%; rhoNL=1.18750; D(0)=0.15338
    LONE 4 1 END
    BOND T 1 2 S 1 3 S 2 5 S 3 7 S 3 8 END
  END
$END
```

B.9. NATURAL BOND-BOND POLARIZABILITY (NBBP)

Reference: H. E. Zimmerman and F. Weinhold, *J. Am. Chem. Soc*. **116**, 1579-1580 (1994); H. E. Zimmerman and F. Weinhold, *J. Org. Chem.* (submitted).

B.9.1 Introduction to NBBP

The "bond-bond polarizability" $\Pi_{rs;tu}$ was originally introduced by Coulson and Longuet-Higgins [C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* **A191**, 39 (1947); **A192**, 16 (1947)] in the framework of Hückel pi-electron theory, but a full *ab initio* SCF-MO generalization can be given with natural hybrid orbitals (NHOs). In Hückel theory the indices *r*, *s*, *t*, *u* of $\Pi_{rs;tu}$ refer to atoms connected by pi bonds, *viz*., pi-bond π_{rs} between atoms *r*, *s* and pi-bond π_{tu} between atoms *t*, *u*. More generally, these indices refer to bonding natural hybrid orbitals h_r, h_s, h_t, h_u forming occupied NBOs of the natural Lewis structure, *viz.*, NBO b_{rs} between hybrids h_r, h_s and NBO b'_{tu} between hybrids h_t, h_u.

The bond-bond polarizability is formally defined as

$$\Pi_{b;b'} = \Pi_{rs;tu} = \sum_j^{occ} \sum_k^{vir} n_j \, (c_{rj}c_{sk} + c_{rk}c_{sj}) \, (c_{tj}c_{uk} + c_{tk}c_{uj})/(\varepsilon_k - \varepsilon_j)$$

where c_{rj}, c_{rk} denote the coefficients of hybrid h_r in an occupied MO φ_j or virtual MO φ_k, with respective orbital energies ε_j, ε_k and occupied orbital occupancy n_j (= 2 for closed-shell systems). When evaluated in this general NHO-based formulation, $\Pi_{rs;tu}$ is referred to as the "natural bond-bond polarizability" (NBBP) index. For open-shell systems, NBBP indices are calculated separately for alpha and beta spin (with $n_j = 1$), consistent with the NBO "different hybrids for different spins" description.

The matrix elements $\Pi_{rs;tu}$ can be formally related to changes in bond order between hybrids *r*, *s*, due to changes in the interaction between hybrids *t*, *u*. The NBBP index therefore allows one to analyze how changes in one part of the molecule affect the strength of bonds (or incipient bonds) elsewhere.

Elements of the natural bond-bond polarizability array may be identified by NBO indices ($\Pi_{b;b'}$) or NHO indices ($\Pi_{rs;tu}$) in the NBBP program output. By default, the program calculates $\Pi_{b;b'}$ values for bonding NBOs of the formal Lewis structure. In addition, the user can request values of other $\Pi_{rs;tu}$ elements by listing desired sets of NHO indices in a supplementary "bracket list" to be described below.

B.9.2 NBBP Keyword Usage and Sample Output

Basic NBBP analysis is requested by simply including the "NBBP" keyword in the $NBO keylist, as in the example below:

```
$NBO  NBBP  FILE=CH3NH2  $END
```

This produces an array of $\Pi_{b;b'}$ elements for each pair of occupied NBOs *b*, *b '* of the natural Lewis structure. Rows and columns of this array are labelled according to the standard NBO numbering. For the simple case of methylamine (RHF/3-21G level, Pople-Gordon geometry), the output is illustrated below:

```
 NBBP: NBO bond-bond polarizability matrix

         NBO        1       2       3       4       5       6       7       8
     ---------- ------- ------- ------- ------- ------- ------- ------- -------
  1.  C 1(cr)     0.0004  0.0000  0.0000  0.0001  0.0002  0.0001  0.0001  0.0000
  2.  N 2(cr)     0.0000  0.0001  0.0000  0.0001  0.0000  0.0000  0.0000  0.0000
  3.  N 2(lp)     0.0000  0.0000  0.0999  0.0004  0.0277  0.0051  0.0051  0.0009
  4.  C 1- N 2    0.0001  0.0001  0.0004  0.0633 -0.0001 -0.0001 -0.0001 -0.0013
  5.  C 1- H 3    0.0002  0.0000  0.0277 -0.0001  0.0755  0.0000  0.0000  0.0004
  6.  C 1- H 4    0.0001  0.0000  0.0051 -0.0001  0.0000  0.0921  0.0012  0.0040
  7.  C 1- H 5    0.0001  0.0000  0.0051 -0.0001  0.0000  0.0012  0.0921  0.0005
  8.  N 2- H 6    0.0000  0.0000  0.0009 -0.0013  0.0004  0.0040  0.0005  0.2102
  9.  N 2- H 7    0.0000  0.0000  0.0009 -0.0013  0.0004  0.0005  0.0040 -0.0014

         NBO        9
     ---------- -------
  1.  C 1(cr)     0.0000
  2.  N 2(cr)     0.0000
  3.  N 2(lp)     0.0009
  4.  C 1- N 2   -0.0013
  5.  C 1- H 3    0.0004
  6.  C 1- H 4    0.0005
  7.  C 1- H 5    0.0040
  8.  N 2- H 6   -0.0014
  9.  N 2- H 7    0.2102
```

In this example, the strongest off-diagonal NBBP element (+0.0277) is that connecting the amine lone pair (NBO 3) with the vicinal antiperiplanar C1-H3 bond (NBO 5), evidence of their strong hyperconjugative coupling. It can also be seen that bond-bond polarizability between CH and NH bonds is stronger for antiperiplanar than gauche orientation (viz., 0.0040 for C1-H4 with N2-H6, vs. 0.0005 for C1-H4 with N2-H7).

In addition, one can request subsidiary $\Pi_{rs;tu} = \Pi(r,s;t,u)$ NBBP values to be computed for an arbitrary list of NHO indices *r*, *s*, *t*, *u*. This is done by including a *bracket list* of the form <*r s t u*/*r ' s ' t ' u '*/ . . . > following the NBBP keyword in the $NBO keylist. For example, to request the additional elements Π(4,5,9,15), Π(7,6,8,12), and Π(8,9,12,13), one could use the $NBO keylist shown below:

```
$NBO NBBP <4 5 9 15/7 6 8 12/8 9 12 13> FILE=CH3NH2 $END
```

The bracket list can also be broken onto multiple lines as illustrated below:

```
$NBO NBBP
<  4  5  9 15 /
   7  6  8 12 /
   8  9 12 13 >
FILE=CH3NH2  $END
```

As illustrated, each field of 4 indices (free format, separated by spaces or commas) is separated by slashes (/) from neighboring fields, with the angle bracket delimiters (<, >) separated by at least one space from adjacent keywords.

The keylist above will produce the usual table of $\Pi_{b;b'}$ values for bonding NBOs as well as the supplementary table shown below with $\Pi_{rs;tu}$ values for the requested NHO indices:

```
 User-requested Pi(r,s;t,u) NBBP Values:

     NHO indices    uncorrected      sign        "corrected"
    -------------   -----------  -------------   -----------
    r   s   t   u   Pi(r,s;t,u)  F(r,s) F(t,u)   Pi(r,s;t,u)
    -------------   -----------  ------ ------   -----------
    4   5   9  15    -0.001658      -      -      -0.001658
    7   6   8  12     0.000412      -      +      -0.000412
    8   9  12  13     0.004018      -      -       0.004018
User-requested Pi(r,s;t,u) NBBP Values:

     NHO indices    uncorrected      sign        "corrected"
    -------------   -----------  -------------   -----------
    r   s   t   u   Pi(r,s;t,u)  F(r,s) F(t,u)   Pi(r,s;t,u)
    -------------   -----------  ------ ------   -----------
    4   5   9  15    -0.001658      -      -      -0.001658
    7   6   8  12     0.000412      -      +      -0.000412
    8   9  12  13     0.004018      -      -       0.004018
```

In this case, the final entry Π(8,9,12,13) of the supplementary table corresponds to the 6-8 entry (0.0040) in the main table, since NBO 6 is composed of hybrids 8, 9 and NBO 8 of hybrids 12, 13. Note that user-selected $\Pi_{rs;tu}$ values are printed with somewhat higher numerical precision than those of the main NBBP table.

As the example above shows, the program prints both the "uncorrected" $\Pi_{rs;tu}$ value (as directly calculated for the actual hybrid phases) as well as a "corrected" value, $sgn(F_{rs}F_{tu})\Pi_{rs;tu}$, whose sign is adjusted to correspond to the intuitive choice of phase with *negative* Fock matrix elements F_{rs}, F_{tu}, i.e., with both *r-s* and *t-u* hybrid pairs chosen to have "in-phase overlap." (The sign information given in this table helps to consistently interpret the physical

significance of negative $\Pi_{rs;tu}$ values, since the sign of $\Pi_{rs;tu}$ can otherwise be reversed by arbitrarily changing the phases of any of its indexed NHOs.) For example, in the second entry of the sample output, the "corrected" value of $\Pi(7,6;8,12)$ is *negative*, as if the phase of hybrid 7 (or 6) were reversed to give a negative Fock matrix element ("positive overlap") between NHOs 7 and 6.

[However, for very small polarizability values, the near-zero Fock matrix elements F_{rs} (weak overlap limit) can become slightly positive even if orbitals *r*, *s* are in-phase. In case of doubt one should therefore check the actual orbital overlap with ORBPLOT, or with the explicit value in the SPNHO overlap matrix, to confirm the presumed phase assignments.]

B.10. NATURAL STERIC ANALYSIS

References: J. K. Badenhoop and F. Weinhold, *J. Chem. Phys.* **107**, 5406-5421, 5422-5432 (1997); *Int. J. Quantum Chem.* **72**, 269-280 (1999).

B.10.1 Introduction

Natural steric analysis expresses steric exchange repulsion as the energy difference due to orbital orthogonalization, in accordance with a well-established physical picture of "steric repulsions" [V. W. Weisskopf, *Science* **187**, 605-612 (1975); P. A. Christiansen and W. E. Palke, *J. Chem. Phys.* **67**, 57 (1977)]. The present implementation improves that introduced in NBO 4.0 by systematic replacement of NBOs by NLMOs, thereby incorporating the coupling of steric repulsions with delocalization effects described by the weak "tails" of NLMOs. This replacement leads to negligible numerical changes for well-localized systems (e.g., rare gas interactions), but it significantly improves the description of steric effects in strongly delocalized species.

The overall NBO/NLMO steric exchange energy is expressed as the sum of orbital orthogonalization energy changes, calculated as differences in diagonal Fock matrix elements for nonorthogonal PNLMOs $\{^{p}\Omega_I\}$ vs. orthogonal NLMOs $(\Omega_I\}$

$$E_x^{NLMO} = \sum_I (F_{I,I}^{NLMO} - F_{I,I}^{PNLMO})$$

where $F_{I,I}^{NLMO} = \langle\Omega_I|\mathbf{F}|\Omega_I\rangle$ and $F_{I,I}^{PNLMO} = \langle{}^{p}\Omega_I|\mathbf{F}|{}^{p}\Omega_I\rangle$. The reference zero in this expression refers to the isolated PNLMO limit in which all atoms are separated to infinity. The steric exchange energy includes effects from *all* occupied orbitals and therefore typically contains contributions from covalent (*intra*bond) groups. In order to calculate intermolecular steric energies, one first performs a calculation with the molecular units separated by a large distance (typically at least 8 Å) as the asymptote, then a second one in the desired geometry, and subtracts the two values.

Natural steric analysis also approximates the pairwise steric exchange interaction $E_{I,J}^{pwx}$ between two semi-localized NLMOs *I*, *J* by using the inverse of a 2 x 2 occupancy-weighted symmetric orthogonalization to obtain two "partial NLMOs" $^{p2}\Omega_I$, $^{p2}\Omega_J$ (labelled "PNLMO/2" orbitals). The steric exchange energy associated with NLMOs *I*, *J* is calculated as

$$E_{I,J}^{pwx} = (F_{I,I}^{NLMO} - F_{I,I}^{PNLMO/2}) + (F_{J,J}^{NLMO} - F_{J,J}^{PNLMO/2})$$

where $F_{I,I}^{PNLMO/2} = < {}^{p2}\Omega_I|\mathbf{F}|\ {}^{p2}\Omega_I>$, etc. The strength of these pairwise interactions between localized orbitals falls off rapidly with distance, so "steric effects" due to interaction of orbitals in close proximity can be exhibited in a short list of the most important terms.

For the total steric exchange energy, both the individual NLMO bond energy changes and the sum E_x^{NLMO} (overall and by molecular unit) are tabulated. This is followed by a list of the pairwise steric interactions between orbitals on different centers above an energy print threshold which can be specified by the user. The user can also specify pairs of NLMO indices in a supplementary bracket list, described below.

B.10.2 STERIC Keyword Usage and Sample Output

Basic NBO/NLMO steric analysis is requested by simply including the "STERIC" keyword in the $NBO keylist, as in the example below:

```
    $NBO  STERIC  FILE=CH3NH2_He  $END
```

This produces a list of orbital contributions to the overall steric exchange energy and their sum organized by molecular unit, followed by a table of PNLMO overlaps and pairwise steric exchange energies.

Sample output will be shown to illustrate both intra- and intermolecular steric interactions for a simple $CH_3NH_2\cdots He$ model, where a helium "probe" atom is placed 2.3 Å (in collinear N-H$\cdots$He arrangement) from an amine hydrogen of methylamine (B3LYP/3-21G, Pople-Gordon geometry). The first segment of output shows the individual NLMO steric exchange energies within each molecular unit, and in total:

```
 NBO/NLMO STERIC ANALYSIS:

 Occupied NLMO contributions dE(i) (kcal/mol) to total steric exchange energy

 NLMOs (i) in unit  1              dE(i)
    1. CR ( 1) C  1                75.90
    2. CR ( 1) N  2               101.45
    3. LP ( 1) N  2               -18.87
    5. BD ( 1) C  1- N  2         -15.57
    6. BD ( 1) C  1- H  3         -11.22
    7. BD ( 1) C  1- H  5         -13.13
    8. BD ( 1) C  1- H  6         -13.16
    9. BD ( 1) N  2- H  4         -11.06
   10. BD ( 1) N  2- H  7         -11.40

 Steric exchange energy, unit 1:    82.95 kcal/mol

 NLMOs (i) in unit  2              dE(i)
    4. LP ( 1)He  8                 0.12

 Steric exchange energy, unit 2:     0.12 kcal/mol
 -------------------------------------------------
   Total steric exchange energy:    83.07 kcal/mol
 -------------------------------------------------
```

As shown, the total steric exchange energy is calculated as +83.07 kcal/mol in this case, arising almost entirely from the CH_3NH_2 unit (82.95 kcal/mol, vs. 0.12 kcal/mol for the He unit). Within CH_3NH_2, the exchange energies are seen to be typically negative for valence NLMOs (*viz.*, −18.87 kcal/mol for the nitrogen lone pair), but strongly positive for core NLMOs (*viz.*, +101.45 kcal/mol for the nitrogen core 1*s* orbital), leading to the expected net positive (repulsive) contribution of steric exchange interactions.

[To obtain the intermolecular steric exchange energy between CH_3NH_2 and He units, one would repeat the calculation with the two units separated by a large distance (e.g., 12 Å). The total steric exchange energy obtained from this calculation (not shown) is +82.66 kcal/mol, so the steric interaction energy would be estimated as +83.07 − 82.66 = +0.41 kcal/mol for the 2.3 Å separation, similar to the room-temperature *kT* value characteristic of van der Waals contact distance.]

The next segment of output shows the corresponding estimates of pairwise steric exchange interactions (and associated pre-NLMO overlap integrals) for "disjoint" pairs of NLMOs (i.e., sharing no common atom):

```
Pairwise steric exchange energies dE(i,j) (kcal/mol) and associated
pre-NLMO overlaps S(i,j) for disjoint (no common atoms) interactions
between NLMOs i,j:

        Threshold for printing:     0.50 kcal/mol
       (Intermolecular threshold:   0.05 kcal/mol)
                                                                 PNLMO    dE(i,j)
     NLMO (i)                          NLMO (j)                 S(i,j)   kcal/mol
================================================================================

within unit  1
   3. LP ( 1) N  2              6. BD ( 1) C  1- H  3        0.1646    10.80
   3. LP ( 1) N  2              7. BD ( 1) C  1- H  5       -0.0770     1.69
   3. LP ( 1) N  2              8. BD ( 1) C  1- H  6        0.0772     1.71
   6. BD ( 1) C  1- H  3        9. BD ( 1) N  2- H  4       -0.0825     1.74
   6. BD ( 1) C  1- H  3       10. BD ( 1) N  2- H  7        0.0826     1.75
   7. BD ( 1) C  1- H  5        9. BD ( 1) N  2- H  4        0.0991     4.05
   7. BD ( 1) C  1- H  5       10. BD ( 1) N  2- H  7        0.0941     2.45
   8. BD ( 1) C  1- H  6        9. BD ( 1) N  2- H  4        0.0937     2.44
   8. BD ( 1) C  1- H  6       10. BD ( 1) N  2- H  7        0.0990     4.02

                                                 sum within unit 1:     31.15

between units  1 and  2
   4. LP ( 1)He  8             10. BD ( 1) N  2- H  7       -0.0282     0.29

                                          sum between units 1 and 2:      0.21

within unit  2

                                                 sum within unit 2:      0.00

--------------------------------------------------------------------------------
      Total disjoint NLMO steric exchange energy from pairwise sum:     31.36
--------------------------------------------------------------------------------
```

As shown, the only appreciable steric interaction between He and CH_3NH_2 (above the default intermolecular printing threshold of 0.05 kcal/mol) is that (+0.29 kcal/mol) with the N_2-H_7 bond pointed directly toward He. The total intermolecular steric exchange interaction estimated from the pairwise sum (+0.21 kcal/mol) differs from the total exchange energy difference calculated above (+0.41 kcal/mol) due to non-pairwise additivity of exchange interactions.

By default, only pairwise steric energies above 0.5 kcal/mol (intramolecular) or 0.05 kcal/mol (intermolecular) are printed. The user can set a different threshold (e.g., 0.4 kcal/mol, with the intermolecular threshold scaled accordingly) by including a real number value after the STERIC keyword, as illustrated below:

```
$NBO  STERIC=0.4  $END
```

The user can also request specific additional pair interaction energies (*I,J*), (*K,L*),... to be printed by specifying pairs of NLMO indices in brackets (cf Sec. B.9.2),

```
STERIC <I J/K L/..>
```

As indicated, each field of two indices (free format, separated by spaces or commas) is separated by slashes (/) from neighboring fields, with the entire list enclosed by angle bracket delimiters () separated by at least one space from adjacent keywords. If desired, the bracket list may be broken up onto separate lines (each terminated by a / field delimiter) as shown below:

```
STERIC <I1 J1/I2 J2/
I3 J3/I4 J4>
```

An altered printing threshold can also be combined with user-requested bracket input as shown below:

```
$NBO  STERIC=0.4 <6 4/5 6/6 1> FILE=CH3NH2_He  $END
```

In the case of the $CH_3NH_2\cdots He$ example (2.3 Å), this would lead to the additional output shown below:

```
User-requested steric interactions:
                                                                  PNLMO    dE(i,j)
     NLMO (i)                          NLMO (j)                   S(i,j)   kcal/mol
 ================================================================================
   6. BD ( 1) C  1- H  3         4. LP ( 1)He  8             -0.0026     0.00
   5. BD ( 1) C  1- N  2         6. BD ( 1) C  1- H  3       -0.1140    15.35
   6. BD ( 1) C  1- H  3         1. CR ( 1) C  1             -0.0421    28.70
 --------------------------------------------------------------------------------
```

As shown, the He probe atom is outside the range in which it has any appreciable steric interaction with the C_1-H_3 bond, but the exchange interactions between NLMOs 5, 6 (the non-disjoint interaction between geminal bonds σ_{CN}, σ_{CH}: +15.35 kcal/mol) or NLMOs 6, 1 (the interaction of bond C_1-H_3 with its own carbon core orbital: +28.70 kcal/mol) are quite significant.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

References: E. D. Glendening and A. Streitwieser, *J. Chem. Phys.* **100**, 2900 (1994). E. D. Glendening, *J. Am. Chem. Soc.* **118**, 2473 (1996). G. K. Schenter and E. D. Glendening, *J. Phys. Chem.* **100**, 17152 (1996). E. D. Glendening, *J. Phys. Chem. A* **109**, 11936 (2005).

B.11.1 Introduction to NEDA

Natural energy decomposition analysis is an energy partitioning procedure for molecular interactions. Electrical interaction (EL), charge transfer (CT), and core repulsion (CORE) contributions are evaluated for self-consistent field (SCF) wavefunctions. The electrical term

$$\mathrm{EL} = \mathrm{ES} + \mathrm{POL} + \mathrm{SE}$$

arises from classical electrostatic (ES) and polarization interactions (POL+SE) that are well described by electrodynamics. SE is the linear response self energy (energy penalty) of polarization. The CORE contribution

$$\mathrm{CORE} = \mathrm{EX} + \mathrm{DEF} - \mathrm{SE}$$

results principally from intermolecular exchange interactions (EX) and deformation (DEF), where the latter is the energy cost to distort a fragment wavefunction in the field of all other fragments of the complex. For DFT-based analysis, EX is replaced by the exchange-correlation interaction (XC). The total interaction energy is then given by

$$\Delta E = \mathrm{EL} + \mathrm{CT} + \mathrm{CORE}$$

A key element of the NEDA approach is the evaluation of "perturbed" fragment wavefunctions, Ψ_A^{def}, one for each of the fragments that comprise the molecular complex. These wavefunctions are constructed from the eigenvectors of local fragment blocks of the Fock or Kohn-Sham matrix expressed in the NAO, NBO, or NLMO basis. Orthogonality of the basis orbitals ensures that the sets of eigenvectors for different fragments are mutually orthogonal. The charge distributions described by the perturbed wavefunctions arise from electric field and quantum mechanical effects experienced by the fragments within the complex. A localized wavefunction, Ψ^{loc}, for the complex is then constructed as an antisymmetrized product of perturbed fragment wavefunctions. NEDA additionally employs the

supermolecule wavefunction, Ψ, of the complex and the SCF-converged wavefunctions of the isolated fragments, Ψ_A.

Given these wavefunctions, the interaction energy and its NEDA components are obtained as follows:

$$\Delta E = E(\Psi) - \sum_A E(\Psi_A)$$

$$\mathrm{CT} = E(\Psi) - E(\Psi^{\mathrm{loc}})$$

$$\mathrm{ES} + \mathrm{POL} + \mathrm{EX} = E(\Psi^{\mathrm{loc}}) - \sum_A E(\Psi_A^{\mathrm{def}})$$

$$\mathrm{DEF} = \sum_A \mathrm{DEF}_A = \sum_A [E(\Psi_A^{\mathrm{def}}) - E(\Psi_A)]$$

Further details of the evaluation of these components are given in the references (especially in the 2005 paper).

ΔE does not account for geometry relaxation of the fragments; that is, all calculations are performed on the unrelaxed fragment geometries of the complex. Additionally, NEDA evaluates all energies in the complete basis set of the complex so that ΔE corresponds to the counterpoise-corrected interaction energy of Boys and Bernardi [*Mol. Phys.* **19**, 553 (1970)]. The NEDA program has been generalized to handle complexes consisting of more than two fragments.

NEDA also evaluates the dipole moments for the fragment wavefunctions Ψ_A^{def} and Ψ_A

$$\boldsymbol{\mu}_A^{\mathrm{def}} = \boldsymbol{\mu}_A^{\mathrm{nuc}} - \langle \Psi_A^{\mathrm{def}} | \boldsymbol{\mu}_{\mathrm{el}} | \Psi_A^{\mathrm{def}} \rangle$$

$$\boldsymbol{\mu}_A^{\mathrm{rel}} = \boldsymbol{\mu}_A^{\mathrm{nuc}} - \langle \Psi_A | \boldsymbol{\mu}_{\mathrm{el}} | \Psi_A \rangle$$

$\boldsymbol{\mu}_A^{\mathrm{def}}$ represents the perturbed dipole of a fragment within the molecular environment, whereas $\boldsymbol{\mu}_A^{\mathrm{rel}}$ is the electronically relaxed dipole of the isolated fragment (in the unrelaxed geometry of the complex). The difference between these two vector quantities is a measure of the induced dipole for a fragment within the complex. These moments are origin independent, except for charged fragments for which the origin is placed at the center of the fragment mass.

B.11.2 Performing NEDA

NEDA is implemented in the energetic (deletions) analysis of the NBO program. NEDA is only available with Gaussian-16 (C.01 or later) and GAMESS, and because the interfaces to these programs differ somewhat, the user input required to initiate and direct NEDA also differs.

B.11.2.1 Performing NEDA with Gaussian

For Gaussian calculations, NEDA is activated by the "NEDA=*n*" keyword in the route section of the input file, where *n* is the number of fragments in the system. Fragments, and their charges and spin multiplicities, are given in the molecule specification section of the input, in format similar to that required of Gaussian's "counterpoise" keyword. For example, the following identifies two fragments (NEDA=2) for the $Na(H_2O)$ complex.

```
0,2  0,2  0,1
Na(fragment=1)     0.000000    0.000000   -0.340466
O(fragment=2)      0.000000    0.000000    2.024020
H(fragment=2)      0.000000    0.762733    2.583246
H(fragment=2)      0.000000   -0.762733    2.583246
```

The three integer pairs that precede the geometry give the charge and spin for the complex, fragment 1, and fragment 2, respectively. In this case, the complex is neutral with one unpaired electron (doublet), the first fragment is the neutral sodium atom with the unpaired electron, and the second fragment is the neutral water molecule.

Gaussian's NEDA keyword automatically activates NBO7 so that no additional NBO input is required. That is, it is unnecessary to add "pop=nbo7" or "pop=nbo7read" to the route section or provide any $NBO or $DEL keylist input when performing NEDA. The user can optionally provide $NBO keylist input, when NEDA is invoked, to direct NBO7 analysis.

By default, Gaussian/NEDA is performed in the NAO basis, with the NAOs of the fragment atoms defining the local fragment blocks of the Fock matrix from which the perturbed fragment wavefunctions are constructed. When using identical methods, basis sets, and geometries, the results of NAO-based Gaussian/NEDA will be identical to those of NBO-based GAMESS/NEDA.

NEDA can be performed for any restricted closed-shell or unrestricted open-shell, SCF-based Gaussian calculation, including those involving effective core potentials (ECPs).

B.11.2.2 Performing NEDA with GAMESS

For GAMESS calculations, NEDA is activated by inserting the keyword NEDA in the $DEL keylist. NEDA input is terminated by the word END. Thus, adding the following lines to the GAMESS input deck runs default NEDA.

```
$NBO  $END
$DEL  NEDA END  $END
```

The first line activates the NBO program. In the second line, the word END terminates NEDA input, and the $END completes the $DEL keylist. This input is entirely free-format and keylists can span more than one line. The $NBO and $DEL keylist identifiers should, however, be the first words appearing on their respective lines.

By default, NEDA analyzes a wavefunction in terms of the molecular units of the NBO program. These units are determined by the connectivity of the NBOs and are printed in the summary table that appears at the bottom of standard NBO output. For instance, a calculation of the water dimer gives two molecular units (the two water molecules), and the analysis of the trimer gives three. Default NEDA would therefore analyze these wavefunctions in terms of two and three water molecules, respectively. For most applications, the set of molecular units calculated by NBO will be exactly that desired for NEDA. In these cases, no input beyond that shown above is required.

To activate NEDA for unrestricted wavefunctions, use a $DEL keylist of the form

```
$DEL
   ALPHA  NEDA END
   BETA   NEDA END
$END
```

which requests NEDA for both the alpha and beta spin systems. For example, NBO analysis of the open-shell Na(H_2O) complex calculates two molecular units in the alpha system, including the Na atom (6 electrons) and H_2O molecule (5 electrons), and two units in the beta system, also a Na atom (5 electrons) and H_2O molecule (5 electrons). Therefore, default input, as shown above, directs NEDA to treat the system as a complex of two fragments, namely a Na atom with unpaired electron (6 alpha electrons and 5 beta) and a H_2O molecule.

Note that NEDA fails for unrestricted systems if the molecular units of the alpha system differ from those of the beta.

In certain cases, it may be desirable to define a set of fragments other than that calculated by the NBO program. Extended NEDA input, $CHOOSE input, and the NBO keyword NOBOND together offer the user several methods to specify an alternate selection.

Extended NEDA input allows one to combine two or more molecular units of the NBO analysis into a single fragment. For example, suppose that NBO calculates eight molecular units, numbered 1 to 8. By default, NEDA would treat these eight units as eight separate fragments. However, the following input forces NEDA to combine these units into only four fragments.

```
$DEL  NEDA (1) (3,4) (2,5,6,7) (8) END  $END
```

In this case, the first fragment is molecular unit 1, the second fragment consists of units 3 and 4, the third includes units 2, 5, 6, and 7. The '(1)' and '(8)' are optional here, because any molecular unit absent in NEDA input is treated as a separate fragment.

NEDA input can be abbreviated by specifying ranges of molecular units instead of listing each unit. For example, the following input is equivalent to that given above:

```
$DEL  NEDA (1) (3-4) (2,5-7) (8) END  $END
```

$CHOOSE input and the NOBOND option can be used to modify the molecular units calculated by the NBO program. For example, consider BH_3NH_3 at its equilibrium geometry. By default, the NBO program calculates a single molecular unit with seven bonds: B1-N2, B1-H3, B1-H4, B1-H5, N2-H6, N2-H7, and N2-H8. To treat this system as an interacting pair of Lewis acid-base molecules BH_3 and NH_3, one can use the $CHOOSE input to specify the pattern of bonds for NBO to calculate.

```
$NBO  $END
$CHOOSE
        LONE 2 1 END
        BOND S 1 3 S 1 4 S 1 5 S 2 6 S 2 7 S 2 8 END
$END
$DEL  NEDA END  $END
```

Alternatively, the NOBOND keyword prevents NBO from calculating any bonding functions. Each molecular unit therefore consists of a single atom and

extended NEDA input can be used to collect atomic centers into the desired fragments.

```
$NBO  NOBOND  $END
$DEL  NEDA (1,3-5) (2,6-8) END  $END
```

By default, the localized (Ψ^{loc}) and perturbed fragment (Ψ_A^{def}) wavefunctions of GAMESS/NEDA are obtained from analysis of the Fock (or Kohn-Sham) matrix in the NBO basis. The user may alternatively request that NEDA construct these wavefunctions from the NAO or NLMO Fock matrices by specifying the desired basis set prior to the NEDA keyword in the $DEL keylist. For example, for the water dimer, separate NAO-, NBO-, and NLMO-based NEDA calculations can be performed using the following input:

```
$DEL
    NAO  NEDA (1-3) (4-6) END
    NBO  NEDA END
    NLMO NEDA END
$END
```

The first analysis is completed, as requested, in the NAO basis, with atoms 1-3 serving as the first molecular fragment (presumably an O and two Hs), and atoms 4-6 as the second. Note that for NAO-based analysis, the "integer units" collected in the input to form fragments correspond to atom numbers. The second analysis performs the default NBO-based analysis (the "NBO", which is the default, could be omitted here), and the third analysis is NLMO-based. As with NBOs, the NLMO-based analysis defaults to molecular units defined by the connectivities of the NLMOs (which are always identical to those of the NBOs).

Because NBOs of a particular molecular unit can be considered to arise from a unitary transformation of the NAOs on that unit, NAO- and NBO-based NEDA will yield identical results (as long as the molecular units are identically defined). NAO-based NEDA is particularly useful when one wants to simply use atom numbers to define molecular units without having to concern oneself with the units that are identified in the NBO summary.

The results of NLMO-based NEDA differ from those of NAO and NBO because the occupied NLMOs of an electron donor unit include the delocalization tails into the electron acceptor that would otherwise be associated with charge transfer. The occupied NLMOs correspond to a unitiary transformation of the occupied MOs. Thus, the NLMOs have integer occupancies (1 for unrestricted wavefunctions, 2 for restricted), and the localized wavefunction (Ψ^{loc}) constructed from NLMOs is identical to the

supermolecular wavefunction (Ψ). The CT term thereby vanishes for NLMO-based NEDA, and the effects nominally associated with CT are shifted into the polarization (POL+SE) and deformation (DEF) terms. See B.11.4.5 for an example.

NEDA can be performed for any restricted closed-shell or unrestricted open-shell, SCF-based GAMESS calculation, including those evaluated by direct SCF methods and those involving effective core potentials (ECPs). The SOSCF, DIIS, damping, and direct energy minimization (DEM) methods of the GAMESS $SCF group can be employed to control the convergence of the fragment SCF wavefunctions.

Symmetry should be disabled (NOSYM=1 in the GAMESS $CONTRL group) *for all NEDA calculations.*

Other NBO deletion types, such as 'LEWIS' and 'DELETE 5 ELEMENTS...' can be placed in the $DEL keylist together with NEDA input, and multiple NEDA evaluations can appear in the keylist (each beginning with NEDA and ending with END). The deletions and NEDA are performed in the order that the keywords are listed in the keylist.

See Section B.6.10 for more details on the NBO energetic analysis and the $DEL keylist.

B.11.3 Sample NEDA Input

B.11.3.1 Water Dimer

The following is sample Gaussian input for the RHF/4-31G calculation of the water dimer, in the geometry of Umeyama and Morokuma [*J. Am. Chem. Soc.* **99**, 1316 (1977)].

```
# rhf/4-31g neda=2

Water dimer...rhf/4-31g//Umeyama, Morokuma, JACS 99, 1316 (1977)

0 1  0 1  0 1
O(fragment=1)    -0.004158   -1.425700    0.000000
H(fragment=1)     0.498701   -1.716026    0.759460
H(fragment=1)     0.498701   -1.716026   -0.759460
O(fragment=2)    -0.004158    1.554300    0.000000
H(fragment=2)    -0.926714    1.804953    0.000000
H(fragment=2)    -0.004158    0.598300    0.000000
```

The two water monomers are explicitly identified in Gaussian input. The following is the same input for GAMESS.

```
 $contrl  scftyp=rhf  runtyp=energy  nosym=1  $end
 $basis  gbasis=n31  ngauss=4  $end
 $nbo  $end
 $del  neda end  $end
 $data
Water dimer...rhf/4-31g//Umeyama, Morokuma, JACS 99, 1316 (1977)
Cs

Oxygen    8.      -0.004158      -1.425700       0.000000
Hydrogen  1.       0.498701      -1.716026       0.759460
Oxygen    8.      -0.004158       1.554300       0.000000
Hydrogen  1.      -0.926714       1.804953       0.000000
Hydrogen  1.      -0.004158       0.598300       0.000000
 $end
```

In this case, NBO analysis calculates two molecular units (water monomers) based on the connectivity of the bonding NBOs. Thus, default NEDA analyzes the wavefunction in terms of these two monomer fragments.

Output for this analysis is shown in Section B.11.4.1.

B.11.3.2 Sodium/Water Complex

The following are sample input files for NEDA of the open-shell wavefunction (UHF/6-31++G**) describing the interaction of a water molecule with a sodium atom:

```
# uhf/6-31++g** neda=2

Na..OH2 (uhf/6-31++G**)

0 2  0 2  0 1
Na      0.000000    0.000000   -0.340466  1
O       0.000000    0.000000    2.024020  2
H       0.000000    0.762733    2.583246  2
H       0.000000   -0.762733    2.583246  2
```

For the Gaussian input here, we have optionally chosen to specify the fragment to which each atom is assigned by an integer appended to the end of each line of the geometry section, rather than using the "fragment=*n*" syntax as shown in Sec. B.11.2.1.

```
 $contrl  scftyp=uhf  runtyp=energy  mult=2  nosym=1  $end
 $basis  gbasis=n31  ngauss=6  ndfunc=1  npfunc=1
         diffsp=.t.  diffs=.t.  $end
 $nbo  $end
 $del
   alpha neda end
    beta neda end
 $end
 $data
Na..OH2 (uhf/6-31++G**)
Cnv 2

 Na          11.0    .0000000000    .0000000000   -.3404656616
 O            8.0    .0000000000    .0000000000   2.0240196206
 H            1.0    .0000000000    .7627333242   2.5832459068
 $end
```

Note that GAMESS input for open-shell systems requires that NEDA be requested in $DEL for both the alpha and beta spin systems.

Output for this analysis is shown in Section B.11.4.2.

B.11.3.3 Covalent Bond in Ethane

The nature of intramolecular forces, such as that of the C-C covalent bond of ethane, can be examined with the Gaussian implementation of NEDA.

Intramolecular NEDA is not implemented for GAMESS.

The following is input for B3LYP/6-311++G** optimized ethane, for which analysis is performed with respect to two separated methyl fragments.

```
# b3lyp/6-311++g** neda=2

Ethane...NEDA of C-C bond

0 1  0 2  0 -2
C        0.000000    0.000000    0.765350  1
C        0.000000    0.000000   -0.765350  2
H        0.000000    1.018574    1.163687  1
H       -0.882111   -0.509287    1.163687  1
H        0.882111   -0.509287    1.163687  1
H        0.882111    0.509287   -1.163687  2
H        0.000000   -1.018574   -1.163687  2
H       -0.882111    0.509287   -1.163687  2
```

Ethane is a singlet spin state, and cleaving the C-C bond yields two doublet fragments, with the alpha bonding electron assigned to one fragment (methyl 1) and the beta electron assigned to the other (methyl 2). Note that "–2" spin multiplicity indicates that methyl fragment 2 is a doublet but with an excess beta electron (rather than the usual alpha).

The resulting open-shell NEDA is performed using an unrestricted SCF method.

Output for this analysis is shown in Section B.11.4.3.

B.11.3.4 Cooperative Effects in Water Trimer

One can use NEDA to examine cooperative effects as, for example, in the C_3 cyclic water trimer. The following input files are for B3LYP/aug-cc-pVTZ optimized trimer, and for the unrelaxed water dimer (identical to the trimer geometry with one of the water molecules eliminated).

The Gaussian input files are:

```
# b3lyp/aug-cc-pvtz neda=3

C3 water trimer...b3lyp/avtz

0 1  0 1  0 1  0 1
O    -0.957406    1.304375   -0.091870 1
H     0.014172    1.244266   -0.037940 1
H    -1.225393    1.975012    0.541376 1
O     1.608343    0.176994   -0.091952 2
H     1.070533   -0.634390   -0.038105 2
H     2.322945    0.073834    0.541511 2
O    -0.650927   -1.481377   -0.091938 3
H    -1.084742   -0.609957   -0.037991 3
H    -1.097527   -2.048758    0.541465 3
```

```
# b3lyp/aug-cc-pvtz neda=2

water dimer (geometry of C3 water trimer)

0 1  0 1  0 1
O    -0.957406    1.304375   -0.091870 1
H     0.014172    1.244266   -0.037940 1
H    -1.225393    1.975012    0.541376 1
O     1.608343    0.176994   -0.091952 2
H     1.070533   -0.634390   -0.038105 2
H     2.322945    0.073834    0.541511 2
```

The corresponding GAMESS input files are:

```
 $contrl  dfttyp=b3lyp  scftyp=rhf  runtyp=energy  nosym=1  ispher=1
    $end
 $system  mwords=100  $end
 $basis  gbasis=acct  $end
 $nbo  $end
 $del  neda end  $end
 $data
C3 water trimer...b3lyp/avtz
Cn 3
```

```
Oxygen     8.    -0.957406    1.304375   -0.091870
Hydrogen   1.     0.014172    1.244266   -0.037940
Hydrogen   1.    -1.225393    1.975012    0.541376
 $end
```

```
$contrl  dfttyp=b3lyp  scftyp=rhf  runtyp=energy  nosym=1  ispher=1
   $end
 $basis  gbasis=acct  $end
 $nbo  $end
 $del  neda end  $end
 $data
water dimer (geometry of C3 water trimer)
C1
Oxygen     8.    -0.957406    1.304375   -0.091870
Hydrogen   1.     0.014172    1.244266   -0.037940
Hydrogen   1.    -1.225393    1.975012    0.541376
Oxygen     8.     1.608343    0.176994   -0.091952
Hydrogen   1.     1.070533   -0.634390   -0.038105
Hydrogen   1.     2.322945    0.073834    0.541511
 $end
```

Output is shown in Section B.11.4.4.

B.11.3.5 NAO-, NBO-, and NLMO-Based NEDA

The following is sample GAMESS input for the NAO-, NBO-, and NLMO-based analysis of RHF/4-31G water dimer:

```
 $contrl  scftyp=rhf  runtyp=energy  nosym=1  $end
 $basis  gbasis=n31  ngauss=4  $end
 $nbo  nlmo  $end
 $del
   nao  neda (1-3) (4-6) end
   nbo  neda end
   nlmo neda end
 $end
 $data
Water dimer...rhf/4-31g//Umeyama, Morokuma, JACS 99, 1316 (1977)
Cs

Oxygen    8.      -0.004158      -1.425700       0.000000
Hydrogen  1.       0.498701      -1.716026       0.759460
Oxygen    8.      -0.004158       1.554300       0.000000
Hydrogen  1.      -0.926714       1.804953       0.000000
Hydrogen  1.      -0.004158       0.598300       0.000000
 $end
```

Because the NBO program does not generate NLMOs by default, we include the NLMO keyword in the $NBO keylist input. Otherwise, NLMO-based NEDA, unable to find NLMOs saved in NBO's direct access file, will fail.

NBO- or NLMO-based NEDA can also be performed with Gaussian but requires identification of the basis using the NEDA keyword in $NBO keylist input, as shown below, for example, for the NLMO-based analysis.

```
# rhf/4-31g neda=2

Water dimer...rhf/4-31g//Umeyama, Morokuma, JACS 99, 1316 (1977)

0 1  0 1  0 1
O(fragment=1)    -0.004158   -1.425700    0.000000
H(fragment=1)     0.498701   -1.716026    0.759460
H(fragment=1)     0.498701   -1.716026   -0.759460
O(fragment=2)    -0.004158    1.554300   -0.000000
H(fragment=2)    -0.926714    1.804953   -0.000000
H(fragment=2)    -0.004158    0.598300   -0.000000

$nbo  neda=nlmo  $end
```

B.11.4 Sample NEDA Output

B.11.4.1 Water Dimer

The following is NEDA output for the hydrogen bond of RHF/4-31G water dimer. The input is given in Sec. B.11.3.1.

NEDA begins by calculating a localized wavefunction in which all interfragment CT effects are deleted. This is accomplished by zeroing all off-diagonal elements of the Fock matrix between orbitals on separate fragments and diagonalizing to obtain localized MOs for each fragment. The first section of output details the occupancy shifts and energy change that occur upon localization.

For Gaussian, the localization is performed in the NAO basis:

```
NEDA: Natural Energy Decomposition Analysis
Deletion of the NAO Fock matrix elements between orbitals:
   1   2   3   4   5   6   7   8   9  10  11  12  13
and orbitals:
  14  15  16  17  18  19  20  21  22  23  24  25  26

Orbital occupancies:

      Orbital                          No deletions  This deletion    Change
------------------------------------------------------------------------------
   1.  O 1( 1s )                         1.99996       1.99996       0.00001
   2.  O 1( 2s )                         1.76340       1.76777       0.00436
   3.  O 1( 3s )                         0.00078       0.00075      -0.00003
   4.  O 1( 2px)                         1.80513       1.80514       0.00001
   5.  O 1( 3px)                         0.00022       0.00021      -0.00001
   6.  O 1( 2py)                         1.92118       1.93099       0.00981
   7.  O 1( 3py)                         0.00060       0.00042      -0.00018
   8.  O 1( 2pz)                         1.47215       1.47215       0.00000
   9.  O 1( 3pz)                         0.00168       0.00167      -0.00001
  10.  H 2( 1s )                         0.50860       0.50922       0.00063
  11.  H 2( 2s )                         0.00123       0.00125       0.00003
  12.  H 3( 1s )                         0.50860       0.50922       0.00063
  13.  H 3( 2s )                         0.00123       0.00125       0.00003
  14.  O 4( 1s )                         1.99995       1.99996       0.00000
  15.  O 4( 2s )                         1.75684       1.75582      -0.00102
  16.  O 4( 3s )                         0.00065       0.00058      -0.00008
  17.  O 4( 2px)                         1.62156       1.62154      -0.00003
  18.  O 4( 3px)                         0.00077       0.00077      -0.00001
  19.  O 4( 2py)                         1.60169       1.59670      -0.00500
  20.  O 4( 3py)                         0.00119       0.00117      -0.00001
  21.  O 4( 2pz)                         1.99952       1.99957       0.00005
  22.  O 4( 3pz)                         0.00044       0.00043       0.00000
  23.  H 5( 1s )                         0.53264       0.53233      -0.00031
  24.  H 5( 2s )                         0.00126       0.00121      -0.00005
  25.  H 6( 1s )                         0.49718       0.48950      -0.00769
  26.  H 6( 2s )                         0.00156       0.00044      -0.00112

NEXT STEP:  Perform one SCF cycle to evaluate the energy of the new density
            matrix constructed from the deleted NAO Fock matrix.

------------------------------------------------------------------------------
```

Localization suppresses charge transfer in the water dimer, returning electron density from the electron acceptor unit (principally 0.0077*e* from the 1*s* of H6 and 0.0050*e* from the $2p_y$ of O4) back to the electron donor (0.0098*e* into the $2p_y$ of O1).

For GAMESS, the same localization is performed, but in the NBO basis:

```
NEDA: Natural Energy Decomposition Analysis
Deletion of the NBO Fock matrix elements between orbitals:
   1   3   4   7   8  11  12  15  16  17  18  19  20
and orbitals:
   2   5   6   9  10  13  14  21  22  23  24  25  26

Orbital occupancies:

      Orbital                          No deletions  This deletion    Change
--------------------------------------------------------------------------------
   1. CR ( 1) O  1                       1.99996        1.99996       0.00001
   2. CR ( 1) O  4                       1.99995        1.99996       0.00000
   3. LP ( 1) O  1                       1.99915        1.99925       0.00010
   4. LP ( 2) O  1                       1.98438        1.99916       0.01478
   5. LP ( 1) O  4                       1.99995        2.00000       0.00005
   6. LP ( 2) O  4                       1.99914        1.99922       0.00008
   7. BD ( 1) O  1- H  2                 1.99904        1.99935       0.00030
   8. BD ( 1) O  1- H  3                 1.99904        1.99935       0.00030
   9. BD ( 1) O  4- H  5                 1.99951        1.99950      -0.00001
  10. BD ( 1) O  4- H  6                 1.99916        1.99936       0.00020
  11. BD*( 1) O  1- H  2                 0.00032        0.00019      -0.00013
  12. BD*( 1) O  1- H  3                 0.00032        0.00019      -0.00013
  13. BD*( 1) O  4- H  5                 0.00028        0.00013      -0.00015
  14. BD*( 1) O  4- H  6                 0.01429        0.00016      -0.01413
  15. RY ( 1) O  1                       0.00003        0.00001      -0.00002
  16. RY ( 2) O  1                       0.00003        0.00003       0.00000
  17. RY ( 3) O  1                       0.00001        0.00000      -0.00001
  18. RY ( 4) O  1                       0.00000        0.00000       0.00000
  19. RY ( 1) H  2                       0.00123        0.00126       0.00003
  20. RY ( 1) H  3                       0.00123        0.00126       0.00003
  21. RY ( 1) O  4                       0.00010        0.00002      -0.00008
  22. RY ( 2) O  4                       0.00002        0.00000      -0.00002
  23. RY ( 3) O  4                       0.00001        0.00001       0.00000
  24. RY ( 4) O  4                       0.00000        0.00000       0.00000
  25. RY ( 1) H  5                       0.00126        0.00121      -0.00005
  26. RY ( 1) H  6                       0.00158        0.00043      -0.00115

NEXT STEP:  Perform one SCF cycle to evaluate the energy of the new density
            matrix constructed from the deleted NBO Fock matrix.

--------------------------------------------------------------------------------T
```

The NBO-based description of localization, like the NAO-based, results in the transfer of electrons from the electron acceptor (loss of 0.014*e* from an OH antibond) back to the electron donor (gain of 0.014*e* by an O lone pair). While the effect of localization is expressed more compactly with NBOs than with NAOs, the two approaches yield identical localized densities for the fragments.

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

The electronic structure system (ESS) evaluates the energy of the localized density using a single SCF cycle.

```
-------------------------------------------------------------------------------
  Energy of deletion :       -151.811801223
    Total SCF energy :       -151.827488227
                       -------------------
       Energy change :          0.015687 a.u.,           9.844 kcal/mol
-------------------------------------------------------------------------------
```

Localization of the water dimer increases the energy from –151.827488 a.u. to –151.811801 a.u., corresponding to CT stabilization of 9.844 kcal/mol.

NEDA and the ESS proceed to evaluate the energies of the perturbed and variationally optimized (relaxed) densities for each fragment. All energies evaluated in the full dimer basis set for fixed fragment geometries (i.e. the monomer geometries within the dimer).

The following summary output results:

```
Natural Energy Decomposition Analysis (Summary):

                                                                  Component
                    Energy(wfn)        Energy(wfn)                (kcal/mol)
-------------------------------------------------------------------------------
H4O2           -151.8274882(scf)  -151.8118012(loc)      CT =   -9.844
                                                         ES =  -10.324
                                                        POL =   -2.916
                                                         EX =   -1.191
1. H2O          -75.8890295(def)   -75.9093357(rel) DEF(SE) =   12.742(  0.118)
2. H2O          -75.8997740(def)   -75.9082470(rel) DEF(SE) =    5.317(  1.296)
                                                              ---------
                                                          E =   -6.216


Electrical (ES+POL+SE) :    -11.826
  Charge Transfer (CT) :     -9.844
      Core (EX+DEF-SE) :     15.454
                         ------------
 Total Interaction (E) :     -6.216


Dipole moments:

  1. H2O
     Dipole (def):    2.3204(x),  -1.2826(y),   0.0000(z);   2.6513(tot) Debye
     Dipole (rel):    2.2512(x),  -1.4100(y),   0.0000(z);   2.6563(tot) Debye
     Dipole (ind):    0.0692(x),   0.1273(y),   0.0000(z);   0.1449(tot) Debye
  2. H2O
     Dipole (def):   -2.0513(x),  -1.8500(y),   0.0000(z);   2.7623(tot) Debye
     Dipole (rel):   -2.0642(x),  -1.5687(y),   0.0000(z);   2.5926(tot) Debye
     Dipole (ind):    0.0128(x),  -0.2813(y),   0.0000(z);   0.2816(tot) Debye
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

The NEDA summary reports the energies (in a.u.) of the delocalized (scf) and localized (loc) dimer, as well as the energies for each of the perturbed (def) and relaxed (rel) monomers. The summary also reports the NEDA components, each expressed in kcal/mol, and dipole moments (perturbed, relaxed, and induced) for each monomer. In GAMESS output, the dipole moments are not listed in the summary, as shown above, but are instead reported immediately following each fragment evaluation, prior to the printing of this summary. Note that the interaction energy is counterpoise-corrected because all calculations are performed in the full AO basis of the dimer.

The monomers of the water dimer are bound by –6.2 kcal/mol at the RHF/4-31G level. NEDA of this interaction suggests the following description.

Electrical interaction (–11.8 kcal/mol) and charge transfer (–9.8 kcal/mol) contribute significantly to hydrogen bonding. Electrical contributions arise principally from the electrostatic interaction (ES = –10.3 kcal/mol) of the relaxed monomer charge distributions with a small contribution from polarization (POL+SE = –1.5 kcal/mol). The induced monomer dipole moments of electron donor and acceptor (0.14 D and 0.28 D, respectively) and the monomer self energies (0.1 and 1.3 kcal/mol, respectively) together suggest that polarization arises principally in the acceptor as its electron density shifts away from the approaching electron donor. The weaker donor polarization is likely a consequence of the donor's inability to fully polarize toward the acceptor as orthogonality of the monomer wavefunctions prevents donor density from significantly penetrating the acceptor. The charge transfer interaction arises nearly entirely from the transfer of electron density from an O lone pair of the donor into the proximal OH antibond. The charge transfer energy is largely consistent with the second-order perturbative estimate of the dominant $n_O \rightarrow \sigma_{OH}^*$ interaction (11.1 kcal/mol) reported elsewhere in NBO output. Core repulsions (15.5 kcal/mol) between the monomers stem most significantly from the deformation of the donor electron density (DEF = 12.7) as Pauli repulsions prevent the donor O lone pair from penetrating the acceptor.

B.11.4.2 Sodium/Water Complex

The following is the summary of open-shell NEDA for the Na(H_2O) complex at the UHF/6-31++G** level.

```
Natural Energy Decomposition Analysis (Summary):

                                                          Component
                    Energy(wfn)        Energy(wfn)         (kcal/mol)
-------------------------------------------------------------------------------
H2ONa          -237.8815329(scf)  -237.8655828(loc)      CT =  -10.009
                                                         ES =  -24.115
                                                        POL =  -19.806
                                                         EX =   -7.635
1. Na          -161.8027550(def)  -161.8414917(rel) DEF(SE) =   24.308(  1.349)
2. H2O          -75.9806681(def)   -76.0324201(rel) DEF(SE) =   32.475(  8.778)
                                                              ---------
                                                          E =   -4.782


Electrical (ES+POL+SE) :    -33.794
  Charge Transfer (CT) :    -10.009
      Core (EX+DEF-SE) :     39.020
                         ------------
 Total Interaction (E) :     -4.782


Dipole moments:

  1. Na
     Dipole (def):    0.0000(x),   0.0000(y),  -1.1756(z);   1.1756(tot) Debye
     Dipole (rel):    0.0000(x),   0.0000(y),   0.0035(z);   0.0035(tot) Debye
     Dipole (ind):    0.0000(x),   0.0000(y),  -1.1790(z);   1.1790(tot) Debye
  2. H2O
     Dipole (def):    0.0000(x),   0.0000(y),  -2.5168(z);   2.5168(tot) Debye
     Dipole (rel):    0.0000(x),   0.0000(y),  -2.1090(z);   2.1090(tot) Debye
     Dipole (ind):    0.0000(x),   0.0000(y),  -0.4078(z);   0.4078(tot) Debye
```

Although interaction of water with Na atom is rather weak (–4.7 kcal/mol), NEDA reveals rather strong electrostatic attraction (ES = –24.1 kcal/mol), polarization (POL+SE = –9.7 kcal/mol), and charge transfer (CT = –10.0 kcal/mol). Water induces a large dipole on the polarizable Na atom (1.18 D). The strong attractive components of the interaction are offset by sizable core repulsions (39.0 kcal/mol) that arise principally from the deformation of the fragment densities as they enter the environment of the complex.

B.11.4.3 Covalent Bond in Ethane

The following is NEDA summary output for cleaving the C-C bond in B3LYP/6-311++G** optimized ethane.

```
Natural Energy Decomposition Analysis (Summary):

                                                          Component
                    Energy(wfn)        Energy(wfn)          (kcal/mol)
-------------------------------------------------------------------------------
C2H6            -79.8565753(scf)   -79.1189303(loc)      CT = -462.879
                                                         ES = -133.294
                                                        POL =   99.255
                                                         XC =  -33.348
1. CH3          -39.5057717(def)   -39.8407865(rel) DEF(SE) =  210.225(-26.689)
2. CH3          -39.5057717(def)   -39.8407865(rel) DEF(SE) =  210.225(-26.689)
                                                          ---------
                                                       E = -109.816


Electrical (ES+POL+SE) :    -87.416
  Charge Transfer (CT) :   -462.879
      Core (XC+DEF-SE) :    440.479
                          ------------
 Total Interaction (E) :   -109.816


Dipole moments:

  1. CH3
     Dipole (def):    0.0000(x),   0.0000(y),  -1.8587(z);   1.8587(tot) Debye
     Dipole (rel):    0.0000(x),   0.0000(y),   0.6658(z);   0.6658(tot) Debye
     Dipole (ind):    0.0000(x),   0.0000(y),  -2.5246(z);   2.5246(tot) Debye
  2. CH3
     Dipole (def):    0.0000(x),   0.0000(y),   1.8587(z);   1.8587(tot) Debye
     Dipole (rel):    0.0000(x),   0.0000(y),  -0.6658(z);   0.6658(tot) Debye
     Dipole (ind):    0.0000(x),   0.0000(y),   2.5246(z);   2.5246(tot) Debye
```

Not surprisingly, the covalent bond energy (–109.8 kcal/mol) is dominated the electron sharing of the charge transfer term (–462.9 kcal/mol). Electrical interactions (–87.4 kcal/mol) are also somewhat stabilizing, but core repulsions (440.5 kcal/mol) are strongly destabilizing.

Intramolecular NEDA may be useful in comparing the nature of bonding in related systems. For example, one might ask how the C-C bond of hexachloroethane (HCE) compares to that of unsubstituted ethane. The following output was obtained for B3LYP/6-311++G** optimized HCE:

```
Natural Energy Decomposition Analysis (Summary):

                                                                  Component
                    Energy(wfn)        Energy(wfn)                (kcal/mol)
-------------------------------------------------------------------------------
C2Cl6         -2837.5324060(scf) -2836.8716070(loc)      CT = -414.658
                                                         ES = -133.329
                                                        POL =  -23.730
                                                         XC =  -58.864
1. CCl3       -1418.2637552(def) -1418.7135904(rel) DEF(SE) =  282.276(  6.872)
2. CCl3       -1418.2637552(def) -1418.7135904(rel) DEF(SE) =  282.276(  6.872)
                                                              ---------
                                                          E =  -66.030


Electrical (ES+POL+SE) :   -143.316
  Charge Transfer (CT) :   -414.658
      Core (XC+DEF-SE) :    491.944
                       ------------
 Total Interaction (E) :    -66.030

Dipole moments:

  1. CCl3
     Dipole (def):    0.0000(x),  -0.0001(y),  -0.5297(z);   0.5297(tot) Debye
     Dipole (rel):    0.0000(x),   0.0000(y),   0.0870(z);   0.0870(tot) Debye
     Dipole (ind):    0.0000(x),  -0.0001(y),  -0.6167(z);   0.6167(tot) Debye
  2. CCl3
     Dipole (def):    0.0000(x),   0.0001(y),   0.5297(z);   0.5297(tot) Debye
     Dipole (rel):    0.0000(x),   0.0000(y),  -0.0870(z);   0.0870(tot) Debye
     Dipole (ind):    0.0000(x),   0.0001(y),   0.6167(z);   0.6167(tot) Debye
```

By comparing NEDA results, we see that the C-C bond of HCE is 43.7 kcal/mol weaker than in ethane and that the weakening stems principally from the loss of charge transfer (by 48.2 kcal/mol) and stronger core repulsions (by 51.4 kcal/mol). Electrical interactions are stronger in HCE than in ethane, likely because the Cl substituents have considerably more electrons than the H atoms of ethane.

When interactions are as strong as those reported here for ethane and HCE there are bound to be important geometry relaxation effects that should be considered too. However, this information must be evaluated separately, through calculations of the individual fragments in the fixed geometries of the complex and relaxed geometries in isolation. Geometry relaxation effects are not provided by NEDA and its treatment of fixed fragment geometries only.

B.11.4.4 Cooperative Effects in Water Trimer

The origin of cooperativity in the C_3 cyclic water trimer can be examined by NEDA. The cooperative (3-body) contribution to the interaction energy, $\Delta E^{(3)}$, is the difference between the total interaction and the sum of all pairwise (2-body) interactions, which by symmetry are equivalent.

$$\Delta E^{(3)} = \Delta E - 3\,\Delta E^{(2)}$$

The individual NEDA components, P, can be similarly expressed in 2- and 3-body form.

$$P^{(3)} = P - 3\,P^{(2)}$$

The following is Gaussian/NEDA output for the B3LYP/aug-cc-pVTZ optimized trimer.

```
Natural Energy Decomposition Analysis (Summary):

                                                                Component
                    Energy(wfn)          Energy(wfn)            (kcal/mol)
-------------------------------------------------------------------------------
H6O3           -229.4201642(scf)  -229.3727411(loc)      CT =  -29.758
                                                         ES =  -25.337
                                                        POL =  -15.250
                                                         XC =  -10.043
1. H2O          -76.4306860(def)   -76.4660473(rel) DEF(SE) =   22.190(  2.626)
2. H2O          -76.4306830(def)   -76.4660474(rel) DEF(SE) =   22.192(  2.625)
3. H2O          -76.4306878(def)   -76.4660475(rel) DEF(SE) =   22.189(  2.625)
                                                          ---------
                                                       E =  -13.819


Electrical (ES+POL+SE) :    -32.711
  Charge Transfer (CT) :    -29.758
      Core (XC+DEF-SE) :     48.651
                         ------------
 Total Interaction (E) :    -13.819


Dipole moments:

  1. H2O
     Dipole (def):   -1.5624(x),   1.0432(y),   1.1353(z);   2.1951(tot) Debye
     Dipole (rel):   -1.3272(x),   0.6298(y),   1.0858(z);   1.8267(tot) Debye
     Dipole (ind):   -0.2352(x),   0.4134(y),   0.0495(z);   0.4782(tot) Debye
  2. H2O
     Dipole (def):    1.6846(x),   0.8311(y),   1.1355(z);   2.1950(tot) Debye
     Dipole (rel):    1.2091(x),   0.8342(y),   1.0860(z);   1.8268(tot) Debye
     Dipole (ind):    0.4756(x),  -0.0031(y),   0.0495(z);   0.4782(tot) Debye
  3. H2O
     Dipole (def):   -0.1223(x),  -1.8745(y),   1.1356(z);   2.1950(tot) Debye
     Dipole (rel):    0.1181(x),  -1.4641(y),   1.0860(z);   1.8268(tot) Debye
     Dipole (ind):   -0.2404(x),  -0.4104(y),   0.0496(z);   0.4781(tot) Debye
```

B.11. NEDA: NATURAL ENERGY DECOMPOSITION ANALYSIS

The following is Gaussian/NEDA output for the unrelaxed water dimer:

```
Natural Energy Decomposition Analysis (Summary):

                                                                 Component
                    Energy(wfn)        Energy(wfn)                (kcal/mol)
-------------------------------------------------------------------------------
H4O2           -152.9380495(scf)  -152.9231543(loc)      CT =   -9.347
                                                         ES =   -8.447
                                                        POL =   -5.224
                                                         XC =   -3.680
1. H2O          -76.4492286(def)   -76.4660031(rel) DEF(SE) =   10.526(  2.415)
2. H2O          -76.4462754(def)   -76.4660209(rel) DEF(SE) =   12.390(  0.231)
                                                               ---------
                                                          E =   -3.781


Electrical (ES+POL+SE) :    -11.024
  Charge Transfer (CT) :     -9.347
      Core (XC+DEF-SE) :     16.590
                           ------------
 Total Interaction (E) :     -3.781


Dipole moments:

  1. H2O
     Dipole (def):   -0.8319(x),  -1.8366(y),   0.2401(z);   2.0305(tot) Debye
     Dipole (rel):   -0.5612(x),  -1.7143(y),   0.2992(z);   1.8285(tot) Debye
     Dipole (ind):   -0.2707(x),  -0.1223(y),  -0.0591(z);   0.3028(tot) Debye
  2. H2O
     Dipole (def):   -0.9637(x),   0.6302(y),   1.6383(z);   2.0025(tot) Debye
     Dipole (rel):   -0.8989(x),   0.4984(y),   1.5099(z);   1.8266(tot) Debye
     Dipole (ind):   -0.0648(x),   0.1318(y),   0.1283(z);   0.1950(tot) Debye
```

We summarize the partitioning of NEDA components into 2- and 3-body contributions as follows (all energies in kcal/mol):

Component	P	$P^{(2)}$	$P^{(3)}$
EL	–32.71	–11.02	0.35
ES	–25.34	–8.45	0.01
POL+SE	–7.37	–2.57	0.34
CT	–29.76	–9.35	–1.71
CORE	48.65	16.59	–1.12
XC	–10.04	–3.68	1.00
DEF–SE	58.69	20.27	–2.12
ΔE	–13.82	–3.78	–2.48

GAMESS/NEDA results are similar but differ very slightly (by generally less than 0.1 kcal/mol) from those of Gaussian due to the differing definitions for B3LYP in the two programs.

NEDA suggests that cooperativity in the water trimer ($\Delta E^{(3)}$ = –2.48 kcal/mol) stems principally from strengthened CT interactions ($CT^{(3)}$ = –1.71 kcal/mol, because a monomer acting as an electron acceptor is an extra-effective electron donor) and reduced CORE repulsions ($CORE^{(3)}$ = –1.12 kcal/mol). As expected, electrostatic interactions ($ES^{(3)}$ = 0.01) contribute nothing to the cooperativity. Polarization is somewhat anti-cooperative, tending to destabilize the trimer somewhat ($POL^{(3)}$+$SE^{(3)}$ = 0.34).

B.11.4.5 NAO-, NBO-, and NLMO-Based NEDA

NAO-based and NBO-based NEDA of RHF/4-31G water dimer are identical, both reporting the following, as described in B.11.4.1:

```
 Natural Energy Decomposition Analysis (Summary):

                                                                 Component
                     Energy(wfn)        Energy(wfn)              (kcal/mol)
 ------------------------------------------------------------------------------
 H4O2           -151.8274882(scf)  -151.8118012(loc)      CT =   -9.844
                                                          ES =  -10.324
                                                         POL =   -2.916
                                                          EX =   -1.191
 1. H2O          -75.8890295(def)   -75.9093357(rel) DEF(SE) =   12.742(  0.118)
 2. H2O          -75.8997740(def)   -75.9082470(rel) DEF(SE) =    5.317(  1.296)
                                                               ---------
                                                           E =   -6.216


 Electrical (ES+POL+SE) :    -11.826
   Charge Transfer (CT) :     -9.844
       Core (EX+DEF-SE) :     15.454
                        ------------
  Total Interaction (E) :     -6.216
```

NLMO-based NEDA differs somewhat:

```
Natural Energy Decomposition Analysis (Summary):

                                                                 Component
                     Energy(wfn)        Energy(wfn)              (kcal/mol)
 ------------------------------------------------------------------------------
 H4O2           -151.8274882(scf)  -151.8274882(loc)      CT =    0.000
                                                          ES =  -10.324
                                                         POL =  -12.299
                                                          EX =   -3.600
 1. H2O          -75.8860575(def)   -75.9093357(rel) DEF(SE) =   14.607(  4.678)
 2. H2O          -75.8996430(def)   -75.9082470(rel) DEF(SE) =    5.399(  1.476)
                                                               ---------
                                                           E =   -6.216


 Electrical (ES+POL+SE) :    -16.468
   Charge Transfer (CT) :      0.000
       Core (EX+DEF-SE) :     10.252
                        ------------
  Total Interaction (E) :     -6.216
```

CT is zero in the NLMO-based analysis, with the charge transfer effect shifting to EL, due to a ~5 kcal/mol strengthening of polarization (POL+SE), and decreasing CORE repulsions by about ~5 kcal/mol.

B.12. CHECKPOINTING OPTIONS

B.12.1 Introduction

It is sometimes desirable to use NBOs (or other set of localized orbitals) in procedures that would otherwise employ canonical MOs (CMOs). For example, one may wish to perform a post-SCF analysis of a wavefunction in terms of NBOs rather than CMOs, or use graphical utilities to plot NBOs instead of CMOs (e.g., using GaussView with a Gaussian checkpoint file). In these cases, it is generally convenient to substitute NBOs in the ESS direct access file where CMOs are usually kept. This operation is referred to as "checkpointing" in the NBO framework, because it was originally implemented in the NBO interface to the Gaussian program to overwrite the CMOs of the Gaussian read-write files (and ultimately the checkpoint file).

Checkpointing presently provides a mechanism for the NBO program to return a localized orbital set to the ESS host. What the ESS does with this orbital set depends on the particular implementation of the ESS/NBO7 interface. Generally these interfaces store the orbitals at some location in a direct access file used by the ESS, potentially the same location the CMOs had previously been stored. Thus, the implementation and uses of checkpointing options are highly ESS-specific. For GenNBO (and ESS/NBO7 implementations based on GenNBO), checkpointing writes a text file having the same filename as the GenNBO input file but with .chk extension. This file lists the transformation matrix elements and orbital energies (if available) in 5(1x,e20.13) format.

One application of NBO checkpointing is to calculate CAS/NBO wavefunctions for localized treatment of electron correlation [A. V. Nemukhin and F. Weinhold, *J. Chem. Phys.* **97**, 1095 (1992)]. Another is to carry out CI in a complete active space of NBOs (CI/NBO), the first step in full CAS/NBO optimization. NBO checkpointing options allow these applications to be performed using either the numbers or labels of NBOs to be included in the active space.

B.12.2 Checkpointing Options

Basic checkpointing is requested by typing a 'C' (checkpointing) in place of 'P' (printing) or 'W' (writing) for selected matrix output keywords (see Sec. B.2.4). Checkpointing is supported for any transformations from AOs to PAO, PNAO, NAO, PNHO, NHO, PNBO, NBO, PNLMO, NLMO, NO, or MO basis sets, hence for the following keywords:

AOPAO AOPNAO AONAO AOPNHO AONHO

AOPNBO AONBO AOPNLMO AONLMO AONO AOMO

For example, the $NBO input

```
$NBO AONBO=C $END
```

will checkpoint the NBOs, while the keyword "AONLMO=C" would checkpoint NLMOs, etc. In the following, we use the example of the NBOs as the orbital set to be checkpointed, but analogous considerations apply to the other localized sets.

In its basic form, the checkpointing command

```
AONBO=C
```

checkpoints NBOs in the standard order of appearance in the NBO output file (e.g., with core orbitals and lone pairs preceding bonds, and antibonds preceding Rydberg orbitals). However, it is also possible to alter the orbital order by occupancy or energy sorting, or by using an explicit "permutation list" that describes a reordering by number or by NBO label. Each option will be described in turn.

Occupancy sorting. One can automatically sort the NBOs by occupancy with a "checkpoint-sort" command of the form

```
AONBO=CS
```

This will order the NBOs according to their populations (diagonal density matrix elements), from most highly to least occupied. Checkpointing of occupancy-sorted NAOs or NLMOs would be accomplished with the corresponding "AONAO=CS" and "AONLMO=CS" keywords.

Occupancy sorting typically brings the most important correlating orbitals into the active-space window around the "Fermi level." For present purposes the Fermi level can be described as the dividing line between the highest occupied ($n_{occ} = N_e/2$) and lowest unoccupied ($n_{occ} + 1$) orbital, i.e., that between the least-occupied Lewis NBO (usually, a high-energy lone pair or bond) and the most-occupied non-Lewis NBO (usually, a valence antibond).

The occupancy-sorted orbital lists are described in the NBO output. A detailed listing is given for NBOs and NLMOs. For example, sorted NBOs for the tutorial methylamine test case (Sec A.3) are reported as (output truncated to first 15 NBOs):

```
Sorting NBOs by occupancy for checkpoint file:

  Sort    Occ       Energy   Orig   Label
 ---------------------------------------------------------
    1.  1.99953   -15.25896    2.   CR ( 1) N  2
    2.  1.99901   -11.04148    1.   CR ( 1) C  1
    3.  1.99863    -0.69256    5.   BD ( 1) C  1- H  3
    4.  1.99849    -0.89737    4.   BD ( 1) C  1- N  2
    5.  1.99443    -0.80927    8.   BD ( 1) N  2- H  6
    6.  1.99443    -0.80927    9.   BD ( 1) N  2- H  7
    7.  1.99402    -0.68912    6.   BD ( 1) C  1- H  4
    8.  1.99402    -0.68912    7.   BD ( 1) C  1- H  5
    9.  1.97845    -0.44752    3.   LP ( 1) N  2
   10.  0.01533     0.68699   11.   BD*( 1) C  1- H  3
   11.  0.00765     0.69611   12.   BD*( 1) C  1- H  4
   12.  0.00765     0.69611   13.   BD*( 1) C  1- H  5
   13.  0.00427     0.68044   14.   BD*( 1) N  2- H  6
   14.  0.00427     0.68044   15.   BD*( 1) N  2- H  7
   15.  0.00176     0.94849   24.   RY ( 1) H  3
```

For all sets other than NBOs and NLMOs, the reordered orbitals are listed by label. For example, "AONAO=CS" for methylamine yields:

```
Sorting NAOs by occupancy for checkpoint file:

   1.  N 2( 1s )   2.  C 1( 1s )   3.  N 2( 2py)   4.  N 2( 2s )   5.  N 2( 2pz)
   6.  N 2( 2px)   7.  C 1( 2pz)   8.  C 1( 2py)   9.  C 1( 2s )  10.  C 1( 2px)
  11.  H 3( 1s )  12.  H 4( 1s )  13.  H 5( 1s )  14.  H 6( 1s )  15.  H 7( 1s )
  16.  N 2( 3py)  17.  H 3( 2s )  18.  C 1( 3px)  19.  H 6( 2s )  20.  H 7( 2s )
  21.  N 2( 3px)  22.  H 4( 2s )  23.  H 5( 2s )  24.  N 2( 3pz)  25.  C 1( 3s )
  26.  C 1( 3py)  27.  C 1( 3pz)  28.  N 2( 3s )
```

Energy sorting. Orbitals can be energy-sorted before checkpointing using a command of the form

```
AONBO=CE
```

This orders the orbitals from lowest to highest energy (diagonal Fock or Kohn-Sham matrix element). If energies are not available, no sorting is performed.

For NBOs and NLMOs (and the corresponding pre-orthogonalized sets), the sorted list is not by strict energy order. The Lewis (occupied) orbitals, consisting of the core orbitals, lone pairs, and bonds, are sorted by energy and listed first. These are immediately followed by energy-sorted lone vacant (LV) orbitals, if any are present in the orbital set. Then the valence antibonds are listed, in the reverse order that the corresponding bonds appear in the Lewis set. Finally, the Rydberg orbitals are listed in energy-sorted order. Note that this sorting generally places the most relevant correlating orbitals around the Fermi level in an order that is probably most convenient for subsequent analysis by post-SCF methods.

The following shows the energy-sorted NLMOs for methylamine (the first 15 NLMOs only):

```
Sorting NLMOs by energy for checkpoint file:

  Sort    Occ       Energy   Orig   Label
 ------------------------------------------------------------
    1.  2.00000   -15.26268    2.   CR ( 1) N  2
    2.  2.00000   -11.04629    1.   CR ( 1) C  1
    3.  2.00000    -0.89836    4.   BD ( 1) C  1- N  2
    4.  2.00000    -0.81272    8.   BD ( 1) N  2- H  6
    5.  2.00000    -0.81272    9.   BD ( 1) N  2- H  7
    6.  2.00000    -0.69397    5.   BD ( 1) C  1- H  3
    7.  2.00000    -0.69333    6.   BD ( 1) C  1- H  4
    8.  2.00000    -0.69333    7.   BD ( 1) C  1- H  5
    9.  2.00000    -0.45790    3.   LP ( 1) N  2
   10.  0.00000     0.70065   13.   BD*( 1) C  1- H  5
   11.  0.00000     0.70065   12.   BD*( 1) C  1- H  4
   12.  0.00000     0.69378   11.   BD*( 1) C  1- H  3
   13.  0.00000     0.68301   15.   BD*( 1) N  2- H  7
   14.  0.00000     0.68301   14.   BD*( 1) N  2- H  6
   15.  0.00000     0.57032   10.   BD*( 1) C  1- N  2
```

Permutations Lists. One can alternatively include an explicit "permutation list" following the checkpoint command to specify the desired order:

```
    $NBO AONBO=C <permutation list> $END
```

As indicated, the permutation list must be enclosed by left-bracket (<) and right-bracket (>) symbols, and the brackets must be separated by at least one space from surrounding keywords. For open-shell systems one can also provide a special form of AOPNBO spin permutation list that allows pairwise exchanges of orbitals between spin sets, as described below.

B.12.3 Checkpoint Permutation Lists

The checkpointing option supports a variety of forms for the permutation bracket list <. . . >.

Permuting by Serial Number. At the simplest level, the permutation list could simply be a list of integers that specifies the permuted order ("n1" is first, "n2" is second, etc.). Orbital numbers not included in the list will be placed after those included. For example, the command

```
AONBO=C <1 2 3 8 5 6 7 4>
```

would interchange orbitals 4 and 8 with respect to the original NBO ordering, but leave other NBOs (including 9, 10,...) in their original positions.

An alternative form of permutation list includes a vertical bar (|) to denote the Fermi level (separation of occupied and unoccupied orbitals). This allows one to permute the orbital ordering by specifying only a few orbitals above and below the Fermi level (e.g., only the few to be included in the active window),

```
<...n2 n1 | m1 m2 ...>
```

Here "n1" identifies the orbital just below the Fermi level, "n2" the next lowest, etc., while "m1" is the first orbital above the Fermi level, "m2" the next highest, etc. This form is most convenient for explicitly specifying the active-space window in CAS procedures.

Orbital numbers not explicitly included in the permutation list are left in their former positions as nearly as possible, or are used to fill in available slots around the specified active window. For example, if one were creating a CAS(5,4) active window, the command

```
AONBO=C <7 8 5 | 10 12>
```

would specify that NBOs 7, 8, and 5 should lie just below the Fermi level, while 10 and 12 should lie just above. If there were originally 15 NBOs with n_{occ} = 8, the permuted order would become [active space enclosed in brackets],

```
1 2 3 4 6 [ 7 8 5 | 10 12 ] 9 11 13 14 15
```

However, if the Fermi-level marker (|) were absent, the corresponding command

```
AONBO=C <7 8 5 10 12>
```

would lead to the permuted order

```
7 8 5 10 12 [ 1 2 3 | 4 6 ] 9 11 13 14 15
```

with the five specified orbitals moved to the beginning of the list, and remaining orbitals occupying the rest of the positions in serial order.

Permuting by Label. It is also possible to identify each permuted orbital by its generic *label* in the NBO output. Since the precise numbering of NBOs may not be known in advance, this option makes it possible to identify an NBO by its unique chemical *type*, avoiding the indeterminacies of numerical ordering.

The form of each label should be chosen to conform to that in the NBO output [such as "BD(1) C3-H15", "LP(2) N11", "BD*(2) C4-C5", etc.], based on the known atom numbering and the expected Lewis structure. Each label should be separated from adjacent labels by at least one comma or space, as in the following example,

```
AONBO=C <BD(1)C3-H15 , LP(2)N11 | BD*(2)C4-C5>
```

Spaces within each label are ignored (so that, e.g., "BD(1) C 3 - H 15" and BD(1)C3-H15" are equivalent). Note that "BD(1)" is typically (but not invariably) the sigma bond and "BD(2)" the pi bond of a double-bonded atom pair, so that the above example would correspond to the NBO ordering [$\sigma_{C3\text{-}H15}$ n_{N11} | $\pi^*_{C4\text{-}C5}$] in a standard notation.

As above, inclusion of a Fermi level "|" marker positions the listed orbitals at the top of the Lewis set (left of |) or bottom of the non-Lewis set (right of |), while omission of "|" requests that these orbitals be moved to the beginning of the list.

Spin Permutations for Open Shells. For open-shell systems (only) and AOPNBO checkpointing (only), one can also provide a special form of *spin permutation list* that allows checkpointed spin-orbitals to be exchanged between alpha and beta spin sets. This is useful in creating customized NBO "guess" configurations for spin states that are difficult to calculate by standard SCF convergence methods. For this purpose, PNBOs provide the most transferable orbitals for specifying a generic electronic configuration in localized Lewis-like terms (i.e., fewest perturbations from the original chemical environment).

Each field of a spin permutation list consists of a pair of NBO indices, each prefixed by 'a' (alpha) or 'b' beta to denote the spin set. Fields are separated as

usual by a slash (/), and the two spin-PNBOs entries of each field are separated by a comma or space. The spin-orbital entries of each field are permuted in pairs, starting with the first field and proceding to the last. For example, the command

```
AOPNBO=C <b8 b9/a9 b8>
```

would first exchange the 8th and 9th PNBOs of the beta set (b8 with b9), then exchange the 8th PNBO of the beta set (formerly b9, now b8) with the 9th PNBO of the alpha set. Note that the ordering of indices within each field is immaterial, but the order of successive fields affects the final orbital ordering (because permutations do not commute).

B.12.4 Example: CAS/NBO and CI/NBO Calculations

A sample Gaussian 9X input deck to carry out a multiconfigurational CAS(2,2)/NBO calculation on methylamine (3-21G basis) is shown below, where the active space consists of the nitrogen lone pair ("LP(1) N 2", NBO 3 in the output) and the antiperiplanar C-H antibond (σ^*_{C1H3}, "BD*(1) C 1- H 3", NBO 11):

```
%chk=ch3nh2.chk
# rhf/3-21g pop=nbo6read

Methylamine...rhf/3-21g//idealized geometry

0 1
C
N   1   1.47
H   1   1.09   2   109.4712
H   1   1.09   2   109.4712   3   120. 0
H   1   1.09   2   109.4712   3   240. 0
H   2   1.01   1   109.4712   3    60. 0
H   2   1.01   1   109.4712   3   300. 0

$nbo  aonbo=c <3 | 11> $end

--Link1--
%chk=ch3nh2.chk
# cas(2,2)/3-21g nosymm guess=read geom=check density=current pop=nbo6

Methylamine...cas(2,2)/3-21g//idealized geometry

0 1
```

The $NBO keylist could equivalently be written as

```
$nbo aonbo=c <lp(1)n2 | bd*(1)c1-h3> $end
```

i.e., in terms of NBO labels rather than serial numbers.

B.13. CMO: CANONICAL MO ANALYSIS

B.13.1 Introduction

The CMO keyword provides an analysis of canonical (delocalized) MOs in terms of their leading NBO contributions. The CMO analysis tables summarize the composition and bonding nature of each MO in a qualitative abbreviated form, providing a convenient alternative to the NBOMO keyword (Sec. B.2.4) which gives full quantitative detail of the LCNBO-MO expansion.

Each MO φ_i can be expressed in terms of the complete orthonormal set of NBOs $\{\Omega_\alpha\}$ by the equation,

$$\varphi_i = \sum_\alpha \Omega_\alpha t_{\alpha i}$$

The coefficients $t_{\alpha i}$ (elements of the NBOMO transformation matrix) determine the percentage contribution ($100*|t_{\alpha i}|^2$) of each NBO to the LCNBO-MO expansion of φ_i. Each coefficient $t_{\alpha i}$ can in turn be identified with an NBO Ω_α of bonding ($t_{\alpha i}^{(b)}$), nonbonding ($t_{\alpha i}^{(n)}$), or antibonding ($t_{\alpha i}^{(a)}$) character. By adding the percentage contributions of each NBO type, one obtains a convenient measure of the total bonding (b), nonbonding (n), or antibonding (a) character of each MO. These in turn can be decomposed into the contributions from individual atomic centers, leading to a detailed description of the "atom-atom bonding character" of each MO.

The CMO keyword summarizes the composition and bonding character of the MOs in two tables. The first table lists the leading LCNBO-MO coefficients and NBO labels (in decreasing order of magnitude) for requested MOs, showing only NBO contributions of 5% or greater. The second table summarizes leading (>5%) atom-atom bond characters for each MO, showing the atoms or atom pairs where the nonbonding, bonding, or antibonding character of the MO is most strongly manifested. The latter information can be useful in predicting structural and vibrational changes that result from changing the occupancy of the MO in an ionization process.

B.13.2 CMO Keyword Usage and Sample Output

Basic CMO analysis is requested by including the "CMO" keyword in the $NBO keylist, as in the example below:

```
    $NBO   CMO   FILE=CH3NH2   $END
```

The first table shows the leading NBO contributions to each MO, as illustrated below for the example of CH_3NH_2 at RHF/3-21G level (selected MOs only):

```
 CMO: NBO Analysis of Canonical Molecular Orbitals

 Leading (> 5%) NBO Contributions to Molecular Orbitals
 ======================================================
  MO   1 (occ): orbital energy = -15.445475 a.u.
               -0.993*[  2]: CR ( 1) N 2(cr)
  MO   2 (occ): orbital energy = -11.182456 a.u.
                0.993*[  1]: CR ( 1) C 1(cr)
  MO   3 (occ): orbital energy =  -1.164751 a.u.
               -0.629*[  4]: BD ( 1) C 1- N 2
               -0.473*[  8]: BD ( 1) N 2- H 6
               -0.473*[  9]: BD ( 1) N 2- H 7
    .
    .
    .
  MO   8 (occ): orbital energy =  -0.517662 a.u.
               -0.593*[  6]: BD ( 1) C 1- H 4
                0.593*[  7]: BD ( 1) C 1- H 5
               -0.382*[  8]: BD ( 1) N 2- H 6
                0.382*[  9]: BD ( 1) N 2- H 7
  MO   9 (occ): orbital energy =  -0.368845 a.u.
                0.900*[  3]: LP ( 1) N 2(lp)
                0.334*[  5]: BD ( 1) C 1- H 3
  MO  10 (vir): orbital energy =   0.265351 a.u.
                0.432*[ 14]: BD*( 1) N 2- H 6*
                0.432*[ 15]: BD*( 1) N 2- H 7*
                0.324*[ 11]: BD*( 1) C 1- H 3*
               -0.284*[ 28]: RY ( 1) H 7(ry)
               -0.284*[ 27]: RY ( 1) H 6(ry)
                0.260*[ 12]: BD*( 1) C 1- H 4*
                0.260*[ 13]: BD*( 1) C 1- H 5*
               -0.249*[ 24]: RY ( 1) H 3(ry)
                0.235*[ 10]: BD*( 1) C 1- N 2*
    .
    .
    .
  MO  28 (vir): orbital energy =   2.843994 a.u.
               -0.723*[ 23]: RY ( 4) N 2(ry)
               -0.651*[ 22]: RY ( 3) N 2(ry)
```

In this example, MO 1 and 2 are both found to be highly localized and transferable, with strong (~99%) contributions from NBO 2 (the nitrogen core orbital) and NBO 1 (the carbon core orbital), respectively. However, MO 3 is a strong admixture of σ_{CN} (NBO 4) and the two σ_{NH} bonds (NBOs 8, 9) with approximate composition

$$\varphi_3 \cong 0.629\,\sigma_{CN} + 0.473(\sigma_{NH} + \sigma_{NH'})$$

and higher MOs show still more strongly mixed NBO character. The HOMO (MO 9) derives primarily (~81%) from the n_N lone pair (NBO 3), with weaker (11%) contribution from the *anti* σ_{CH} bond (NBO 5). However, the LUMO (MO 10) has significant contributions from at least *nine* NBOs, including three Rydberg orbitals (NBOs 24, 27, 28) from outside the formal valence shell, and hence exhibits little transferability to other molecules.

The table of "atom-atom bonding character" follows (truncated to the same seven MOs as above):

```
          Molecular Orbital Atom-Atom Bonding Character
         ================================================
             bonding          nonbonding       antibonding
  MO        (2c, 3c)           (1c, 1c*)         (2c*, 3c*)
------  ---------------    ----------    ---------------
  1(o)                     0.987  N 2
         -----              -----          -----
         0.011(b)           0.989(n)       0.000(a)  total
-------------------------------------------------------------
  2(o)                     0.986  C 1
         -----              -----          -----
         0.013(b)           0.987(n)       0.000(a)  total
-------------------------------------------------------------
  3(o)  0.396  C 1- N 2
        0.224  N 2- H 7
        0.224  N 2- H 6
         -----              -----          -----
         0.954(b)           0.045(n)       0.000(a)  total
-------------------------------------------------------------
 .
 .
 .
-------------------------------------------------------------
  8(o)  0.352  C 1- H 5
        0.352  C 1- H 4
        0.146  N 2- H 7
        0.146  N 2- H 6
         -----              -----          -----
         0.997(b)           0.001(n)       0.003(a)  total
-------------------------------------------------------------
  9(o)  0.112  C 1- H 3    0.811  N 2
         -----              -----          -----
         0.179(b)           0.812(n)       0.009(a)  total
-------------------------------------------------------------
 10(v)                     0.081  H 7     0.186  N 2- H 7
                           0.081  H 6     0.186  N 2- H 6
                           0.062  H 3     0.105  C 1- H 3
                                          0.068  C 1- H 5
                                          0.068  C 1- H 4
                                          0.055  C 1- N 2
         -----              -----          -----
         0.001(b)           0.331(n)       0.668(a)  total
-------------------------------------------------------------
 .
 .
 .
-------------------------------------------------------------
 28(v)                     0.946  N 2
         -----              -----          -----
         0.000(b)           0.993(n)       0.007(a)  total
-------------------------------------------------------------
         6.000(b)          16.000(n)       6.000(a)  Sum total for MOs
```

This table shows, e.g., that MOs 1, 2 have predominantly (>98%) nonbonding character, whereas MO 3 is predominantly (95.4%) of bonding character, primarily at CN (39.6%) and the two NH bonds (22.4% each). Similarly, the entries for MO 9 suggest that the HOMO is about 81% non-bonding (on N) and only 18% bonding (primarily on the C1-H3 bond). Hence, in the spirit of simple Koopmans-type reasoning, ionization of an electron from the HOMO might be expected to result in only slight bond weakening (primarily at C1-H3), whereas ionization from MO 8 (SOMO) should significantly weaken C1-H4 and C1-H5, as well as (to a lesser extent) both NH bonds.

The “Sum total” shown after the last MO entry reflects that the sum of tabulated MO bond characters must correspond to the total of 6 bond NBOs, 16 nonbonding NBOs (cores, lone pairs, Rydbergs), and 6 antibond NBOs of the full NBO basis.

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

Reference: J. A. Bohmann, F. Weinhold, and T. C. Farrar, *J. Chem. Phys*. **107**, 1173-1184 (1997).

B14.1 Introduction to Natural Chemical Shielding Analysis

The GIAO (gauge-including atomic orbitals) treatment [R. Ditchfield, *Mol. Phys.* **27**, 789 (1974); K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.* **112**, 8251 (1990)] of nuclear magnetic moments (***m***) in external magnetic fields (***B***) leads to the expression for the anisotropic NMR chemical shielding tensor components $\sigma_{\alpha\beta}$ as a sum of "unperturbed" (u) and "induced" (i) contributions,

(1) $\sigma_{\alpha\beta} = \mathrm{Tr}\{\mathbf{D}^{00}\,\mathbf{h}^{\alpha\beta}\} + \mathrm{Tr}\{\mathbf{D}^{\alpha 0}\,\mathbf{h}^{0\beta}\} = \sigma_{\alpha\beta}^{(u)} + \sigma_{\alpha\beta}^{(i)}$

where the matrices $\mathbf{D}^{00}$, $\mathbf{D}^{\alpha 0}$, $\mathbf{h}^{0\beta}$, and $\mathbf{h}^{\alpha\beta}$ represent, respectively, the Fock-Dirac density matrix, the density derivative with respect to field component B_α, the derivative of the 1-e Hamiltonian (**h**) with respect to magnetic moment component m_β, and the crossed second derivative of **h** with respect to M_α and m_β, all in the basis of atomic orbitals $\{\chi_p\}$. For the full chemical shielding anisotropy, the tensor indices α, β range over the Cartesian components *x*, *y*, *z*, but the simpler isotropic scalar shielding (average diagonal component)

(2) $\sigma_{iso} = {}^1\!/_3 \sum_\alpha \sigma_{\alpha\alpha}$

is usually the quantity of principal chemical interest. The distinction between "unperturbed" (field-free) and "induced" (field-dependent) GIAO contributions is parallel to that between "diamagnetic" and "paramagnetic" terms in Ramsey's non-GIAO theory. In both cases the labels distinguish contributions associated with the unperturbed ground state ($\sigma_{\alpha\beta}^{(u)}$) from those associated with excited states ($\sigma_{\alpha\beta}^{(i)}$).

To carry out localized analysis of $\sigma_{\alpha\beta}$ (or σ_{iso}), we make use of the following transformations that relate the canonical MOs (φ_k^{MO}) to the NLMOs (φ_j^{NLMO}), NBOs (Ω_n) and AOs (χ_p), viz.,

(3a) $\varphi_j^{NLMO} = \sum_n^{NBO} a_{nj}\,\Omega_n$ (NBONLMO)

(3b) $\Omega_n = \sum_q^{AO} b_{qn}\,\chi_q$ (AONBO)

(3c) $\varphi_k^{MO} = \sum_p^{AO} c_{pk}\,\chi_p$ (AOMO)

(3d) $\varphi_j^{NLMO} = \sum_q^{AO} d_{qj}\, \chi_q$ (AONLMO)

(3e) $\varphi_k^{MO} = \sum_j^{NLMO} t_{jk}\, \varphi_j^{NLMO}$ (NLMOMO)

The program analyzes $\sigma_{\alpha\beta}$ in terms of localized NBO contributions

(4) $\sigma_{\alpha\beta} = \sum_j^{L} [{}^{j}\sigma_{\alpha\beta} + \sum_n^{NL} {}^{j\to n}\sigma_{\alpha\beta}]$

where ${}^{j}\sigma_{\alpha\beta}$ is a Lewis-type (L) contribution from the parent NBO (Ω_j) of φ_j^{NLMO}, and ${}^{j\to n}\sigma_{\alpha\beta}$ is a non-Lewis-type (NL) contribution from the "delocalization tail" Ω_n of this NLMO (the same label serving to identify both the NLMO and its parent NBO). Each ${}^{j\to n}\sigma_{\alpha\beta}$ is therefore the shielding associated with a particular $\Omega_j \to \Omega_n$ donor-acceptor (L → NL) interaction of NBO energetic analysis (Sec. A.3.5), contributing only when conjugative or hyperconjugative delocalization is present. Note that such delocalization occurs in both ground and excited states, so NL contributions of both "unperturbed" and "induced" type are possible.

To evaluate the terms in (4), the program first calculates $\sigma_{\alpha\beta}^{(u)}$ (corresponding to contributions from occupied field-free MOs φ_k^{MO}) from localized contractions of the form

(5) ${}^{j\to n}\sigma_{\alpha\beta}^{(u)} = \mathrm{Tr}\{{}^{j\to n}\mathbf{D}^{00}\mathbf{h}^{\alpha\beta}\}$

where the partial density matrix for localized $j \to n$ NBO interaction is

(6) ${}^{j\to n}\mathbf{D}^{00}{}_{pq} = 2\, a_{nj}\, b_{pn}\, d_{qj}$

This follows from writing the Fock-Dirac density matrix elements $\mathbf{D}^{00}{}_{pq} = 2\sum_k c_{pk}c_{qk}$ in the alternative NLMO form

(7) $\mathbf{D}^{00}{}_{pq} = 2\sum_j^{NLMO} d_{pj}\, d_{qj}$

and using (3a) to write NLMO j in terms of its parent NBO Ω_j and delocalization tail Ω_n.

The program next calculates $\sigma_{\alpha\beta}^{(i)}$ (corresponding to contributions from virtual MOs φ_v^{MO}) from localized contractions of the form

(8) ${}^{j\to n}\sigma_{\alpha\beta}^{(i)} = \mathrm{Tr}\{{}^{j\to n}\mathbf{D}^{\alpha 0}\mathbf{h}^{0\beta}\}$

where the $j \to n$ contribution to the density derivative matrix can be written as

(9) $^{j\rightarrow n}\mathbf{D}^{\alpha 0}{}_{pq} = 2\sum_k^{occ} t_{jk}\, a_{nj}\, [b_{pn}\, c^{\alpha 0}{}_{qk} - c^{\alpha 0}{}_{pk}\, b_{qn}]$

The coefficients $c^{\alpha 0}{}_{pk}$ describe the field-dependent correction to the field-free LCAO coefficient c_{qk} in the 1st-order perturbative expression

(10) $c_{pk}{}^{(1)}(B_\alpha, m_\beta) = c_{pk} + iB_\alpha\, c^{\alpha 0}{}_{pk} + im_\beta\, c^{0\beta}{}_{pk} + \ldots$

They are evaluated by the formalism of Pulay in the form

(11) $c^{\alpha 0}{}_{pk} = \sum_q^{AO} \sum_r^{AO} c_{rk}\, [^k\mathbf{W}_{pq}(\mathbf{F}^{\alpha 0}{}_{qr} - \varepsilon_k \mathbf{S}^{\alpha 0}{}_{qr}) + {}^1\!/_4\, \mathbf{D}^{00}{}_{pq}\, \mathbf{S}^{\alpha 0}{}_{qr}]$

where $\mathbf{F}^{\alpha 0}$ and $\mathbf{S}^{\alpha 0}$ are the first-order Fock matrix and overlap matrix derivatives and $^k\mathbf{W}$ is the Ditchfield weighting matrix

(12) $^k\mathbf{W}_{pq} = \sum_v^{vir} c_{pv}\, c_{qv}/(\varepsilon_k - \varepsilon_v)$

for MO k with orbital energy ε_k. The final L, NL contributions in (4) are obtained as the sum of unperturbed and induced terms (5), (8).

B.14.2 NCS Keyword Usage

The NCS module is currently implemented only for Gaussian versions of NBO. To calculate GIAO shieldings and perform NCS analysis, one should include the Gaussian keyword NMR on the Gaussian route card, together with chosen NCS options in the $NBO keylist.

Basic natural chemical shielding (NCS) analysis is requested by simply including the "NCS" keyword in the $NBO keylist. A sample Gaussian input deck for the idealized RHF/3-21G calculation of CH_3NH_2 is illustrated below:

```
# rhf/3-21g nmr pop=nbo6read

Methylamine...rhf/3-21g//idealized geometry

0 1
C
N   1   1.47
H   1   1.09   2   109.4712
H   1   1.09   2   109.4712   3   120. 0
H   1   1.09   2   109.4712   3   240. 0
H   2   1.01   1   109.4712   3    60. 0
H   2   1.01   1   109.4712   3   300. 0

$nbo ncs $end
```

This produces a table of localized contributions to isotropic chemical shielding constants (σ_{iso}) for each nucleus for which GIAO calculations were performed, showing the Lewis "L" ($^{j}\sigma_{\alpha\beta}$) and non-Lewis "NL" ($\sum_{n}^{j\rightarrow n}\sigma_{\alpha\beta}$) contributions arising from each occupied NBO *j*.

One can request additional details of the shielding tensors by including one or more of the following options (separated by commas or spaces) immediately after the NCS keyword:

OPTION	*OPTION DESCRIPTION*
CSA	Request analysis of diagonal tensor components (in the principal shielding axes) and chemical shielding anisotropy (CSA) for each nucleus. The transformation matrix from the molecular Cartesian frame to the principal shielding frame of each nucleus is also printed.

XYZ	Request analysis of full chemical shielding tensor in the molecular Cartesian axes (x,y,z). This keyword automatically sets the CSA option.
U	Request separate analysis of the "unperturbed" (field-free or diamagnetic) contribution $\sigma_{\alpha\beta}^{(u)}$ to chemical shielding.
I	Request separate analysis of the "induced" (field-dependent or paramagnetic) contribution $\sigma_{\alpha\beta}^{(i)}$ to chemical shielding. (Because the total shielding is analyzed by default, this contribution can be determined from the analysis by difference.)
MO	Request analysis of the shielding tensor in terms of canonical MOs (in addition to localized NBO/NLMO analysis), following Ditchfield's original treatment.

For example, a sample $NBO keylist to request NCS analysis including both total and induced anisotropic shielding tensor components in the principal shielding axes is shown below:

```
$NBO  NCS=I,CSA  $END
```

The keywords "NCS=I,XYZ" would request analogous analysis with respect to the molecular Cartesian axes (in addition to CSA printout). Note that each NCS option "compounds" the effect of others, so that, e.g., a combination such as "NCS=I,XYZ,MO" gives ~8 *times* the printout of "NCS=CSA".

Each table produced by NCS analysis includes all $j \rightarrow n$ delocalization contributions that exceed the default threshold for printing, 0.1 ppm. This threshold is also the minimum off-diagonal element that characterizes the tensor as "non-symmetric" and leads to full printout of antisymmetric tensor components.

The default print threshold can be altered as illustrated in the following example,

```
$NBO  NCS=0.02  $END
```

which lowers the threshold to 0.02 ppm. Modified forms of the NCS keyword can be combined, as in the following example,

```
$NBO  NCS=0.5,CSA  $END
```

which requests printing of delocalized anisotropic and isotropic shielding contributions exceeding 0.5 ppm.

B.14. NCS: NMR CHEMICAL SHIELDING ANALYSIS

When the NMR keyword is included on the Gaussian route card and the ARCHIVE keyword in the $NBO keylist, the NBO program will write additional NCS-related keylists to FILE47 output that allow NCS analysis to be repeated at the stand-alone GenNBO level. These keylists include MO derivative coefficiencts ($C01 keylist) and GIAO Hamiltonian 1st derivatives ($H01 keylist) and 2nd derivatives ($H11 keylist) that are collections of the matrices needed to perform NCS analysis.

B.14.3 NCS Sample Output

Sample default NCS output is shown below for the CH_3NH_2 molecule (RHF/3-21G level, idealized Pople-Gordon geometry):

```
NATURAL CHEMICAL SHIELDING ANALYSIS:

Summary of isotropic NMR chemical shielding
Total Lewis (L) and non-Lewis (NL) contributions: (ppm)

       NBO           C  1    N  2    H  3    H  4    H  5    H  6    H  7
---------------    ------- ------- ------- ------- ------- ------- -------
  1.  C 1(cr)   L   202.40   -0.07    0.16    0.13    0.13   -0.03   -0.03
                NL    0.15    0.00    0.00   -0.01   -0.01    0.00    0.00
  2.  N 2(cr)   L     0.08  238.43    0.05    0.03    0.03    0.07    0.07
                NL    0.00    0.10    0.00    0.00    0.00    0.00    0.00
  3.  N 2(lp)   L    -0.11    6.57   -0.46    0.19    0.19    5.43    5.43
                NL   -0.08    0.75   -0.34   -0.01   -0.01    0.05    0.05
  4.  C 1- N 2  L    -6.54    6.39    0.56    0.50    0.50    2.42    2.42
                NL    0.16   -0.36    0.03    0.08    0.08   -0.10   -0.10
  5.  C 1- H 3  L    -4.23    0.48   26.52    1.85    1.85    0.10    0.10
                NL   -0.59   -0.37    0.07   -0.05   -0.05   -0.01   -0.01
  6.  C 1- H 4  L    -2.61    2.12    2.10   25.73    2.04    0.13    0.22
                NL   -0.24   -1.42   -0.02    0.05    0.03   -0.04   -0.07
  7.  C 1- H 5  L    -2.61    2.12    2.10    2.04   25.73    0.22    0.13
                NL   -0.24   -1.42   -0.02    0.03    0.05   -0.07   -0.04
  8.  N 2- H 6  L     0.08    7.16    0.34    0.29    0.24   22.87    3.36
                NL    0.00    0.16   -0.02   -0.12   -0.01    0.03   -0.04
  9.  N 2- H 7  L     0.08    7.16    0.34    0.24    0.29    3.36   22.87
                NL    0.00    0.16   -0.02   -0.01   -0.12   -0.04    0.03
---------------    ------- ------- ------- ------- ------- ------- -------
          Lewis     186.56  270.36   31.71   31.00   31.00   34.56   34.56
      non-Lewis      -0.84   -2.39   -0.32   -0.02   -0.02   -0.19   -0.19
---------------    ------- ------- ------- ------- ------- ------- -------
          Total     185.72  267.97   31.39   30.99   30.99   34.38   34.38
```

For each NBO *j*, the table gives the sum of "L" ($^{j}\sigma_{\alpha\beta}$) and total "NL" ($\sum_{n}^{NL} {}^{j\rightarrow n}\sigma_{\alpha\beta}$) contributions to σ_{iso}.

An example of the output produced by keyword option "NCS=CSA" is shown below for the H(3) atom of methylamine:

```
Principal components of the tensor (ppm) for atom  H(  3):
This tensor is non-symmetric.  The antisymmetric part will be printed.

                  Principal components     Antisymmetric part
      NBO           11      22      33      12      13      23      CSA     ISO
================================================================================
   1. C 1(cr)      0.01    0.19    0.28    0.00    0.00    0.11    0.18    0.16
   3. N 2(lp)     -1.81   -0.13    0.55    0.00    0.00    0.03    1.52   -0.46
    NL  11. BD*   -0.56   -0.49    0.40    0.00    0.00   -0.13    0.93   -0.22
    NL  16. RY     0.13    0.03   -0.01    0.00    0.00    0.04   -0.09    0.05
    NL  24. RY    -0.15   -0.14   -0.01    0.00    0.00    0.01    0.13   -0.10
   4. C 1- N 2     0.28   -0.82    2.23    0.00    0.00   -0.09    2.50    0.56
    NL  24. RY    -0.10   -0.10    0.02    0.00    0.00    0.05    0.12   -0.06
   5. C 1- H 3    25.65   25.79   28.12    0.00    0.00    0.35    2.40   26.52
   6. C 1- H 4     1.14    3.00    2.18   -0.15    0.84   -0.17    0.11    2.10
   7. C 1- H 5     1.14    3.00    2.18    0.15   -0.84   -0.17    0.11    2.10
   8. N 2- H 6     0.16   -0.08    0.92   -0.18   -0.51    0.23    0.88    0.34
```

```
   9. N 2- H 7     0.16   -0.08    0.92    0.18    0.51    0.23    0.88    0.34
-------------------------------------------------------------------------------
          Lewis   26.78   30.93   37.43    0.00    0.00    0.50    8.57   31.71
      non-Lewis   -0.66   -0.65    0.34    0.00    0.00    0.12    0.99   -0.32
-------------------------------------------------------------------------------
          Total   26.13   30.27   37.77    0.00    0.00    0.63    9.57   31.39
-------------------------------------------------------------------------------

Cartesian XYZ to principal shielding axes for atom  H (  3):

       1         2         3
------------------------------
 X  0.000000  0.729704 -0.683763
 Y  0.000000  0.683763  0.729704
 Z  1.000000  0.000000  0.000000
```

This table displays contributions to the individual tensor components in the principal axes of the nuclear shielding tensor. "ISO" denotes $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$, the isotropic shielding, and "CSA" denotes $\sigma_{33} - (\sigma_{11} + \sigma_{22})/2$, the chemical shielding anisotropy (with conventional axis ordering $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$). Off-diagonal contributions are displayed ("Antisymmetric Part") only if the magnitude of at least one σ_{ij} exceeds the print threshold. Note that individual NL contributions $^{j \rightarrow n}\sigma_{\alpha\beta}$ (> 0.1 ppm, the default threshold) are printed in this more detailed analysis of the shielding tensor. The printout includes the matrix of direction cosines from the overall Cartesian XYZ system (as chosen by the ESS) to the principal shielding axes for each nucleus.

Similarly, the keyword option "NCS=XYZ" leads to the additional output for H(3) shown below:

```
Full Cartesian NMR shielding tensor (ppm) for atom  H(  3):
Lewis (L) and non-Lewis (NL) contributions

    NBO
   L  NL     XX      XY      XZ      YX      YY      YZ      ZX      ZY      ZZ
===============================================================================
   1.       0.48    0.05    0.00   -0.17   -0.02    0.00    0.00    0.00    0.01
   3.      -0.82   -0.24    0.00   -0.31    1.24    0.00    0.00    0.00   -1.81
     11.    0.01   -0.58    0.00   -0.32   -0.10    0.00    0.00    0.00   -0.56
     12.   -0.04    0.03    0.05   -0.05   -0.01    0.01   -0.01    0.14   -0.06
     13.   -0.04    0.03   -0.05   -0.05   -0.01   -0.01    0.01   -0.14   -0.06
     16.    0.02    0.05    0.00   -0.02    0.00    0.00    0.00    0.00    0.13
     24.   -0.07   -0.05    0.00   -0.07   -0.07    0.00    0.00    0.00   -0.15
   4.       0.45   -1.60    0.00   -1.42    0.96    0.00    0.00    0.00    0.28
     24.   -0.05   -0.01    0.00   -0.10   -0.04    0.00    0.00    0.00   -0.10
   5.      28.96   -0.95    0.00   -1.65   24.95    0.00    0.00    0.00   25.65
   6.       2.35    0.25   -0.59    0.60    2.82   -0.85    0.78   -1.86    1.14
   7.       2.35    0.25    0.59    0.60    2.82    0.85   -0.78    1.86    1.14
   8.       0.04   -0.24    0.03   -0.71    0.80   -0.88   -0.41    0.11    0.16
   9.       0.04   -0.24   -0.03   -0.71    0.80    0.88    0.41   -0.11    0.16
-------------------------------------------------------------------------------
      L    33.91   -2.74    0.00   -3.75   34.44    0.00    0.00    0.00   26.78
     NL    -0.14   -0.37    0.00   -0.62   -0.17    0.00    0.00    0.00   -0.66
-------------------------------------------------------------------------------
  Total    33.78   -3.11    0.00   -4.37   34.26    0.00    0.00    0.00   26.13
-------------------------------------------------------------------------------
```

This table displays all tensor elements $\sigma_{\alpha\beta}$ (regardless of magnitude) in the Cartesian axis system of the ESS. Due to space limitations, contributing L-type and NL-type NBOs are identified by number only. Note that the fixed printing threshold may lead to slightly different lists of leading NL contributions in the CSA and XYZ tables.

Finally, option "NCS=MO" adds delocalized MO analysis of isotropic shieldings for all nuclei, as shown below:

Summary of isotropic NMR chemical shielding
Canonical MO contributions: (ppm)

MO	C 1	N 2	H 3	H 4	H 5	H 6	H 7
1.	0.35	234.43	0.18	0.13	0.13	-0.11	-0.11
2.	199.51	0.35	-0.13	-0.24	-0.24	0.17	0.17
3.	5.19	22.23	1.12	1.42	1.42	4.69	4.69
4.	28.33	12.26	6.11	6.08	6.08	3.74	3.74
5.	-3.52	-19.19	0.82	3.49	3.49	10.44	10.44
6.	-11.52	-3.19	16.99	2.95	2.95	2.19	2.19
7.	-4.33	20.38	3.21	5.43	5.43	4.04	4.04
8.	-20.93	0.80	-0.41	11.25	11.25	4.34	4.34
9.	-7.35	-0.11	3.49	0.48	0.48	4.89	4.89
Total	185.72	267.97	31.39	30.99	30.99	34.38	34.38

The MO contributions of this table are typically much less transferable than corresponding NBO contributions.

B.15. NJC: NATURAL J-COUPLING ANALYSIS

Reference: S. J. Wilkens, W. M. Westler, J. L. Markley, and F. Weinhold, *J. Am. Chem. Soc.* **123**, 12026-12036 (2001).

B.15.1 Introduction to Natural J-Coupling Analysis

The Fermi-contact contribution to scalar J-coupling J[A,B] between magnetic nuclei A,B can be conveniently evaluated in the framework of HF/DFT theory by the finite-field perturbative method [J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.* **49**, 2960-2964, 2965-2970 (1968); T. Onak, J. Jaballas, and M. Barfield, *J. Am. Chem. Soc.* **121**, 2850-2856 (1999)]. In this method, a Fermi contact (Dirac delta function) α-spin perturbation $\delta(\mathbf{r}_B)$ with formal perturbative field strength λ_B is added at the position $\mathbf{r}_B$ of nucleus B, and the resulting spin-density distribution $\Delta\rho(\mathbf{r}) = \rho^{(\alpha)}(\mathbf{r}) - \rho^{(\beta)}(\mathbf{r})$ is evaluated at the position $\mathbf{r}_A$ of nucleus A. If $\Delta_B\rho(\mathbf{r}_A)$ denotes the spin density at A induced by perturbation of strength λ_B at B, the J-coupling (Hz) can be evaluated as

(1) $$J[A,B] = (16h\mu_b^2\,\gamma_A\gamma_B/9)\,\Delta_B\rho(\mathbf{r}_A)\,/\lambda_B$$

where h is Planck's constant, μ_b is the Bohr magneton, and γ_A, γ_B are nuclear gyromagnetic ratios. The perturbative field strength should be taken sufficiently small (e.g., $\lambda_B = 0.02$ a.u.) that the ratio $\Delta_B\rho/\lambda_B$ is numerically independent of λ_B.

To obtain a localized decomposition of the densities ($\rho^{(\alpha)}$, $\rho^{(\beta)}$) of either spin, one can replace the usual expansion over occupied MOs $\{\varphi_i^{(\sigma)}\}$ by the corresponding expansion over NLMOs $\{\Omega_i^{(\sigma)}\}$

(2) $$\rho^{(\sigma)} = \sum_i^{occ} |\Omega_i^{(\sigma)}|^2\ ,\ (\sigma = \alpha, \beta)$$

Each semi-localized NLMO Ω_i can in turn be expanded in the complete set of localized NBOs $\{\sigma_j\}$, viz., for α spin,

(3) $$\Omega_i^{(\alpha)} = c_{ii}^{(\alpha)}\sigma_i^{(\alpha)} + \sum_{jj}^{NL} c_{ji}^{(\alpha)}\sigma_j^{(\alpha)}$$

where the $\{c_{ji}^{(\alpha)}\}$ are elements of the NBO → NLMO transformation matrix.

Eqs. (1)-(3) lead to a localized decomposition of J[A,B] into Lewis (L) and non-Lewis (NL) contributions of the form

(4) $$J[A,B] = \sum_i^L \{J_i^{(L)}[A,B] + \sum_j^{NL} J_{ji}^{(NL)}[A,B]\}$$

analogous to that previously described for the dipole operator (Sec. B.6.3). Each Lewis-type $J_i^{(L)}$ corresponds to the contribution of a completely localized NBO σ_i [i.e., the result of setting $c_{ji} \neq 0$ for all $j \neq i$ in Eq. (3)], whereas $J_{ji}^{(NL)}$ is the contribution of $\sigma_i \rightarrow \sigma_j^*$ interactions in each spin set. Because Eq. (1) expresses J[A,B] unsymmetrically in terms of the perturbation "from B to A," a second evaluation of J[A,B] is performed with the roles of A and B reversed, and each term in Eq. (4) is evaluated as the average of these unsymmetrical contributions in order to restore the physical symmetry of the A,B spin coupling.

The $\sigma_i \rightarrow \sigma_j^*$ interactions can in turn be partitioned into two sets:

Repolarization: Those ("internal") in which σ_j^* is centered on one or both of the *same* atoms as σ_i, viz.,

(4) $\sigma_{AB} \rightarrow \sigma^*_{AB}, r^*_A, r^*_B$ ("internal")

Delocalization: Those ("external") in which σ_i, σ_j^* are centered in *distinct* bonding regions, viz.,

(5) $\sigma_{AB} \rightarrow \sigma^*_{CD}, r^*_C, r^*_D$ ("external")

Each J[A,B] can thereby be expressed as a sum of "Lewis," "repolarization," and "delocalization" contributions

(6) $J = J^{(L)} + J^{(repol)} + J^{(deloc)}$

or, in terms of individual NBOs, as

(7) $J = \sum_i^L \{J_i^{(L)} + J_i^{(repol)} + \sum_j^{NL} J_{ji}^{(deloc)}\}$

Physically, the $J_i^{(L)}$ contributions represent primarily the *steric* (exchange antisymmetry) effects that are present even in the completely localized natural Lewis structure wavefunction, the $J_i^{(repol)}$ contributions describe how the electron pair in each NBO can repolarize (altering the left-right, radial, or angular separation of α and β electrons) in response to the perturbation, and the $J_{ji}^{(deloc)}$ contributions represent the effect of hyperconjugative or conjugative $\sigma_i \rightarrow \sigma_j^*$ delocalizations of "resonance" type (irreducible departures from a single localized Lewis structure). See Wilkens et al. for further discussion.

In each case the gyromagnetic ratios γ_A, γ_B (taken from a standard compilation of NMR properties <www.webelements.com> are chosen to correspond to the

"most important" magnetic isotope, i.e., the isotope of half-integer nuclear spin (I) of greatest natural abundance. J-couplings for other isotopic nuclei can then be obtained by correcting for the change in γ values. For cases where isotopic spin and γ are unknown, the program uses the value γ = 1 (x10^7), so that calculated J values can be easily rescaled to correct physical units when the proper γ becomes known. (A similar rescaling procedure can be used to correct for possible future revisions of the γ values.) The table below summarizes the selected isotope, nuclear spin, γ value (in units of 10^7 rad $T^{-1}s^{-1}$) and percentage terrestrial abundance for all atoms Z = 1-103.

Z	isotope	I	γ(x10^{-7})	%−abund.
1	^{1}H	1/2	26.7522	99.98
2	^{3}He	1/2	−20.3802	0.00
3	^{7}Li	3/2	10.3977	92.57
4	^{9}Be	3/2	−3.7597	100.00
5	^{11}B	3/2	2.8747	80.10
6	^{13}C	1/2	6.7283	1.10
7	^{15}N	1/2	−2.7126	0.37
8	^{17}O	5/2	−3.6281	0.04
9	^{19}F	1/2	25.1815	100.00
10	^{21}Ne	3/2	−2.1131	0.27
11	^{23}Na	3/2	7.0808	100.00
12	^{25}Mg	5/2	−1.6389	10.05
13	^{27}Al	5/2	6.9763	100.00
14	^{29}Si	1/2	−5.3190	4.67
15	^{31}P	1/2	10.8394	100.00
16	^{33}S	3/2	2.0557	0.75
17	^{35}Cl	3/2	2.6242	75.78
18	^{39}Ar	7/2	1.0000	0.00
19	^{39}K	3/2	1.2501	93.26
20	^{43}Ca	7/2	−1.8031	0.13
21	^{45}Sc	7/2	6.5088	100.00
22	^{47}Ti	5/2	−1.5105	7.30
23	^{51}V	7/2	7.0455	99.75

24	^{53}Cr	3/2	−1.5152	9.50
25	^{55}Mn	5/2	6.6453	100.00
26	^{57}Fe	1/2	0.8681	2.25
27	^{59}Co	7/2	6.3320	100.00
28	^{61}Ni	3/2	−2.3948	1.14
29	^{63}Cu	3/2	7.1118	69.17
30	^{67}Zn	5/2	1.6767	4.12
31	^{69}Ga	3/2	6.4389	60.11
32	^{73}Ge	9/2	−0.9360	7.73
33	^{75}As	3/2	4.5962	100.00
34	^{77}Se	1/2	5.1254	7.63
35	^{79}Br	3/2	6.7256	50.69
36	^{83}Kr	9/2	−1.0331	11.55
37	^{85}Rb	5/2	2.5927	72.17
38	^{87}Sr	9/2	−1.1639	7.00
39	^{89}Y	1/2	−1.3163	100.00
40	^{91}Zr	5/2	−2.4974	11.22
41	^{93}Nb	9/2	6.5674	100.00
42	^{95}Mo	5/2	−1.7880	15.92
43	^{99}Tc	9/2	6.0460	0.00
44	^{101}Ru	5/2	−1.3770	16.98
45	^{103}Rh	1/2	−0.8468	100.00
46	^{105}Pd	5/2	−1.2300	22.33
47	^{107}Ag	1/2	−1.0889	51.84
48	^{111}Cd	1/2	−5.6983	12.80
49	^{115}In	9/2	5.8972	95.70
50	^{119}Sn	1/2	−10.0317	8.59
51	^{121}Sb	5/2	6.4435	57.36
52	^{125}Te	1/2	−8.5108	7.14
53	^{127}I	5/2	5.3896	100.00
54	^{129}Xe	1/2	−7.4521	26.40
55	^{133}Cs	7/2	3.5333	100.00
56	^{137}Ba	3/2	2.9930	11.23
57	^{139}La	7/2	3.8083	99.91
58	^{141}Ce	7/2	1.0000	0.00

59	^{141}Pr	5/2	8.1907	100.00
60	^{143}Nd	7/2	−1.4570	12.18
61	^{147}Pm	7/2	3.6130	0.00
62	^{147}Sm	7/2	−1.1150	15.07
63	^{153}Eu	5/2	2.9369	52.20
64	^{157}Gd	7/2	−1.0769	15.65
65	^{159}Tb	3/2	6.4310	100.00
66	^{163}Dy	7/2	1.2890	24.90
67	^{165}Ho	7/2	5.7100	100.00
68	^{167}Er	7/2	−0.7716	22.95
69	^{169}Tm	1/2	−2.2180	100.00
70	^{173}Yb	5/2	−1.3025	16.12
71	^{175}Lu	7/2	3.0552	97.41
72	^{177}Hf	7/2	1.0860	18.61
73	^{181}Ta	7/2	3.2438	99.99
74	^{183}W	1/2	1.1282	14.28
75	^{187}Re	5/2	6.1057	62.60
76	^{189}Os	3/2	2.1071	16.10
77	^{193}Ir	3/2	0.5227	62.70
78	^{195}Pt	1/2	5.8385	33.80
79	^{197}Au	3/2	0.4731	100.00
80	^{199}Hg	1/2	4.8458	16.87
81	^{205}Tl	1/2	15.6922	70.48
82	^{207}Pb	1/2	5.5805	22.10
83	^{209}Bi	9/2	4.3750	100.00
84	^{209}Po	1/2	7.4000	0.00
85	$^{?}$At	?	1.0000	0.00
86	$^{?}$Rn	?	1.0000	0.00
87	^{223}Fr	?	1.0000	0.00
88	$^{?}$Ra	?	1.0000	0.00
89	^{227}Ac	3/2	3.5000	0.00
90	^{229}Th	5/2	0.4000	0.00
91	^{231}Pa	3/2	3.2100	100.00
92	^{235}U	7/2	−0.5200	0.72
93	^{237}Np	5/2	3.1000	0.00

94	^{239}Pu	1/2	0.9720	0.00
95	^{241}Am	5/2	1.4000	0.00
96	^{247}Cm	9/2	0.2000	0.00
97	^{247}Bk	3/2	1.0000	0.00
98	^{251}Cf	1/2	1.0000	0.00
99	$^{?}$Es	?	1.0000	0.00
100	^{257}Fm	?	1.0000	0.00
101	$^{?}$Md	?	1.0000	0.00
102	^{259}No	?	1.0000	0.00
103	$^{?}$Lr	?	1.0000	0.00

B.15.2 NJC Keyword Usage and Sample Input

The NJC keyword is currently implemented only for Gaussian host programs. Default natural J-coupling analysis is invoked by simply including the NJC keyword in the $NBO keylist. However, evaluation of all $J_{A,B}$ couplings in a closed-shell molecule of *N* magnetic nuclei requires a separate open-shell Fermi FIELD calculation for each perturbed nucleus. These calculations should be prepared as a chained sequence of "Link1" jobs, each requesting perturbation of a different nucleus *n*, and each having a FILE name of the form JOB_*n* (as well as the NJC keyword) in the $NBO keylist. The NJC output from JOB_*n* will contain the couplings to previously perturbed atoms of the chain (i.e., JOB_1 output contains no couplings, JOB_2 output contains $J_{1,2}$ coupling, JOB_3 output contains $J_{1,3}$ and $J_{2,3}$ couplings, and so forth).

[Note that each JOB_*n* of the chain creates a file "JOB_*n*.njc" that is read by subsequent JOB_*m* links to analyze $J_{n,m}$ coupling. Thus, the individual jobs of the chain can also be run separately, provided the JOB_*n*.njc files from previous runs remain accessible on the default directory.]

The following input deck creates a chain of seven jobs for the example of CH_3NH_2 (7 nuclei), using a field strength of "200" (0.02 a.u.) for each perturbation. The field strength "200" is assumed by NJC and should always be chosen on the Gaussian route card. [If it is necessary to alter this field strength for numerical reasons, one can always use Eq. (1) to re-scale the calculated J value for the actual λ_B employed.] In the present case the J-couplings will be evaluated with gyromagnetic ratios for ^{1}H, ^{13}C, and ^{15}N nuclei. Note that the "PRINT=0" keyword is included in the $NBO keylist after the first job to suppress repetitive printing of NBO output that differs infinitesimally from that of the first job.

```
%mem=2000000
%chk=ch3nh2
HF/3-21G POP=NBORead field=f(1)200

Methylamine: perturb C1

0   1
C
N   1   1.47
H   1   1.09 2   109.47
H   1   1.09 2   109.47   3   120.  0
H   1   1.09 2   109.47   3   240.  0
H   2   1.01 1   109.47   3    60.  0
H   2   1.01 1   109.47   3   300.  0
```

```
$NBO FILE=CH3NH2_1 NJC $END

--Link1--
%mem=2000000
%chk=ch3nh2
HF/3-21G POP=NBORead field=f(2)200 guess=read geom=allcheckpoint

$NBO FILE=CH3NH2_2 NJC PRINT=0 $END

--Link1--
   .
   .
   .
--Link1--
%mem=2000000
%chk=ch3nh2
HF/3-21G POP=NBORead field=f(7)200 guess=read geom=allcheckpoint

$NBO FILE=CH3NH2_7 NJC PRINT=0 $END
```

By default, all J-coupling contributions are printed that exceed a printing threshold of 0.1 Hz. This can be altered by including a chosen print threshold with the NJC keyword, as illustrated below (e.g., to increase the print threshold to 0.5 Hz)

```
$NBO FILE=CH3NH2_7 NJC=0.5 $END
```

(Note that NJC table entries are only printed to 0.01 Hz precision, so that setting the print threshold below 0.01 only results in additional rows and colums with zero entries.)

B.15.3 NJC Sample Output

A sample of NJC output produced (on the CH3NH2_7 step) for the J[H5,H7] spin coupling in the idealized methylamine example is shown below:

```
 J[H5,H7] = 8.35 Hz:  3-J[H5-C1-N2-H7]
    Threshold for printing:   0.10 Hz
                     1.         3.         4.         5.         6.
                | C 1- N 2   C 1- H 4   C 1- H 5   N 2- H 6   N 2- H 7
-------------------------------------------------------------------------
         Lewis |    0.03      -0.06       1.74      -0.08       4.07
         Repol.|    0.00       0.00      -0.08       0.00      -0.08
-------------------------------------------------------------------------
      C 1(ry*) |                                    -0.00 v     0.17 v
      N 2(ry*) |              -0.01 v    -0.28 v
  20. H 5(ry*) |   -0.04 v    -0.03 v                -0.05 r    -0.25 r
  22. H 7(ry*) |   -0.07 v    -0.05 r    -0.25 r     -0.04 v
  26. C 1- H 5*|    0.08 g     0.08 g                 0.18 v     1.21 v
  28. N 2- H 7*|    0.11 g     0.12 v     1.38 v      0.11 g
         Others|   -0.01       0.00      -0.05       0.00       0.10
(Total deloc.)|   (0.07)     (0.12)     (0.80)     (0.20)     (1.23)
-------------------------------------------------------------------------
          NLMO |    0.10       0.06       2.47       0.12       5.23

                    9.
                | N 2(lp)     Others |    Total
-------------------------------------------------
         Lewis |    0.10       0.03 |     5.84
         Repol.|    0.00       0.00 |    -0.15
-------------------------------------------------
      C 1(ry*) |    0.01 v     0.00 |     0.18
      N 2(ry*) |              -0.01 |    -0.30
  20. H 5(ry*) |   -0.05 r    -0.02 |    -0.44
  22. H 7(ry*) |   -0.11 v    -0.04 |    -0.56
  26. C 1- H 5*|    0.27 v     0.04 |     1.86
  28. N 2- H 7*|    0.09 g     0.07 |     1.88
         Others|   -0.00      -0.01 |     0.04
(Total deloc.)|   (0.20)     (0.05)|    (2.66)
-------------------------------------------------
          NLMO |    0.30       0.08 |     8.35
```

As shown in the output heading, the J[H5,H7] coupling is evaluated as 8.35 Hz, and the coupling pattern is identified as being of "3-J" (^{3}J, vicinal, through-3-bonds) type, bridged by bonds to C1 and N2. In the chosen geometry (Sec. B.15.2), the H5, H7 protons are in the vicinal antiperiplanar orientation that is expected to favor strong J-coupling, according to the well-known Karplus equation. (In accordance with Karplus-like torsional dependence, the *gauche*-oriented H5, H6 protons have much weaker 4.62 Hz J-coupling in this molecule.) From the final "Total" column, the total Lewis, repolarization, and delocalization contributions to J[H5,H7] can be identified as

$$J^{(L)} = 5.84 \text{ Hz}, J^{(repol)} = -0.15 \text{ Hz}, J^{(deloc)} = 2.66 \text{ Hz}$$

The final "NLMO" row gives the total contribution of each NLMO identified in the column heading, showing that the leading contributions are from NLMOs 4 (the C1-H5 NLMO) and 6 (the N2-H7 NLMO),

$$J_4^{(NLMO)} = 2.47 \text{ Hz}, J_6^{(NLMO)} = 5.23 \text{ Hz}$$

with relatively insignificant contributions (< 0.3 Hz) from other NLMOs. The "Lewis" entry at the head of the column gives the corresponding NBO contribution, viz.,

$$J_4^{(NBO)} = 1.74 \text{ Hz}, J_6^{(NBO)} = 4.07 \text{ Hz}$$

the following "Repol." entry gives the (relatively negligible) repolarization correction for the NBO, and the remaining column entries give the $\sigma_i \rightarrow \sigma_j^*$ delocalization corrections. The two most important such corrections are seen to be

$$J_{4\rightarrow 28} = 1.38 \text{ Hz} (\sigma_{C1H5} \rightarrow \sigma^*_{N2H7}), J_{6\rightarrow 26} = 1.21 \text{ Hz} (\sigma_{N2H7} \rightarrow \sigma^*_{C1H5})$$

corresponding to the expected strong hyperconjugative interaction in the vicinal *trans*-like relationship between these NBOs. These $J_{4\rightarrow 28}$ and $J_{6\rightarrow 26}$ delocalizations are expected to vary with torsional angle in a Karplus-like manner (showing strong proportionality to the corresponding entries in the table of 2nd-order stabilization energies). This example illustrates how the J-coupling is often dominated by a relatively small number of localized (and transferable) NBO interactions of clear physical origin and distinctive dihedral dependence. In the present case, increasing the print threshold to 0.5 Hz would eliminate all but the few entries listed above, compacting the output table considerably.

As seen in the output table, each delocalization entry is labelled as vicinal (v), geminal (g), or "remote" (r) to identify the through-bonds relationship of the interacting σ_i, σ_j^* NBOs. The table also shows how multiple Rydberg-type (ry*) orbitals on a single atom are grouped together in a single entry (unnumbered, unless there is only one such ry* orbital in the group). Due to this condensation of ry* contributions, the size of the NJC output table tends to remain relatively constant as the basis set is extended. Note that setting the print threshold NJC=0.0 bypasses condensation and forces printing of table entries for all individual orbitals.

NJC analysis also recognizes and flags J-coupling through hydrogen bonds. In this case the coupling is identified by a label of the form "2h-J[H1-O2:H4],"

where “2h” denotes geminal through-H-bond coupling and the colon (:) denotes the coordinative H-bond.

B.16. 3-CENTER, 4-ELECTRON HYPERBOND SEARCH

Reference: F. Weinhold and C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective* (Cambridge U. Press, London, 2005), Secs 3.E, 4.F

B.16.1 Introduction

By default, the NBO program initiates a subsidiary "3CHB" search for 3-center, 4-electron "hyperbonds" (ω-bonds). As described in the 3-center MO picture [G. C. Pimentel, *J. Chem. Phys.* **19**, 446 (1951); R. E. Rundle, *J. Chem. Phys.* **17**, 671 (1941)] a hyperbonded triad of atoms A, B, C, with strongly interacting valence hybrids h_A, h_B, h_C, can give rise to *two* doubly-occupied MOs accommodating four electrons. Such 3-c, 4-e triads are more aptly described in Coulson's picture [C. A. Coulson, *J. Chem. Soc.* **1964**, 1442 (1964)] as a strong resonance hybrid of the two localized Lewis structure representations

(1) A-B :C ↔ A: B-C

which is denoted in NBO output as A:-B-:C.

In NBO language, each A:-B-:C triad corresponds to strong $n_C \rightarrow \sigma_{AB}^*$ delocalization in the A-B :C Lewis structure, or equivalently, strong $n_A \rightarrow \sigma_{BC}^*$ delocalization in the alternative A: B-C Lewis structure, leading to nearly equivalent NRT weightings of these structures ($w_{A\text{-}B:C} \approx w_{A:B\text{-}C}$; cf. Sec. B.8). The 3CHB search attempts to locate such A:-B-:C triads and to identify the participating NHOs and NBOs in the framework of the parent A-B :C Lewis structure. While 3-c, 4-e hyperbonding is a somewhat unusual feature of main-group compounds, it is a ubiquitous feature of transition metal bonding, as illustrated in the gold carbine complex example below.

An estimate of the %A-B vs. %B-C character of the resonance hybrid (1) can be obtained from the approximate inverse relationship to relative occupancies of σ_{AB}^*, σ_{BC}^* antibond NBOs in the respective Lewis structures, viz.,

(2) $\%A\text{-}B / \%B\text{-}C \approx occ(\sigma_{BC}^*) / occ(\sigma_{AB}^*)$

The σ_{BC}^* occupancy can in turn be estimated from the eigenvalues of the 2×2 density matrix in the basis of h_B, h_C NHOs. [Because these NHOs belong to the "wrong" (A-B :C) resonance structure, the estimates of $occ(\sigma_{BC}^*)$ and %A-B vs. %B-C are only qualitatively correct; however, these approximations allow

the hyperbonds to be efficiently recognized and characterized in terms of a *single* parent NBO Lewis structure, bypassing alternative $CHOOSE structures or full NRT search.]

The total occupancy of the A:-B-:C resonance triad (i.e., of the occupied $\omega_{AB:C}$, $\omega_{A:BC}$ hyperbonds, or of the interacting h_A, h_B, h_C valence NHOs) can be estimated by adding the delocalized σ_{AB}* occupancy to the localized n_C, σ_{AB} occupancies of the nominal A-B :C Lewis structure,

(3) $\quad \text{occ(A:-B-:C)} \approx \text{occ}(n_C) + \text{occ}(\sigma_{AB}) + \text{occ}(\sigma_{AB}^*)$

With the approximations noted above, the A:-B-:C hyperbonds can be characterized in terms of NHOs (h_A, h_B, h_C) and NBOs (σ_{AB}, n_C) of only the A-B :C parent NBO Lewis structure.

In principle, the resonance hybrid (1) could exhibit a continous range of weightings, and thus continuously variable %A-B vs. %B-C values in (2). By default, the 3CHB search flags as a hyperbond only those A, B, C triads in which the apparent %B-C weighting is at least half that of %A-B, i.e.,

(4) $\quad \%\text{B-C} > 33\%$

Although this numerical cut-off is rather arbitrary, it corresponds approximately to the limit where A-B :C and A: B-C must both be considered as NRT "reference" structures (Sec. B.8). Threshold (4) therefore corresponds to the onset of pronounced chemical effects that signal a uniquely distinctive "hyperbond" element of the skeletal bonding framework.

B.16.2 Sample Output

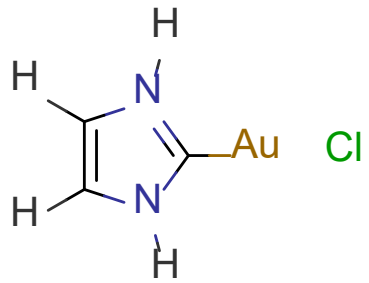
Let us illustrate 3CHB output for the transition metal-carbene complex with Gaussian input file

```
#b3lyp/lanl2dz pop=nbo6

imidazol-2-ylidene gold(i) chloride...b3lyp/lanl2dz

0  1
Au          0.000000    0.000000    0.581586
Cl          0.000000    0.000000    2.973055
C           0.000000    0.000000   -1.419815
N           0.000000    1.078828   -2.271212
N           0.000000   -1.078828   -2.271212
C           0.000000    0.686265   -3.619328
C           0.000000   -0.686265   -3.619328
H           0.000000    2.031939   -1.932775
H           0.000000   -2.031939   -1.932775
H           0.000000    1.387301   -4.436958
H           0.000000   -1.387301   -4.436958
```

and resulting NBO bonding pattern shown below:



Default NBO search yields two molecular units with the Au center interacting with the heterocyclic carbene through a coordinate covalent Au-C bond, and a detached Cl ligand. The 3CHB search gives the output shown below:

```
 3-Center, 4-Electron A:-B-:C Hyperbonds (A-B :C <=> A: B-C)
             [threshold for detection: 33.3%]

                                                        NBOs       3-center hybrids
                                                    -------------  ----------------
      Hyperbond A:-B-:C    %A-B/%B-C    occ      BD(A-B) LP(C)  h(A)  h(B)  h(C)
    ------------------   ---------  ------  ------- -----  ----  ----  ----
  1.  C  3:-Au  1-:Cl  2  53.1/46.9  3.9550      20     18    20    21    18
  2.  N  4:- C  3-: N  5  50.0/50.0  3.9423      22     19    24    25    19
```

The search discovers two hyperbonds (C_3:-Au_1-:Cl_2 and N_4:-C_3-:N_5), each with occupancy of roughly 3.95*e*. The first hyperbond exhibits slightly higher Au-C bonding character (53.1%) than Au-Cl (46.9%), whereas the second, allyl-type hyperbond shows equivalent C-N_4 and C-N_5 character. For the C:-Au-:Cl hyperbond, the NBOs 20 (σ_{AuC}) and 18 (n_{Cl}) are composed of NHOs 20, 21, and 18, which have approximate hybrid compositions:

$$(sp^{1.4})_C\text{-}(sd^{2.1})_{Au}\text{-}(sp^{7.4})_{Cl}$$

As also found in other segments of the NBO analysis, the low occupancy of n_{Cl} (1.67*e*), high occupancy of σ_{AuC}* (0.32*e*), and large estimated n_{Cl}-σ_{AuC}* 2nd-order interaction energy (114 kcal/mol) are all consistent with strong C:-Au-:Cl hyperbond character.

B.17. NBCP: NATURAL BOND CRITICAL POINT ANALYSIS

Reference: F. Weinhold, *J. Comput. Chem.* **33**, 2440-2449 (2012)

B.17.1 Introduction to Natural Bond Critical Point Analysis

The bond path (BP) and bond critical point (BCP) concepts are associated with topological analysis of electron density $\rho(\mathbf{r})$, as formulated in the "quantum theory of atoms in molecules" (QTAIM) theory of Bader and coworkers [R. F. W. Bader, *Atoms in Molecules: A Quantum Theory* (Oxford U. Press, London, 1990)]. In this approach, the gradient vector ($\nabla\rho(\mathbf{r})$) and Laplacian ($\nabla^2\rho(\mathbf{r})$) of $\rho(\mathbf{r})$ provide topological "curvature" descriptors of density at each spatial position $\mathbf{r}$, allowing one to locate the nuclear peaks $\mathbf{r}_A$, $\mathbf{r}_B$ and connecting ridge lines that may lead to a continuous "bond path" $BP_{AB}(\mathbf{r})$ between atoms A and B. In general, $BP_{AB}(\mathbf{r})$ is expected to descend steeply from each nucleus toward the unique intermediate stationary point BCP_{AB} that satisfies the characteristic "critical point" requirements of (3,−1) saddle-type topology: (i) vanishing gradient, $\nabla\rho(\mathbf{r})|_{BCP} = 0$, and (ii) proper curvature characteristics (one positive and two negative eigenvalues) of the Hessian matrix $(\mathbf{H})_{ij} = (\partial^2\rho/\partial\mathbf{r}_i\partial\mathbf{r}_j)_{BCP}$, $(i, j = 1\text{-}3)$.

Because both gradient and Laplacian are linear operators, their action on $\rho(\mathbf{r})$ can be decomposed unambiguously into distinct orbital contributions. In terms of delocalized MOs $\{\varphi_i\}$, semi-localized NLMOs $\{^{sl}\Omega_i\}$, localized NBOs $\{\Omega_i\}$, or atomic NAOs $\{\Theta_i^{(A)}\}$, $\rho(\mathbf{r})$ can be equivalently decomposed as

(1a) $\rho(\mathbf{r}) = \sum_i n_i^{(MO)} |\varphi_i(\mathbf{r})|^2$

(1b) $\rho(\mathbf{r}) = \sum_i n_i^{(NLMO)} |^{sl}\Omega_i(\mathbf{r})|^2$

(1c) $\rho(\mathbf{r}) = \sum_i n_i^{(NBO)} |\Omega_i(\mathbf{r})|^2 + \sum_{j\neq i} (\gamma^{(NBO)})_{ij}\Omega_i(\mathbf{r})\Omega_j(\mathbf{r})$

(1d) $\rho(\mathbf{r}) = \sum_i n_i^{(NAO)} |\Theta_i^{(A)}(\mathbf{r})|^2 + \sum_{j\neq i} (\gamma^{(NAO)})_{ij}\Theta_i^{(A)}(\mathbf{r})\Theta_j^{(A)}(\mathbf{r})$

where each diagonal MO or NLMO orbital occupancy $n_i^{(MO)} = n_i^{(NLMO)} = 1$ or 2 for open- or closed-shell species, respectively, and $(\gamma^{(basis)})_{ij}$ denotes an off-diagonal coupling element of the 1-particle density matrix in the non-diagonal NBO or NAO basis.

The conventional BP_{AB} and BCP_{AB} descriptors, as determined from total density $\rho(\mathbf{r})$, can be compared with the corresponding "natural" bond path

(NBP_{AB}) and bond critical point ($NBCP_{AB}$) as obtained from the *partial* density $\rho_{AB}^{(NAO)}(\mathbf{r})$ of contributions from idealized "natural atoms" A and B,

(2) $\rho_{AB}^{(NAO)}(\mathbf{r}) = \rho_{A}^{(NAO)}(\mathbf{r}) + \rho_{B}^{(NAO)}(\mathbf{r})$

Consistency (or inconsistency) between BCP and NBCP properties can then be taken as a measure of how accurately the NAO-based formulation of "natural atoms in molecules" (NAIM) leads to topological features that are consistent with those actually found in the total electron density.

Each NAIM-based "natural atomic density" $\rho_{A}^{(NAO)}(\mathbf{r})$ in Eq. (2) arises from the NAOs $\{\Theta_i^{(A)}\}$ of a particular atom A,

(3) $\rho_{A}^{(NAO)}(\mathbf{r}) = \sum_i n_i^{(NAO)} |\Theta_i^{(A)}(\mathbf{r})|^2 + \sum_{j\neq i} (\gamma^{(NAO)})_{ij}\Theta_i^{(A)}(\mathbf{r})\Theta_j^{(A)}(\mathbf{r})$

Consistent with general NPA properties, the integrated $\rho_{A}^{(NAO)}(\mathbf{r})$ densities (total NPA populations) for each atom sum properly to the total number of electrons (N) of the system,

(4) $N = \int \rho(\mathbf{r})\, d\mathbf{r} = \sum_A \int \rho_A^{(NAO)}(\mathbf{r})\, d\mathbf{r}$

The NAIM-based partitioning (4) of total electron density therefore serves as a useful alternative to the virial-based spatial partitioning that underlies the conventional QTAIM definition of "atoms in molecules".

Numerical evaluation of the idealized $NBCP_{AB}$ from idealized $\rho_{AB}^{(NAO)}(\mathbf{r})$ proceeds in exact analogy to corresponding evaluation of conventional BCP_{AB} from total $\rho(\mathbf{r})$. The differences (if any) between BCP_{AB} vs. $NBCP_{AB}$ location, density, and Laplacian density give a quantitative measure of deviations from a simple picture of localized natural atom contributions, reflecting "spill-over" density from atomic centers other than A and B. Such BCP vs. NBCP differences are tabulated for each atom pair in the first section of NBCP output to illustrate the high accuracy of the alternative NAIM-based topological model of electron density.

In the second section of NBCP output, the electron density and Laplacian density at each BCP are analyzed in terms of individual orbital contributions (1a-c) of NBO, NLMO, or MO type. In the simplest NAIM picture, each BCP arises essentially from a *single* localized NBO or NLMO, or if multiply bonded, from the summed bond-type NBO/NLMO contributions between the same two atoms. Absolute and percentage differences of BCP properties from the idealized NAIM limit provide an alternative measure of resonance or spill-

over effects (strictly absent in corresponding NBCP descriptors) that may strongly affect the chemical interpretation of BCP descriptors. If MO-based analysis of BCP properties is selected, one may also employ the results of CMO analysis (Sec. B.13) to anticipate how a *single* dominant NBO/NLMO contribution may be portrayed as a confusing mixture of delocalized contributions in conventional MO framework.

B.17.2 NBCP Keyword Usage

The NBCP keyword is implemented for all ESS host programs and stand-alone GenNBO configurations.

Basic NBCP analysis is requested by simply including the "NBCP" keyword in the $NBO keylist. A sample Gaussian input deck to request default NBCP analysis for formamide (B3LYP/6-311++G** level) is shown below:

```
#b3lyp/6-311++g** pop=nboread

H3NCHO, E=-169.9548513

0 1
7    1.084401   -0.157302   -0.000171
6   -0.162865    0.386721   -0.000029
8   -1.196169   -0.246396    0.000027
1    1.187639   -1.161267    0.000459
1    1.908579    0.420705    0.000529
1   -0.140489    1.492514    0.000162

$nbo file=h2ncho nbcp $end
```

This produces the basic table comparing conventional BCP and localized NBCP topological descriptors, as well as a second table showing individual NBO contributions to each BCP. The NAIM description makes no provision for spatial dissection of $\rho(\mathbf{r})$ into the virial-based "atomic basins" of QTAIM theory, nor is it restricted to equilibrium geometries in which the virial theorem is satisfied.

[It should be noted that computed entries of NBCP output tables are obtained by finite-difference rather than analytic differentiation procedures. Particularly for the case of Laplacian density, the numerical accuracy may not extend to the apparent precision (±0.0001e) of printed output, which attempts to display the small BCP vs. NBCP differences near the limits of machine accuracy.]

The basic NBCP keyword can be modified to specify alternative NLMO-based ("NBCP=NLMO") or MO-based ("NBCP=MO") analysis of BCP properties in the second table. In orbital-type density expansions based on NBOs, the non-diagonal coupling terms are gathered with neglected small diagonal terms as "others" in tabulated decompositions.

One can also append a bracket list of selected atom pairs to be specified for analysis of BCP/NBCP features, using a command of the form

```
NBCP[=basis] [IA1 IB1/IA2 IB2/.../IAn IBn]
```

to bypass the exhaustive search over all possible atom pairs of a large molecule. For example, the modified $NBO keylist

```
$nbo file=h2ncho nbcp=nlmo  1 2/1 3/2 3  $end
```

would request NLMO-based analysis of only the non-hydride (atoms 1-3: C, N, O) BCP features in the formamide example above.

B.17.3 Additional NBCP_BP and NBCP_PT Keyword Options

One can also request additional details of bond-path coordinates by including the "NBCP_BP" keyword. This prints a summary of computed bond path coordinates and atomic composition to an external ".50" file. This keyword can also be used in the optional form "NBCP_BP[=nstep]" to alter the granularity of computed bond paths by specifying a chosen NSTEP parameter that controls the number of path-segments from A to B (default NSTEP=100). Thus, to specify more coarse-grained (faster) path searches of 20 steps between atoms, one could employ the keylist shown below:

```
$nbo file=h2ncho nbcp nbcp_bp=20 $end
```

After usage of the NBCP_BP keyword, the complete set of bond path coordinates for successful BCP searches will be found in the output file "h2ncho.50" (or corresponding name specified by FILE keyword). Cartesian coordinates of each point on the A-B bond path are shown together with the NAIM-based percentage of density contributed by the atom at each terminus.

One can also employ the "NBCP_PT" keyword to analyze the density at arbitrary points of interest, as specified in bracket-list format. The general form of command is

```
NBCP_PT[=ibas] <x1 y1 z1/x2 y2 z2/.../xn yn zn>
```

where *ibas* = [NBO], NLMO, or MO is the basis set in which the density-point is analyzed. For example, to analyze the density at Cartesian points (0.461, 0.115, 1.0) and (–0.680, 0.070, 1.0) in terms of NLMO contributions, the command would be

```
NBCP_PT=NLMO <0.461 0.115, 1.0/-0.68 0.07 1.0>
```

In this manner, one can analyze the electron density at ring or cage critical points (RCP, CCP) or other points of interest that are not located by the NBCP program itself.

B.17.4 NBCP Sample Output

The first table of default NBCP output is shown below for the formamide input file of the previous section:

```
NATURAL BOND CRITICAL POINT (NBCP) ANALYSIS

[Topological (3,-1) bond critical points:
   BCP (total density); NBCP (NAO atomic densities)]

  Atoms             Rho    Lapl.   Laplacian curvatures        Coordinates
----------       ------- -------  ----------------------  ----------------------
N  1- C  2  BCP   0.3161 -0.8805  0.4240 -0.6221 -0.6824  0.2969  0.1851  0.0000
            NBCP  0.3175 -0.6776  0.4672 -0.5329 -0.6118  0.3227  0.1764 -0.0001
                                                        [|R(BCP)-R(NBCP)|=  0.0272]
N  1- H  4  BCP   0.3372 -1.6445  0.8714 -1.2256 -1.2903  1.1615 -0.8970  0.0003
            NBCP  0.3374 -1.5771  0.8786 -1.2182 -1.2374  1.1598 -0.8956  0.0003
                                                        [|R(BCP)-R(NBCP)|=  0.0022]
N  1- H  5  BCP   0.3397 -1.6392  0.8779 -1.2240 -1.2931  1.6892  0.2683  0.0003
            NBCP  0.3399 -1.5960  0.8719 -1.2213 -1.2466  1.6890  0.2694  0.0003
                                                        [|R(BCP)-R(NBCP)|=  0.0011]
C  2- O  3  BCP   0.4122 -0.2203  1.8546 -1.0044 -1.0705 -0.5137  0.1637  0.0000
            NBCP  0.4203 -0.1661  1.7268 -0.8540 -1.0390 -0.5226  0.1553  0.0000
                                                        [|R(BCP)-R(NBCP)|=  0.0123]
C  2- H  6  BCP   0.2772 -0.9466  0.5480 -0.7382 -0.7564 -0.1431  1.1029  0.0001
            NBCP  0.2746 -0.8296  0.6229 -0.7220 -0.7305 -0.1426  1.1107  0.0001
                                                        [|R(BCP)-R(NBCP)|=  0.0078]
```

For each listed pair of atoms in the first column, the successive columns describe the density ("Rho"), Laplacian density ("Lapl."), the three Hessian eigenvalues ("Laplacian curvatures"), and the Cartesian position vector ("Coordinates") for the listed BCP and/or NBCP, with the spatial separation ("|R(BCP)-R(NBCP)|", in Å) listed below. As seen in the table, the five atom pairs exhibit BCP features that are generally in close proximity to an idealized NBCP (within 0.01-0.03Å in all cases). The BCP and NBCP are also found to have similar density (within 2% in all cases), and the corresponding Laplacian densities are also of similar magnitude and sign (but with significantly larger differences, ranging up to ca. 35%). Such close agreement of total $\rho(\mathbf{r}_{BCP})$ and idealized $\rho(\mathbf{r}_{NBCP})$ densities is rather typical, suggesting why NAO/NBO descriptors are often highly correlated with measures of chemical bonding interactions inferred from topological BCP densities (although corresponding correlations with Lagrangian densities are significantly weaker).

In the second portion of default NBCP output, the five BCP features are analyzed in terms of individual NBO contributions, as shown below:

```
NBO-based contributions to   5 bond critical points

BCP  1.  N  1- C  2: (  0.2969,  0.1851,  0.0000)
-------------------------------------------------
  NBO   1.  N 1- C 2 : Rho = 0.3032 ( 95.9%), LaplRho = -1.6879
  NBO   2.  N 1- H 4 : Rho = 0.0038 (  1.2%), LaplRho = -0.0312
  NBO   3.  N 1- H 5 : Rho = 0.0042 (  1.3%), LaplRho = -0.0344
```

```
  NBO   6.  C 2- H 6 : Rho = 0.0005 (  0.2%), LaplRho =  0.1338
  NBO   7.  N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0026
  NBO   8.  C 2(cr)  : Rho = 0.0007 (  0.2%), LaplRho =  0.2435
  NBO  12.  O 3(lp)  : Rho = 0.0027 (  0.8%), LaplRho = -0.0220
  NBO  30.  C 2(ry*) : Rho = 0.0004 (  0.1%), LaplRho = -0.0009
  NBO  31.  C 2(ry*) : Rho = 0.0014 (  0.4%), LaplRho = -0.0226
  NBO  82.  N 1- C 2*: Rho = 0.0084 (  2.7%), LaplRho = -0.0184
                  [others =-0.0098 ( -3.1%)             0.5622]
                      Total 0.3161                     -0.8805

BCP  2.  N  1- H  4: (  1.1615, -0.8970,  0.0003)
-------------------------------------------------
  NBO   2.  N 1- H 4 : Rho = 0.3352 ( 99.4%), LaplRho = -1.8259
  NBO   3.  N 1- H 5 : Rho = 0.0005 (  0.1%), LaplRho =  0.0301
  NBO   6.  C 2- H 6 : Rho = 0.0002 (  0.1%), LaplRho =  0.0030
  NBO   7.  N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0041
  NBO  64.  H 4(ry*) : Rho = 0.0001 (  0.0%), LaplRho =  0.0005
  NBO  83.  N 1- H 4*: Rho = 0.0006 (  0.2%), LaplRho =  0.0218
                  [others = 0.0000 (  0.0%)             0.1301]
                      Total 0.3372                     -1.6445

BCP  3.  N  1- H  5: (  1.6892,  0.2683,  0.0003)
-------------------------------------------------
  NBO   2.  N 1- H 4 : Rho = 0.0004 (  0.1%), LaplRho =  0.0334
  NBO   3.  N 1- H 5 : Rho = 0.3378 ( 99.4%), LaplRho = -1.8298
  NBO   5.  C 2- O 3 : Rho = 0.0001 (  0.0%), LaplRho =  0.0005
  NBO   6.  C 2- H 6 : Rho = 0.0002 (  0.1%), LaplRho =  0.0003
  NBO   7.  N 1(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0043
  NBO  84.  N 1- H 5*: Rho = 0.0004 (  0.1%), LaplRho =  0.0152
                  [others = 0.0003 (  0.1%)             0.1454]
                      Total 0.3397                     -1.6392

BCP  4.  C  2- O  3: ( -0.5137,  0.1637,  0.0000)
-------------------------------------------------
  NBO   1.  N 1- C 2 : Rho = 0.0002 (  0.0%), LaplRho =  0.1604
  NBO   2.  N 1- H 4 : Rho = 0.0010 (  0.2%), LaplRho = -0.0036
  NBO   3.  N 1- H 5 : Rho = 0.0012 (  0.3%), LaplRho = -0.0121
  NBO   5.  C 2- O 3 : Rho = 0.3676 ( 89.2%), LaplRho = -2.7691
  NBO   6.  C 2- H 6 : Rho = 0.0017 (  0.4%), LaplRho =  0.2275
  NBO   8.  C 2(cr)  : Rho = 0.0107 (  2.6%), LaplRho =  1.6365
  NBO   9.  O 3(cr)  : Rho = 0.0006 (  0.2%), LaplRho = -0.0011
  NBO  11.  O 3(lp)  : Rho = 0.0175 (  4.3%), LaplRho = -0.2191
  NBO  30.  C 2(ry*) : Rho = 0.0017 (  0.4%), LaplRho =  0.0020
  NBO  31.  C 2(ry*) : Rho = 0.0002 (  0.0%), LaplRho =  0.0006
  NBO  82.  N 1- C 2*: Rho = 0.0003 (  0.1%), LaplRho =  0.0282
  NBO  86.  C 2- O 3*: Rho = 0.0012 (  0.3%), LaplRho = -0.0123
  NBO  87.  C 2- H 6*: Rho = 0.0003 (  0.1%), LaplRho =  0.0225
                  [others = 0.0081 (  2.0%)             0.7192]
                      Total 0.4122                     -0.2203

  BCP  5.  C  2- H  6: ( -0.1431,  1.1029,  0.0001)
-------------------------------------------------
  NBO   2.  N 1- H 4 : Rho = 0.0001 (  0.0%), LaplRho =  0.0019
  NBO   3.  N 1- H 5 : Rho = 0.0003 (  0.1%), LaplRho =  0.0005
  NBO   6.  C 2- H 6 : Rho = 0.2735 ( 98.6%), LaplRho = -1.0297
  NBO   8.  C 2(cr)  : Rho = 0.0003 (  0.1%), LaplRho = -0.0036
  NBO  12.  O 3(lp)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0016
                  [others = 0.0021 (  0.8%)             0.0859]
                      Total 0.2772                     -0.9466
```

For each BCP, the table displays an exhaustive list of all orbitals contributing at least 0.0001e to $\rho(\mathbf{r}_{NBCP})$. Nevertheless, the table shows that the hydride BCP densities derive ca. 99% from the *single* NBO that is "expected" to link the atoms in elementary Lewis structure representation. The resonance-delocalized C-N (BCP 1) and C-O (BCP 4) BCP densities exhibit somewhat weaker contributions from the dominant "parent" NBOs (96% and 89%, respectively).

However, both the reduced percentages and the unusually large NBO contributions from off-diagonal couplings (included in “others”) are characteristic signatures of the important *resonance* delocalization in these bonds, as expected on chemical grounds.

For comparison, we show the corresponding NLMO-based decompositions (as obtained from “NBCP=NLMO” keyword):

```
 NLMO-based contributions to   5 bond critical points

 BCP  1.  N  1- C  2: (  0.2969,  0.1851,  0.0000)
 -------------------------------------------------
  NLMO   1.  N 1- C 2 : Rho = 0.3055 ( 96.7%), LaplRho = -1.7129
  NLMO   2.  N 1- H 4 : Rho = 0.0042 (  1.3%), LaplRho = -0.0144
  NLMO   3.  N 1- H 5 : Rho = 0.0044 (  1.4%), LaplRho = -0.0186
  NLMO   5.  C 2- O 3 : Rho = 0.0003 (  0.1%), LaplRho =  0.0697
  NLMO   6.  C 2- H 6 : Rho = 0.0001 (  0.0%), LaplRho =  0.1557
  NLMO   7.  N 1(cr)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0056
  NLMO   8.  C 2(cr)  : Rho = 0.0007 (  0.2%), LaplRho =  0.2488
                    [others = 0.0000 (  0.0%)             0.3968]
                        Total 0.3161                     -0.8805

 BCP  2.  N  1- H  4: (  1.1615, -0.8970,  0.0003)
 -------------------------------------------------
  NLMO   2.  N 1- H 4 : Rho = 0.3347 ( 99.3%), LaplRho = -1.8243
  NLMO   3.  N 1- H 5 : Rho = 0.0007 (  0.2%), LaplRho =  0.0329
  NLMO   6.  C 2- H 6 : Rho = 0.0007 (  0.2%), LaplRho = -0.0023
  NLMO   7.  N 1(cr)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0084
                    [others = 0.0001 (  0.0%)             0.1576]
                        Total 0.3372                     -1.6445

 BCP  3.  N  1- H  5: (  1.6892,  0.2683,  0.0003)
 -------------------------------------------------
  NLMO   2.  N 1- H 4 : Rho = 0.0006 (  0.2%), LaplRho =  0.0374
  NLMO   3.  N 1- H 5 : Rho = 0.3373 ( 99.3%), LaplRho = -1.8288
  NLMO   5.  C 2- O 3 : Rho = 0.0002 (  0.1%), LaplRho = -0.0008
  NLMO   6.  C 2- H 6 : Rho = 0.0003 (  0.1%), LaplRho = -0.0027
  NLMO   7.  N 1(cr)  : Rho = 0.0009 (  0.3%), LaplRho = -0.0086
  NLMO  12.  O 3(lp)  : Rho = 0.0004 (  0.1%), LaplRho =  0.0015
                    [others = 0.0000 (  0.0%)             0.1629]
                        Total 0.3397                     -1.6392

 BCP  4.  C  2- O  3: ( -0.5137,  0.1637,  0.0000)
 -------------------------------------------------
  NLMO   1.  N 1- C 2 : Rho = 0.0006 (  0.2%), LaplRho =  0.1449
  NLMO   5.  C 2- O 3 : Rho = 0.3696 ( 89.6%), LaplRho = -2.7707
  NLMO   6.  C 2- H 6 : Rho = 0.0021 (  0.5%), LaplRho =  0.1976
  NLMO   8.  C 2(cr)  : Rho = 0.0103 (  2.5%), LaplRho =  1.6401
  NLMO   9.  O 3(cr)  : Rho = 0.0011 (  0.3%), LaplRho = -0.0066
  NLMO  11.  O 3(lp)  : Rho = 0.0285 (  6.9%), LaplRho = -0.3482
                    [others = 0.0001 (  0.0%)             0.9226]
```

```
                      Total 0.4122                    -0.2203

 BCP  5.  C  2- H  6: ( -0.1431,  1.1029,  0.0001)
 ------------------------------------------------
  NLMO   3.  N 1- H 5 : Rho = 0.0003 (  0.1%), LaplRho = -0.0020
  NLMO   6.  C 2- H 6 : Rho = 0.2755 ( 99.4%), LaplRho = -1.0524
  NLMO   8.  C 2(cr)  : Rho = 0.0004 (  0.1%), LaplRho = -0.0043
  NLMO  12.  O 3(lp)  : Rho = 0.0009 (  0.3%), LaplRho =  0.0149
                    [others = 0.0001 (  0.0%)             0.0972]
                      Total 0.2772                    -0.9466
```

For NLMOs (as for MOs), the individual orbital contributions are strictly non-negative and additive, with no off-diagonal couplings to complicate orbital analysis of $\rho(\mathbf{r}_{BCP})$. Note that the Laplacian density $\nabla^2\rho(\mathbf{r}_{BCP})$ ("LaplRho") is much more sensitive than $\rho(\mathbf{r}_{BCP})$ to distracting spill-over contributions from nearby NBOs or NLMOs of little chemical interest [see, e.g., the large contribution of the C core orbital to $\nabla^2\rho(\mathbf{r}_{BCP})$ in BCP 4]. These results are typical of strong correlations that are generally found between NBO and $\rho(\mathbf{r}_{BCP})$ density descriptors, as well as the weaker NBO correlations with $\nabla^2\rho(\mathbf{r}_{BCP})$ Laplacian descriptors. In the latter context, NBCP output can be helpful in identifying the sources of unexpected variability in Laplacian $\nabla^2\rho(\mathbf{r}_{BCP})$ values, which carry the "image" of the parent NBO in less clear-cut form.

Next, we show sample output from the "NBCP_BP=20" command for the CN bond path (atoms 1, 2), as printed to the "h2ncho.50" file:

```
atoms   1   2 (NSTEP =  20)
STEP LAMBDA      x         y         z         rho      %-A     %-B   %-other
  0  0.000 (   1.0844,  -0.1573,  -0.0002) 193.8574e, 99.79%,  0.10%,  0.10%
  1  0.070 (   0.9976,  -0.1195,  -0.0001)  17.6962e, 99.62%,  0.00%,  0.37%
  2  0.117 (   0.9380,  -0.0936,  -0.0001)   3.7513e, 98.86%,  0.38%,  0.76%
  3  0.165 (   0.8784,  -0.0677,  -0.0001)   1.1643e, 97.09%,  1.85%,  1.06%
  4  0.214 (   0.8179,  -0.0415,  -0.0001)   0.6837e, 96.49%,  2.65%,  0.86%
  5  0.261 (   0.7582,  -0.0157,  -0.0001)   0.5677e, 97.28%,  2.11%,  0.61%
  6  0.309 (   0.6985,   0.0101,  -0.0001)   0.5062e, 98.24%,  1.30%,  0.46%
  7  0.358 (   0.6380,   0.0364,  -0.0001)   0.4522e, 98.14%,  1.47%,  0.39%
  8  0.405 (   0.5783,   0.0622,  -0.0001)   0.4053e, 94.52%,  5.08%,  0.40%
  9  0.453 (   0.5187,   0.0881,  -0.0001)   0.3680e, 82.96%, 16.49%,  0.55%
 10  0.502 (   0.4582,   0.1144,  -0.0001)   0.3413e, 59.94%, 39.17%,  0.89%
 11  0.549 (   0.3986,   0.1403,  -0.0001)   0.3253e, 33.02%, 65.69%,  1.29%
 12  0.597 (   0.3391,   0.1665,  -0.0001)   0.3174e, 13.88%, 84.55%,  1.57%
 13  0.631 (   0.2969,   0.1851,   0.0000)   0.3157e,  6.76%, 91.55%,  1.70%
 14  0.679 (   0.2374,   0.2116,   0.0000)   0.3198e,  2.72%, 95.44%,  1.84%
 15  0.727 (   0.1780,   0.2381,   0.0000)   0.3436e,  1.93%, 96.04%,  2.03%
 16  0.775 (   0.1185,   0.2643,   0.0000)   0.4466e,  1.71%, 96.10%,  2.19%
 17  0.823 (   0.0580,   0.2908,   0.0000)   0.9058e,  0.86%, 97.29%,  1.85%
 18  0.871 (  -0.0016,   0.3167,   0.0000)   2.8502e,  0.14%, 98.78%,  1.08%
 19  0.919 (  -0.0612,   0.3426,   0.0000)  10.9306e,  0.01%, 99.49%,  0.50%
 20  1.000 (  -0.1629,   0.3867,   0.0000) 119.7722e,  0.10%, 99.82%,  0.08%
```

Each step of the bond path is shown with the associated fractional progress parameter ("lambda"), Cartesian coordinates (x,y,z), and the NAO-based

percentage contribution from each "natural atom" (terminal atoms A. B or "others") along the path. As seen, the C-N BCP is at step 13 ($\lambda_{BCP} = 0.631$), with 6.76% contribution from NAOs on C, 91.55% from those on N, and 1.70% from other atoms. The calculated λ_{BCP} is in sensible agreement with the "Perrin estimate" that can be directly inferred from the σ_{CN} NBO polarization coefficients ($c_C = 0.6158$, $c_N = 0.7879$), viz.,

$$\lambda_{BCP} \approx |c_N|^2/(|c_C|^2 + |c_N|^2) = 0.621$$

in accordance with the expected dominant contribution of the single σ_{CN} NBCP.

Finally, we show sample output from the illustrative NBCP_PT command for two density points, as given in the previous section. The chosen points, (0.461, 0.115, 1.0) and (–0.680, 0.070, 1.0), correspond to the midpoints of CN and CO bonds, respectively, but are placed 1.0Å above the molecular *xy* plane to sample possible π-type as well as σ-type contributions to electron density.

```
NLMO-based contributions to   2 density points

Density point  1: (  0.4610,  0.1150,  1.0000)
-----------------------------------------------
                            Rho                 GradRho          LaplRho
                       ---------------   ----------------------  -------
 NLMO   1.  N 1- C 2 : 0.0092 ( 32.0%)   0.0011 -0.0005 -0.0271   0.0520
 NLMO   4.  C 2- O 3 : 0.0024 (  8.4%)  -0.0058  0.0013 -0.0035   0.0104
 NLMO   6.  C 2- H 6 : 0.0001 (  0.4%)  -0.0003  0.0008  0.0000   0.0040
 NLMO  10.  N 1(lp)  : 0.0169 ( 58.6%)   0.0148 -0.0053 -0.0263   0.0249
             [others = 0.0002 (  0.6%)  -0.0002 -0.0002 -0.0004  -1.0377]
                 Total 0.0288            0.0095 -0.0038 -0.0573  -0.9464

Density point  2: ( -0.6800,  0.0700,  1.0000)
-----------------------------------------------
                            Rho                 GradRho          LaplRho
                       ---------------   ----------------------  -------
 NLMO   4.  C 2- O 3 : 0.0219 ( 75.4%)  -0.0039 -0.0019 -0.0394   0.0365
 NLMO   5.  C 2- O 3 : 0.0067 ( 22.9%)   0.0001  0.0001 -0.0220   0.0497
 NLMO   6.  C 2- H 6 : 0.0002 (  0.7%)   0.0003  0.0011 -0.0001   0.0035
             [others = 0.0003 (  0.9%)   0.0012 -0.0003 -0.0003  -1.0361]
                 Total 0.0290           -0.0023 -0.0011 -0.0619  -0.9464
```

In this example, the two spatial points are found to have distinctly non-zero values of the $\nabla\rho(\mathbf{r})$ ("GradRho") gradient vector , but quite similar values of $\rho(\mathbf{r})$ ("Rho": 0.0288 vs. 0.0290) and Laplacian $\nabla^2\rho(\mathbf{r})$ ("LaplRho": both –0.9464). As expected, the second point draws largest $\rho(\mathbf{r})$ contribution from π_{CO} (NLMO 4) and the first point from n_N (NLMO 10), consistent with the strong amide resonance delocalization that is expected to spread appreciable π-character into the CN bonding region.

B.18. NCE: NATURAL COULOMB ELECTROSTATICS ANALYSIS

Reference: F. Weinhold and C. R. Landis, *Discovering Chemistry with Natural Bond Orbitals* (Wiley-VCH, Hoboken NJ, 2012), p. 145ff.

B.18.1 Introduction to Natural Coulombic Energy Analysis

A simplified picture of long-range electrostatic interactions can be based on the concept of effective atomic point charges Q_A that interact according to the classical law of Coulomb electrostatics,

(1) $E_{Coulomb} = \Sigma_{A,B}\, Q_A\, Q_B/R_{AB}$

where R_{AB} is the interatomic distance between nuclei A, B. The classical Coulomb formula (1) is highly questionable in the short-range domain of quantal exchange interactions. Nevertheless, Eq. (1) may provide a useful estimate of "electrostatic effects" when R_{AB} separations sufficiently exceed the sum of atomic van der Waals radii. When Eq. (1) is evaluated with *natural* atomic charges, the formula defines what may be called the "Natural Coulomb Electrostatics" (E_{NCE}) potential energy for the species and geometry in question.

The "NCE" keyword provides the simple NPA-based evaluation of Coulomb electrostatic potential energy E_{NCE}. The variations of E_{NCE} with respect to geometry changes thereby provide simple estimates of "electrostatic" contributions to intra- or intermolecular interaction energy, which may be compared with independent estimates of "steric" and "donor-acceptor" contributions. Such simplified estimates complement the more sophisticated dissection of interaction energy in "energy decomposition analysis" methods such as NEDA.

An issue in such energy decompositions is the *coupling* between localized Lewis (L) and delocalized non-Lewis (NL) contributions to perceived "classical type" electrostatic or steric components. For E_{NCE}, one can quantitatively assess such L/NL coupling by comparing the actual NPA charge Q_A with that ($Q_A^{(L)}$) for the ideally localized "natural Lewis structure" (NLS), in which each L-type NBO is constrained to exact double-occupancy. In this manner, one can separate the L-type charge distribution of an idealized Lewis structural model from the NL-type "charge transfer" delocalizations of non-classical origin. The NCE analysis module displays such L/NL contributions to E_{NCE} for each atom pair, providing a direct estimate of non-classical CT corrections to Coulomb electrostatics.

B.18. NCE: NATURAL COULOMB ELECTROSTATICS ANALYSIS

The NL-induced charge shifts are often found to be leading contributors to chemically important “electrostatic effects”, providing an important quantal correction to quasi-classical interpretation of total E_{NCE}. For open shells, an additional spin-charge NCE table shows the distinct α-NCE and β-NCE contributions of each spin set, again emphasizing the limitations of naive classical interpretations.

B.18.2 NCE Keyword Usage and Sample Output

The NCE keyword is implemented for all ESS host programs and stand-alone GenNBO configurations.

NCE analysis is requested by simply including the "NCE" keyword in the $NBO keylist. A sample Gaussian input deck to request NCE analysis for formamide (RHF/3-21G level) is shown below:

```
#rhf/3-21g pop=nboread

H2NCHO

0 1
1       -1.913380       -0.349570        0.000000
1       -0.655700       -1.514100        0.000000
7       -0.940200       -0.557500        0.000000
6        0.000000        0.415950        0.000000
8        1.198300        0.232820        0.000000
1       -0.435920        1.407901        0.000000

$nbo file=h2ncho nce $end
```

This produces the first NCE output table comparing L and NL contributions to total NPA charge for each atom:

```
NATURAL COULOMB ELECTROSTATICS (NCE):

  Lewis(L) and non-Lewis(NL) contributions to NPA atomic charge
  and Coulomb potential energy

                      atomic charge
                  ----------------------------
  atom   unit       L        NL       total
  ----   ----   --------  --------  --------
  H  1     1     0.41730  -0.00287   0.41443
  H  2     1     0.42685  -0.00681   0.42004
  N  3     1    -1.12743   0.18029  -0.94714
  C  4     1     0.81557  -0.21133   0.60423
  O  5     1    -0.70603   0.06755  -0.63848
  H  6     1     0.17375  -0.02683   0.14691
-------------------------------------------
Total unit  1    0.00000   0.00000   0.00000
-------------------------------------------
Total species    0.00000   0.00000   0.00000
```

The second output table then evaluates L and NL contributions to total Coulomb potential energy $E_{Coulomb}$ both within and between units:

		NCE Potential Energy (au)		
unit	unit	L	NL	total
within	1	-0.79462	0.21469	-0.57993
	Total	-0.79462	0.21469	-0.57993

B.19. NCU: NATURAL CLUSTER UNIT ANALYSIS

B.19.1 Introduction to Natural Cluster Unit Analysis

For conceptual purposes, one often envisions the sequential aggregation of particulate matter into ever-larger "building blocks" of macroscopic phases, viz.,

(1) (elementary particles →) atoms → molecules
→ supramolecular clusters → ... → "condensation"

From a chemistry perspective (assuming existence of nuclei and electrons), the focal step in (1) is formation of molecules from atoms, under the influence of quantum mechanical exchange-type forces. From a biochemical perspective, the focus is on H-bonding and other supramolecular clustering processes (often attributed to so-called "noncovalent forces") that are active in the domain of near-ambient terrestrial conditions. From a materials perspective, attention focuses on higher-order clustering processes that lead finally to the aggregated liquid and solid phases of the macroscopic world. Advances in each domain can be associated with successful identification and characterization of fundamental "units" or "building blocks" that underlie steps of sequence (1).

To address the broader aspects of sequence (1), we can envision a formal interaction parameter τ_{NCU} that varies *continuously* from the weakest interatomic forces (i.e., those characteristic of London dispersion and long-range Casimir-Polder interactions) to the powerful exchange-type forces of chemical bonding. Each range of τ_{NCU} values leads to characteristic "natural cluster units" (NCUs) that are intrinsic building blocks of that range. The NCU module determines the numerical τ_{NCU} transition values and associated NCU building blocks that characterize a chosen system of nuclei and electrons in specified nuclear geometry.

Mathematically, the τ_{NCU} interaction parameter can be expressed as the strength (matrix norm) of off-diagonal couplings between atomic blocks of the NAO density matrix, viz.,

(2) $\tau_{NCU}(A,B) = Tr\{D_A * D_B\}^{1/2}$

where "Tr" denotes matrix trace and D_A, D_B are respective density matrix blocks for atoms A, B. Alternatively, the $\tau_{NCU}(A,B)$ value can be related to the square-root of the NAO-based Wiberg bond index (Sec. B.6.5), which

represents a type of "bond order" between atoms A, B. Conceptually, the τ_{NCU} coupling-strength parameter can also be pictured as an "effective temperature" that leads to complete atomic dissociation at sufficiently high values, or complete condensation at sufficiently low values, but with distinctive alternative NCU cluster patterns at characteristic τ_{NCU} transition values.

For a given interaction strength τ_{NCU}, each pair of atoms A, B is considered to form a connective "link" if and only if

(3) $\tau_{NCU} \leq \tau_{NCU}(A,B)$

Each contiguously linked network of atoms identifies a distinct NCU for the chosen τ_{NCU} value, analogous to the usual identification of NBO-linked networks as "molecular units." In the appropriate range of τ_{CU} values, the NCU assignments will agree with NBO-based molecular unit assignments. However, alternative NCU patterns are generally found in other τ_{NCU} ranges.

For a chosen input system of nuclei and electrons, the NCU module displays the list of distinct τ_{NCU} transition values and associated NCU clustering patterns for all possible interaction strengths, $0 \leq \tau_{NCU} \leq 1$. As shown in Eq. (2), NCU analysis depends only NAO-based definitions of underlying constituent atoms, with no other dependence on NBO-based description of intramolecular or intermolecular interactions. Nevertheless, subsequent NBO analysis of individual NCU species and their mutual interactions may further illuminate the composite system initially selected for NCU study.

B.19.2 NCU Sample Output

A simple illustration of NCU analysis can be given for the model water dimer (RHF/4-31G level), with Gaussian input file:

```
#RHF/4-31G POP=NBORead

water dimer

0  1
O       0.699995      -1.217080       0.000000
H       1.280646      -1.217080      -0.759460
H       1.280646      -1.217080       0.759460
O      -0.740005       1.277073       0.000000
H      -1.664288       1.032867       0.000000
H      -0.262005       0.449153       0.000000

$NBO FILE=dimer ncu $END
```

Corresponding output from the NCU module is shown below:

```
Natural Cluster Unit (NCU) Analysis:

 NCU       Unit        Unit
 thr      formula     charge  Atom list
----- --------------- ------ ----------------------------------------------------
1.000  1. O           -0.924  O1
       2. H            0.477  H2
       3. H            0.477  H3
       4. O           -0.952  O4
       5. H            0.447  H5
       6. H            0.474  H6
----- --------------- ------ ----------------------------------------------------
0.890  1. O           -0.924  O1
       2. H            0.477  H2
       3. H            0.477  H3
       4. HO          -0.505  O4,H5
       5. H            0.474  H6
----- --------------- ------ ----------------------------------------------------
0.870  1. H2O          0.031  O1,H2,H3
       2. HO          -0.505  O4,H5
       3. H            0.474  H6
----- --------------- ------ ----------------------------------------------------
0.850  1. H2O          0.031  O1,H2,H3
       2. H2O         -0.031  O4,H5,H6
----- --------------- ------ ----------------------------------------------------
0.210  1. H4O2         0.000  O1,H2,H3,O4,H5,H6
----- --------------- ------ ----------------------------------------------------
```

In this case, five distinct τ_{NCU} transition values and associated NCU aggregation regimes were found, with atomic constitution and net charge shown for each NCU unit. For $\tau_{NCU} = 0.210$ (and below), the full water dimer aggregate is found as the single NCU, with zero net charge. Up to τ_{NCU} =

0.850, the NCU units are the usual monomer "molecular units" found in default NBO analysis, with the expected charge transfer (±0.031) on each unit. At higher τ_{NCU} values up to 0.870, the bridging H_6 and residual O_4H_5 of the former Lewis acid (acceptor) monomer are recognized as a distinct NCU "ion pair" (with respective charges +0.474, –0.505). Further breakup of the remaining $O_1H_2H_3$ monomer leads to five NCU fragments (up to $\tau_{NCU} = 0.890$) and thereafter to final breakup of anionic O_4H_5 into mononuclear fragments (up to final $\tau_{NCU} = 1.000$).

B.20. PROP: GENERAL 1e PROPERTY ANALYSIS

Reference: Cf. DIPOLE analysis (Sec. B.6.3).

The PROP (property) keyword provides a powerful tool to perform NBO analysis of *any* 1e property that is available from the host ESS program (or input .47 file). Familiar examples of 1e properties include

- kinetic energy (PROP=KINETIC)
- nuclear-electron attraction (PROP=V)
- Fock or Kohn-Sham operator (PROP=F),
- dipole moment (PROP=DIPOLE)
- electron density (PROP=DM)

or any other property that depends solely on electron density. The above list includes properties that are generally computed by all host ESS programs and included in the .47 file, but many additional properties may be available from individual ESS hosts. If your ESS can calculate a property, the PROP keyword can perform its NBO analysis.

As indicated by examples given above, the PROP keyword must include an identifying label (id_label) of the chosen property

```
PROP=id_label
```

(e.g., PROP=KINETIC). The proper "id_label" is matched to .47 file input (e.g., $KINETIC keylist) or provided by the host ESS program through ESS/NBO message-passing protocol. Consult the ESS program documentation for available properties and labels from each host.

For any chosen property, the format of PROP output resembles that of DIPOLE or NJC output. The overall expectation value of the property is expressed as a sum of Lewis (L) and non-Lewis (NL) contributions, with subsidiary correlation correction for post-SCF methods.

The PROP keyword can be illustrated for the kinetic energy operator (PROP=KINETIC) of formamide (RHF/3-21G level), with input file

```
#rhf/3-21g pop=nboread

RHF/3-21G for formamide (H2NCHO)

0 1
```

```
  H   -1.91338       -0.34957       0.00000
  H   -0.65570       -1.51410       0.00000
  N   -0.94020       -0.55750       0.00000
  C    0.00000        0.41595       0.00000
  O    1.19830        0.23282       0.00000
  H   -0.43592        1.40790       0.00000

$nbo prop=kinetic $end
```

The corresponding PROP output segment is shown below:

```
 PROPerty Analysis for P = K   (all values in a.u.)

                Lewis(L)                 Non-Lewis(NL)       L + NL
     ================================  ====================  =========
           NBO                P(NBO)    NL    P(NL)  (%-NL)    P(NLMO)   e-corr
 ------------------------------------------------------------------------------
   1. CR ( 1) N  1            22.8091    24    0.0214 (  0.1)   22.8453   0.0000
                                         13    0.0208 (  0.1)
                                         22    0.0156 (  0.1)
                                        rem   -0.0216 ( -0.1)
   2. CR ( 1) C  2            16.4799    17   -0.0105 ( -0.1)   16.4996   0.0000
                                         25   -0.0103 ( -0.1)
                                         13    0.0084 (  0.1)
                                        rem    0.0322 (  0.2)
   3. CR ( 1) O  3            30.4278    23    0.0432 (  0.1)   30.4976   0.0000
                                         29    0.0181 (  0.1)
                                         17   -0.0166 ( -0.1)
                                        rem    0.0250 (  0.1)
   4. LP ( 1) N  1             1.7328    16   -0.1434 ( -8.3)    1.5892   0.0000
                                         28   -0.0049 ( -0.3)
                                         26    0.0046 (  0.3)
                                        rem    0.0000 (  0.0)
   5. LP ( 1) O  3             1.9631    23   -0.0549 ( -2.8)    1.8970   0.0000
                                         24   -0.0050 ( -0.3)
                                         14   -0.0025 ( -0.1)
                                        rem   -0.0037 ( -0.2)
   6. LP ( 2) O  3             2.5600    13   -0.1009 ( -3.9)    2.2837   0.0000
                                         18   -0.0999 ( -3.9)
                                         24   -0.0474 ( -1.9)
                                        rem   -0.0282 ( -1.1)
   7. BD ( 1) N  1- C  2       1.3642    27   -0.0018 ( -0.1)    1.3588   0.0000
                                         18   -0.0013 ( -0.1)
                                         14   -0.0010 ( -0.1)
                                        rem   -0.0014 ( -0.1)
   8. BD ( 1) N  1- H  5       1.2331    18   -0.0081 ( -0.7)    1.2178   0.0000
                                         17   -0.0072 ( -0.6)
                                         13   -0.0041 ( -0.3)
                                        rem    0.0042 (  0.3)
   9. BD ( 1) N  1- H  6       1.2267    17   -0.0102 ( -0.8)    1.2125   0.0000
                                         13   -0.0034 ( -0.3)
                                         24    0.0028 (  0.2)
                                        rem   -0.0034 ( -0.3)
  10. BD ( 1) C  2- O  3       1.7983    20   -0.0047 ( -0.3)    1.7936   0.0000
                                        rem    0.0000 (  0.0)
  11. BD ( 2) C  2- O  3       1.6619    15   -0.0031 ( -0.2)    1.6585   0.0000
                                        rem   -0.0003 (  0.0)
  12. BD ( 1) C  2- H  4       0.9525    14   -0.0075 ( -0.8)    0.9381   0.0000
                                         27   -0.0042 ( -0.4)
                                         19   -0.0035 ( -0.4)
                                        rem    0.0008 (  0.1)
                              ----------------------------------------------------
                  * Sum *     84.2095        -0.4218 ( -0.5)   83.7917   0.0000
                                                               ----------
                                                 * Total *     83.7917
```

As expected, the total kinetic energy (83.7917 a.u.) is dominated by well-localized CR (core) NBOs 1-3, with relatively small NL corrections (ca. 79 kcal/mol, 0.1%, acting to increase K.E.) . However, the resonance-type NL effects act to significantly *reduce* K.E. in valence NBOs, particularly for the lone pairs on oxygen [NBOs 6 (ca. 173 kcal/mol, 11%) and 4 (ca. 41 kcal/mol, 3%)] and nitrogen [NBO 4 (ca. 90 kcal/mol, 9%)]. The final column shows (unsurprisingly) that each electron correlation "e-corr" contribution vanishes in RHF level.

B.21. MATRIX: GENERAL MATRIX OPERATOR AND TRANSFORMATION OUTPUT

Reference: Sec. B.2.4, "Matrix Output Keywords"

The MATRIX keyword provides a powerful utility for obtaining general matrix elements of one or more chosen operators (*OP*) or basis set (*BAS*) transformations of interest. General MATRIX keyword input supplements and extends the "old-style" specific matrix output keywords listed in Sec. B.2.4, offering a vitually unlimited set of new output options as enabled by ESS hosts.

As in Sec. B.2.4, matrix output may refer to an operator matrix [the matrix representation of an operator (*OP*) in a chosen basis (*BAS*)] or a transformation matrix [transforming one basis (*BAS1*) to another (*BAS2*)] The particular choice of matrix is specified by the entries of a bracket list that follows the MATRIX keyword.

To specify a chosen operator matrix for a chosen operator *OP* in a chosen basis *BAS*, the input form is

MATRIX <*OP*/*BAS*>

For example, "MATRIX <F/NBO>" specifies the Fock (or Kohn-Sham) matrix in the NBO basis, and "MATRIX <K/PNLMO>" specifies the kinetic energy matrix in the PNLMO basis.

To specify a chosen transformation matrix from one basis (*BAS1*) to another (*BAS2*), the input form is

MATRIX <*BAS1*/*BAS2*>

For example, "MATRIX <AO/MO>" specifies the LCAO-MO transformation from basis AOs to MOs, whereas "MATRIX <NAO/NLMO>" specifies the LCNAO-NLMO transformation from NAOs to NLMOs (reported as "NLMOs in the NAO basis" in the NBO output).

Note that "MATRIX <NLMO/NAO>" reports the "NAOs in the NLMO basis", that is, the inverse of the <NAO/NLMO> transformation. Matrix inversion is trivial for orthogonal transformations (simply the transpose of the original transformation) but requires rather time-intensive Gauss-Jordan elimination for non-orthogonal basis sets. For non-square transformations, i.e. when linear dependence is encountered in the basis set, matrix inversion is not possible and

NBO will not report the inverse transformation. Note that matrices <AO/AO>, <PAO/PAO>, etc. will report the unit matrix (i.e. "AOs in the AO basis set", "PAOs in the PAO basis set", etc.).

In the above commands the chosen *BAS* name may be chosen from any of the twelve recognized basis sets:

BAS: AO, PAO, PNAO, NAO, PNHO, NHO, PNBO, NBO, PNLMO, NLMO, NO, MO

The chosen *OP* name may be chosen from *any* 1e operator included in the input archive (.47) file, such as

- "DM" or "Density" (density operator),
- "S" or "Overlap" (unit operator),
- "F" or "Fock" (Fock/Kohn-Sham operator),
- "K" or "Kinetic" (kinetic energy operator),
- "V" or "Nuclear" (nuclear-electronic potential),
- "DI" or "Dipole" (electric dipole moment)

In addition, the SD (spin-density) operator is available for all open-shell NBO options.

Alternatively, *OP* might be any operator provided to NBO from the host ESS program through general ESS/NBO message-passing protocol. Check the ESS User Manual for valid *OP* options available in your host ESS program. Symbolic names or abbreviations for *OP* or *BAS* entries are generally case-insensitive.

A single MATRIX keyword may be followed by multiple (up to 25) bracket lists for different matrices, such as

MATRIX <S/PNBO> <DIPOLE/NLMO> <NAO/NO>

Old-style keywords such as SPNBO or DINLMO are still recognized for popular options, but many new possibilities become available. Note however that additional keyword parameters as provided for old-style matrix output keywords (see Sec. B.2.4) are unrecognized by MATRIX.

The sample Gaussian input file below illustrates requests for the Fock matrix in the NBO basis ("matrix <fock/nbo>") and the AO → NAO transformation matrix ("matrix <ao/nao>") for formamide.

```
#rhf/3-21g pop=nboread

RHF/3-21G for formamide (H2NCHO)

0 1
  H   -1.91338       -0.34957       0.00000
  H   -0.65570       -1.51410       0.00000
  N   -0.94020       -0.55750       0.00000
  C    0.00000        0.41595       0.00000
  O    1.19830        0.23282       0.00000
  H   -0.43592        1.40790       0.00000

$nbo matrix <fock/nbo> <ao/nao> $end
```

In each case, the output format is identical to that for the respective old-style keywords FNBO and AONAO (which are still recognized in NBO 7).

B.22. STRUCTURAL AND GRAPHICAL OUTPUT KEYWORDS

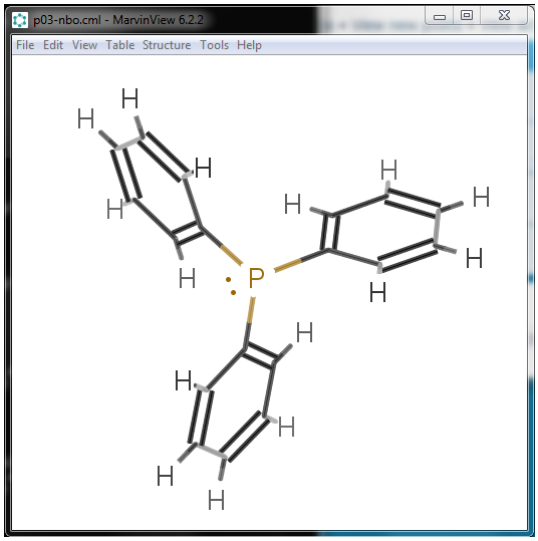
The NBO program offers additional keywords to write details of molecular structure and bonding in alternative file formats that serve as input to popular "molecular editor" and "cheminformatics" utilities. Graphical utilities are particularly useful for visualizing orbitals of the NBO program and for representing the 2D/3D bonding properties of resonance structures, providing a visualizable alternative of the NRT output of Sec. B.8.4. Non-graphical utilities can also convert output to a variety of ESS input file formats, derive proper IUPAC names, or make other use of the information.

We give brief details of each keyword in turn:

NBOCML

The NBOCML keyword produces a valid CML (chemical markup language) format file that specifies the pattern of bond and lone pairs of the NBO natural Lewis structure (NLS).

The CML file (written with the "-nbo.cml extension") provides convenient input to the *MarvinView* applet (see <www.chemaxon.com/products/marvin>). The illustration below shows sample NBOCML/MarvinView output for triphenylphosphine:



Multi-center bonds (like the B-H-B bridge bonds in diborane), if present in the NLS, are not correctly displayed.

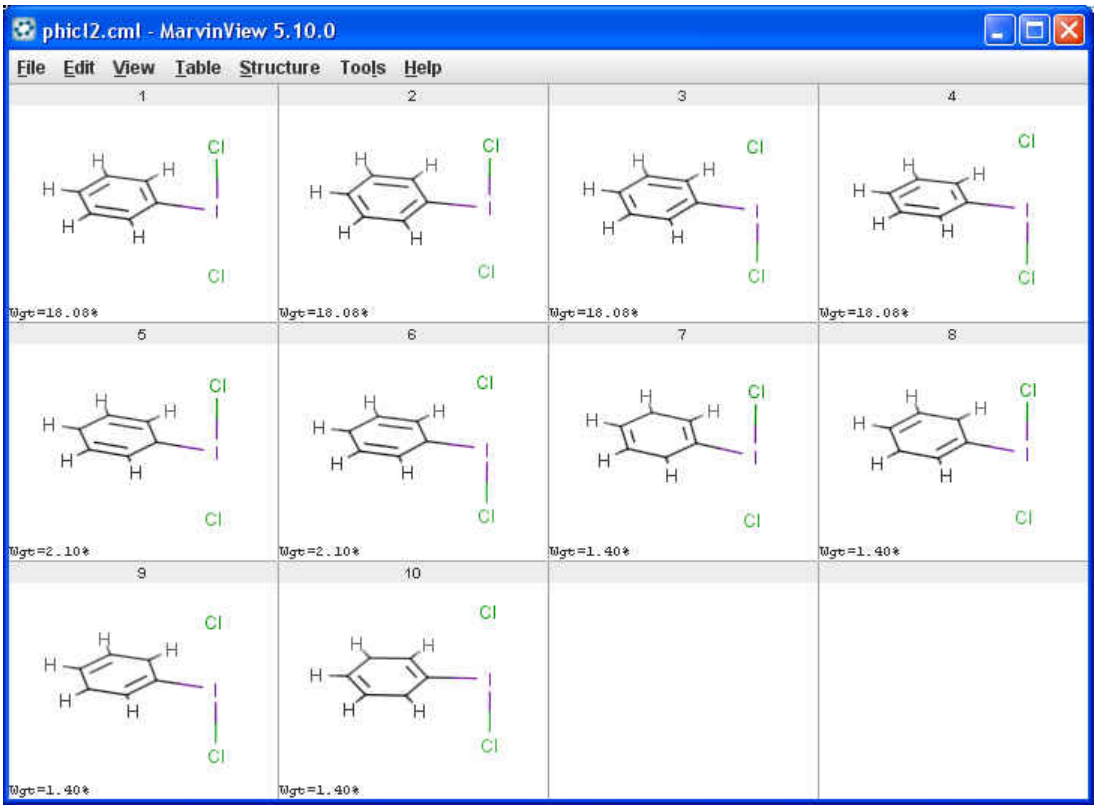
NBOMOL

The NBOMOL keyword produces a valid MDL (Molfile) format file that, like NBOCML, specifies the pattern of bonds and lone pairs of the NBO NLS. The external file, with "-nbo.mol" extension, is written in either V2000 (default) or V3000 format. The latter is requested using NBOMOL=V3000. NBOMOL does not support multi-center bonding.

NRTCML

The NRTCML keyword produces a valid CML format file that report structural and connectivity information for the leading resonance structures of NRT. NRTCML only writes resonance forms having greater than threshold weight (1%, by default) to the CML file. The default threshold can be modified (e.g. NRTCML=5 would write only those resonance structures have weights greater than 5%).

The illustration below shows sample NRTCML/MarvinView output for $C_6H_5ICl_2$:



NRTMOL

The NRTMOL keyword produces one valid MDL format file for each of the resonance structures of NRT analysis. By default, only structures having weights larger than 1% are written to these files. The user can modify the 1% threshold by appending the desired percentage threshold to the NRTMOL keyword. For example, NRTMOL=5 will allow NRT analysis to write only those structures having weight greater than 5%.

NRTMOL can write an MDL file in either V2000 (default) or V3000 format. To request the latter, use NRTMOL=V3000. Either format can be combined with the weight threshold, e.g. NRTMOL=V2000,10 for which structures having weight greater than 10% are written in V2000 format.

XMOL

The XMOL keyword writes a valid XMol XYZ format file that can be used with many programs, such as XMol, RasMol, JMol, and Molden, to display molecular geometry. Atom coordinates are reported in Angstrom units, in the same molecular orientation as provided by the host ESS program.

By default, the XMol file is written to FILE45 (with .45 extension). An alternative file can be specified by appending the logical file number to the XMOL keyword (e.g. XMOL=99 writes the XMol file with the .99 extension).

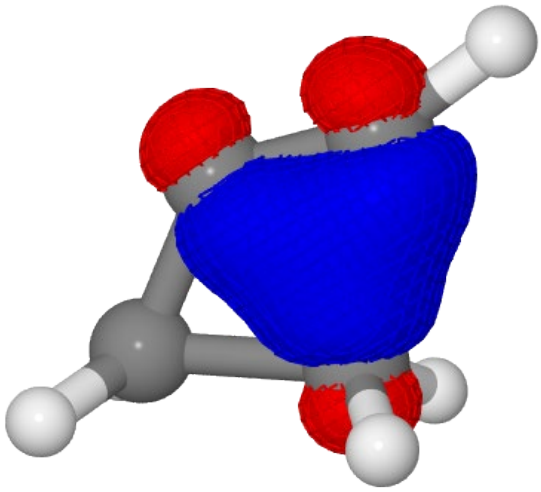
MOLDEN

The MOLDEN keyword writes geometry and orbital specifications to an external file in Molden format (with .molden extension). By default, this keyword writes the NBOs (that is, the AO to NBO transformation) to the external file, but an alternate orbital set can be selected by using the general MOLDEN=*basis* form of the keyword, where *basis* is one of the following orbital basis sets:

PAO, PNAO, NAO, PNHO, NHO, PNBO, NBO, PNLMO, NLMO, MO, NO

The orbitals are listed in the Molden file in the same order that they are reported in the NBO output. No reordering is performed.

The Molden file can be used as input for a number of molecular graphics programs, including Molden and Jmol. The following is a Jmol image of the 3-center 2-electron PNBO of the 1-cyclobutenyl cation, $C_4H_5^+$.



Note to Jmol users: By default, Jmol sorts orbitals by energy. To prevent Jmol from sorting so that the orbitals are numbered in Jmol exactly as they are in the NBO output, load the Molden file with "nosort" filtering using the Jmol script console. For example, the above image (of PNBO 14) was produced by creating a Molden file using MOLDEN=PNBO and then entering the following into the Jmol console.

```
cd /path/to/moldenfile
load c4h5+.molden filter "nosort"
mo 14
mo fill
background white
```

B.23. EFFECTIVELY UNPAIRED ELECTRON DISTRIBUTION

Radical character in molecules is often of interest. For UHF-based methods, the open-shell NBO analysis of Sec B.6.11 is recommended, in which one determines radical character directly by comparing separate analyzes of the α and β electron densities. For methods that are otherwise based on a spin-averaged density matrix, assessing the nature of the unpaired electron distribution is rather problematic. For these methods NBO implements an interesting measure of radical character proposed by Head-Gordon [*Chem. Phys. Lett.*, **372**, 508-511 (2003)] and based on the "distribution of effectively unpaired electrons." This approach, although not unique, is intuitive and useful.

An unpaired electron density matrix **U** is defined as

$$\mathbf{U} = \mathbf{V} f_U(\mathbf{n}) \mathbf{V}^\dagger$$

where the columns of **V** represent the natural orbitals (NOs) of the full density, **n** is the diagonal matrix of NO occupation numbers, and f_U is Head-Gordon's definition of the unpaired electron distribution,

$$f_U(n_i) = 1 - \mathrm{abs}(1 - n_i).$$

NOs that have no occupancy (n_i=0) or are doubly occupied (n_i=2) contribute nothing (f_U=0) to the unpaired electron distribution, whereas NOs that are singly occupied (n_i=1) contribute one electron. For an N-electron molecule, the total unpaired electron density

$$n_U = \mathrm{Tr}(\mathbf{U}) = \Sigma_i f_U(n_i)$$

satisfies the condition $0 \le n_U \le N$.

The user requests an analysis of the effectively unpaired electron distribution by including the RADICAL keyword in the $NBO keylist. The output reports the NAO distribution (the diagonal elements of **U** in the NAO basis), the NBO distribution (the diagonal elements of **U** in the NBO basis), the distribution by atoms (NAO values summed over atoms), and the total unpaired electron density.

As an example of RADICAL analysis, we consider the dissociation of ethane into two methyl radicals calculated at the CAS(2,2)/cc-pVDZ level. The

following is a sample Gaussian input file for ethane with its C-C bond stretched by about 1 Å from equilibrium (R_{CC}=2.5 Å):

```
# cas(2,2)/cc-pVDZ pop=nbo6read

Ethane...stretched C-C bond...cas(2,2)/VDZ

0 1
C
C  1  CC
H  1  CH  2  HCC
H  1  CH  2  HCC  3  120. 0
H  1  CH  2  HCC  3  240. 0
H  2  CH  1  HCC  3   60. 0
H  2  CH  1  HCC  3  180. 0
H  2  CH  1  HCC  3  300. 0

CH     1.0836
HCC  101.9121

CC     2.5

$nbo radical $end
$choose bond s 1 2 s 1 3 s 1 4 s 1 5 s 2 6 s 2 7 s 2 8 end $end
```

At this geometry the C-C distance is sufficiently elongated that the default NBO search favors a "broken bond" description with 1-center orbitals on the separate C centers, rather than the usual $\sigma_{CC}/\sigma_{CC}^*$ bond-antibond pair. We prefer to analyze stretched ethane using the conventional Lewis structure (that is, with the C-C bond) and therefore direct NBO to search for the desired bonding pattern using the $CHOOSE keylist as shown above. (Note that using $CHOOSE to specify an alternate bonding pattern only impacts the NBO summary output shown below; NAO output is unchanged.)

The NPA/NAO output segment is:

```
NATURAL POPULATIONS:  Natural atomic orbital occupancies

  NAO Atom No lang   Type(AO)    Occupancy    Radical
 -----------------------------------------------------
    1    C  1  s      Cor( 1s)     2.00000     0.00000
    2    C  1  s      Val( 2s)     1.21527     0.01420
    3    C  1  s      Ryd( 3s)     0.00067     0.00027
    4    C  1  px     Val( 2p)     1.16310     0.00000
    5    C  1  px     Ryd( 3p)     0.00108     0.00000
    6    C  1  py     Val( 2p)     1.16310     0.00000
    7    C  1  py     Ryd( 3p)     0.00108     0.00000
    8    C  1  pz     Val( 2p)     0.98061     0.22173
    9    C  1  pz     Ryd( 3p)     0.00531     0.00080
   10    C  1  dxy    Ryd( 3d)     0.00125     0.00000
   11    C  1  dxz    Ryd( 3d)     0.00060     0.00000
   12    C  1  dyz    Ryd( 3d)     0.00060     0.00000
   13    C  1  dx2y2  Ryd( 3d)     0.00125     0.00000
```

14	C	1	dz2	Ryd(3d)	0.00085	0.00010
15	C	2	s	Cor(1s)	2.00000	0.00000
16	C	2	s	Val(2s)	1.21527	0.01420
17	C	2	s	Ryd(3s)	0.00067	0.00027
18	C	2	px	Val(2p)	1.16310	0.00000
19	C	2	px	Ryd(3p)	0.00108	0.00000
20	C	2	py	Val(2p)	1.16310	0.00000
21	C	2	py	Ryd(3p)	0.00108	0.00000
22	C	2	pz	Val(2p)	0.98061	0.22173
23	C	2	pz	Ryd(3p)	0.00531	0.00080
24	C	2	dxy	Ryd(3d)	0.00125	0.00000
25	C	2	dxz	Ryd(3d)	0.00060	0.00000
26	C	2	dyz	Ryd(3d)	0.00060	0.00000
27	C	2	dx2y2	Ryd(3d)	0.00125	0.00000
28	C	2	dz2	Ryd(3d)	0.00085	0.00010
29	H	3	s	Val(1s)	0.81900	0.00050
30	H	3	s	Ryd(2s)	0.00059	0.00001
31	H	3	px	Ryd(2p)	0.00194	0.00001
32	H	3	py	Ryd(2p)	0.00003	0.00000
33	H	3	pz	Ryd(2p)	0.00019	0.00003
34	H	4	s	Val(1s)	0.81900	0.00050
35	H	4	s	Ryd(2s)	0.00059	0.00001
36	H	4	px	Ryd(2p)	0.00051	0.00000
37	H	4	py	Ryd(2p)	0.00146	0.00000
38	H	4	pz	Ryd(2p)	0.00019	0.00003
39	H	5	s	Val(1s)	0.81900	0.00050
40	H	5	s	Ryd(2s)	0.00059	0.00001
41	H	5	px	Ryd(2p)	0.00051	0.00000
42	H	5	py	Ryd(2p)	0.00146	0.00000
43	H	5	pz	Ryd(2p)	0.00019	0.00003
44	H	6	s	Val(1s)	0.81900	0.00050
45	H	6	s	Ryd(2s)	0.00059	0.00001
46	H	6	px	Ryd(2p)	0.00051	0.00000
47	H	6	py	Ryd(2p)	0.00146	0.00000
48	H	6	pz	Ryd(2p)	0.00019	0.00003
49	H	7	s	Val(1s)	0.81900	0.00050
50	H	7	s	Ryd(2s)	0.00059	0.00001
51	H	7	px	Ryd(2p)	0.00194	0.00001
52	H	7	py	Ryd(2p)	0.00003	0.00000
53	H	7	pz	Ryd(2p)	0.00019	0.00003
54	H	8	s	Val(1s)	0.81900	0.00050
55	H	8	s	Ryd(2s)	0.00059	0.00001
56	H	8	px	Ryd(2p)	0.00051	0.00000
57	H	8	py	Ryd(2p)	0.00146	0.00000
58	H	8	pz	Ryd(2p)	0.00019	0.00003

Summary of Natural Population Analysis:

Atom	No	Natural Charge	Natural Population				
			Core	Valence	Rydberg	Total	Radical
C	1	-0.53476	2.00000	4.52207	0.01270	6.53476	0.23711
C	2	-0.53476	2.00000	4.52207	0.01270	6.53476	0.23711
H	3	0.17825	0.00000	0.81900	0.00275	0.82175	0.00054
H	4	0.17825	0.00000	0.81900	0.00275	0.82175	0.00054
H	5	0.17825	0.00000	0.81900	0.00275	0.82175	0.00054
H	6	0.17825	0.00000	0.81900	0.00275	0.82175	0.00054
H	7	0.17825	0.00000	0.81900	0.00275	0.82175	0.00054
H	8	0.17825	0.00000	0.81900	0.00275	0.82175	0.00054
* Total *		0.00000	3.99999	13.95811	0.04189	18.00000	0.47747

Analysis reveals significant radical character (0.23712*e*) at the two C centers and negligible character at the H centers, consistent with the breaking of the C-C bond. The radical character is principally localized in the C $2p_z$ NAOs (aligned with the C-C line of centers), with small contributions from the 2*s* NAOs.

The total number of unpaired electrons is 0.47747. Because the overall spin symmetry is singlet, half of the unpaired electron density must have α spin, the other half β spin. Note, however, that RADICAL analysis provides no spin information (e.g. that the unpaired electrons at C1 are of α spin, and those at C2 of β spin, or vice versa). Such information requires analysis of the spin density, which is often unavailable.

Radical character of the NBOs appears in the NBO summary:

```
NATURAL BOND ORBITALS (Summary):

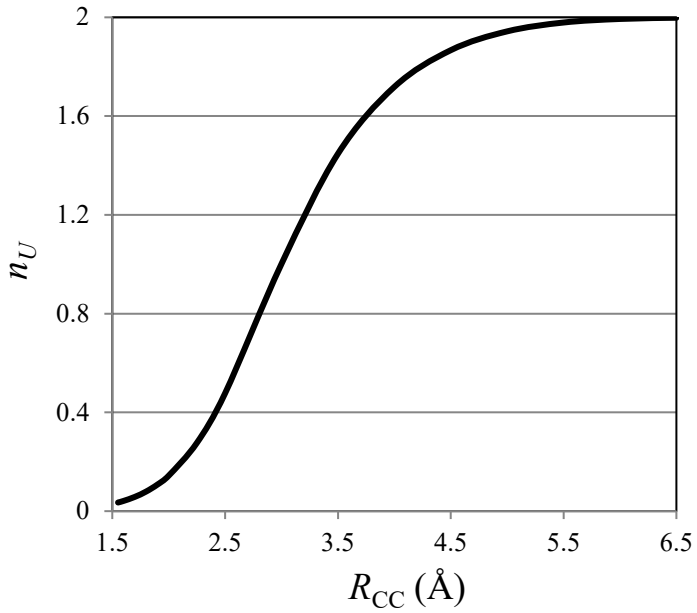
           NBO                 Occupancy    Radical
 ========================================================
 Molecular unit  1  (C2H6)
 ------ Lewis -----------------------------------------
    1. CR ( 1) C  1             2.00000     0.00000
    2. CR ( 1) C  2             2.00000     0.00000
    3. BD ( 1) C  1- C  2       1.76227     0.23536
    4. BD ( 1) C  1- H  3       1.99771     0.00061
    5. BD ( 1) C  1- H  4       1.99771     0.00061
    6. BD ( 1) C  1- H  5       1.99771     0.00061
    7. BD ( 1) C  2- H  6       1.99771     0.00061
    8. BD ( 1) C  2- H  7       1.99771     0.00061
    9. BD ( 1) C  2- H  8       1.99771     0.00061
 ------ non-Lewis -------------------------------------
   10. BD*( 1) C  1- C  2       0.24148     0.23712
   11. BD*( 1) C  1- H  3       0.00047     0.00010
   12. BD*( 1) C  1- H  4       0.00047     0.00010
   13. BD*( 1) C  1- H  5       0.00047     0.00010
   14. BD*( 1) C  2- H  6       0.00047     0.00010
   15. BD*( 1) C  2- H  7       0.00047     0.00010
   16. BD*( 1) C  2- H  8       0.00047     0.00010
   17. RY ( 1) C  1             0.00052     0.00003
   18. RY ( 2) C  1             0.00026     0.00000
   19. RY ( 3) C  1             0.00026     0.00000
   20. RY ( 4) C  1             0.00023     0.00021
   21. RY ( 5) C  1             0.00000     0.00000
   22. RY ( 6) C  1             0.00000     0.00000
   23. RY ( 7) C  1             0.00000     0.00000
   24. RY ( 8) C  1             0.00000     0.00000
   25. RY ( 9) C  1             0.00000     0.00000
   26. RY ( 1) C  2             0.00052     0.00003
   27. RY ( 2) C  2             0.00026     0.00000
   28. RY ( 3) C  2             0.00026     0.00000
   29. RY ( 4) C  2             0.00023     0.00021
   30. RY ( 5) C  2             0.00000     0.00000
   31. RY ( 6) C  2             0.00000     0.00000
   32. RY ( 7) C  2             0.00000     0.00000
```

```
 33. RY ( 8) C  2             0.00000     0.00000
 34. RY ( 9) C  2             0.00000     0.00000
 35. RY ( 1) H  3             0.00060     0.00001
 36. RY ( 2) H  3             0.00015     0.00003
 37. RY ( 3) H  3             0.00003     0.00000
 38. RY ( 4) H  3             0.00000     0.00000
 39. RY ( 1) H  4             0.00060     0.00001
 40. RY ( 2) H  4             0.00015     0.00003
 41. RY ( 3) H  4             0.00003     0.00000
 42. RY ( 4) H  4             0.00000     0.00000
 43. RY ( 1) H  5             0.00060     0.00001
 44. RY ( 2) H  5             0.00015     0.00003
 45. RY ( 3) H  5             0.00003     0.00000
 46. RY ( 4) H  5             0.00000     0.00000
 47. RY ( 1) H  6             0.00060     0.00001
 48. RY ( 2) H  6             0.00015     0.00003
 49. RY ( 3) H  6             0.00003     0.00000
 50. RY ( 4) H  6             0.00000     0.00000
 51. RY ( 1) H  7             0.00060     0.00001
 52. RY ( 2) H  7             0.00015     0.00003
 53. RY ( 3) H  7             0.00003     0.00000
 54. RY ( 4) H  7             0.00000     0.00000
 55. RY ( 1) H  8             0.00060     0.00001
 56. RY ( 2) H  8             0.00015     0.00003
 57. RY ( 3) H  8             0.00003     0.00000
 58. RY ( 4) H  8             0.00000     0.00000
       -------------------------------
              Total Lewis   17.74852  ( 98.6029%)
        Valence non-Lewis    0.24428  (  1.3571%)
        Rydberg non-Lewis    0.00721  (  0.0400%)
       -------------------------------
            Total unit  1   18.00000  (100.0000%)
           Charge unit  1    0.00000
```

The output reveals transfer of electron density from the C-C bond into its own antibond, as would be expected for bond dissociation. At this elongated geometry, nearly a quarter of an electron (0.24148*e*) has transferred into the σ_{CC}* antibond, principally from the σ_{CC} bond. The antibond density is essentially entirely unpaired [$n_U(\sigma_{CC}^*) = 0.23712$] with the corresponding unpaired density (nominally of opposite spin) predominantly residing in the bond [$n_U(\sigma_{CC}) = 0.23536$].

The following plot shows how the total unpaired electron density (n_U) varies as ethane undergoes C-C bond dissociation, from its equilibrium geometry to separated methyl radical monomers. As expected, the unpaired density is negligible at the equilibrium geometry and rises to a value of 2 as the C-C bond cleaves.

B.23. EFFECTIVELY UNPAIRED ELECTRON DISTRIBUTION



B.24. NATURAL POLY-ELECTRON POPULATION ANALYSIS (NPEPA)

References: P. Karafiloglou and G. Ohanessian, *J. Chem. Educ.* **68**, 583-586 (1991); R. M. Parrondo, P. Karafiloglou, and E. Sanchez Marcos, *Int. J. Quantum Chem.* **52**, 1127-1144 (1994); P. Karafiloglou, *J. Comp. Chem.* **22**, 306-315 (2001); P. Karafiloglou, *Chem. Educ. Res. Pract.* **3**, 119-127 (2002); E. D. Glendening and F. Weinhold, *Chem. Phys.Lett.* **711**, 23-26 (2018); K. Kyriakidou, P. Karafiloglou, E. D. Glendening, and F. Weinhold, *J. Comput. Chem.* **40**, 1509-1520 (2019).

B.24.1 Introduction to NPEPA

The concept of l-electron "orbital population," as evaluated by Natural Population Analysis (NPA), can be generalized to the populations (occupation probabilities) of more complex poly-electron patterns. The *Natural Poly-Electron Population Analysis* (NPEPA) module allows the probabilities of quite general "hole/electron" patterns of vacant/occupied NBOs or other localized orbitals to be rigorously evaluated in a manner that parallels (but generalizes) the simple l-e NPA concept.

Let the N-electron wavefunction Ψ be expressed in configuration interaction (CI) form as a linear combination of normalized Slater determinants $D_I^{(MO)}$

$$(1)\quad \Psi(1,2,...,N) = \sum_I c_I D_I^{(MO)}(1,2,...,N)$$

with coefficients (probability amplitudes) c_I. Index I represents a unique set of N occupied molecular spin-orbitals $\{\psi_i\}$ from which the determinant is constructed. Each Slater determinant can, in turn, be expressed as a linear combination of "localized orbital determinants" $D_K^{(LO)}$

$$(2)\quad D_I^{(MO)} = \sum_K d_K^{(I)} D_K^{(LO)}$$

constructed from a complete, orthonormal basis of localized spin-orbitals $\{\varphi_k\}$, such as the NAOs, NHOs, or NBOs. The total probability $P(k)$ that l-e spin-orbital φ_k is occupied in Ψ (the "electron occupancy" of φ_k) is evaluated as the summed probability of determinants D_K that contain φ_k (denoted $k\in K$), viz.,

$$(3a)\quad P(k) = \sum_I |c_I|^2 \sum_{k\in K} |d_K^{(I)}|^2$$

The corresponding "hole occupancy" *P(~k)* (i.e., the probability that φ_k is *not* occupied; $k \notin K$*)* is similarly evaluated as

(3b) $P(\sim k) = \sum_I |c_I|^2 \sum_{k \notin K} |d_K^{(I)}|^2 = 1 - P(k)$

For a general poly-electron pattern of occupied ("electron" *e*) $\{\varphi_i , \varphi_j , \ldots \varphi_e\}$ and vacant ("hole" *h*) orbitals $\{\varphi_k , \varphi_l , \ldots \varphi_h\}$,

(4a) $\underline{\mathbf{e}} = \{\varphi_i , \varphi_j , \ldots \varphi_e\}$
(4b) $\underline{\mathbf{h}} = \{\varphi_k , \varphi_l , \ldots \varphi_h\}$

we can similarly define the *poly*-electron probability $P(\underline{\mathbf{h}}/\underline{\mathbf{e}})$ as

(5) $P(\underline{\mathbf{h}}/\underline{\mathbf{e}}) = \sum_I |c_I|^2 \sum_{\underline{\mathbf{h}} \notin K; \underline{\mathbf{e}} \in K} |d_K^{(I)}|^2$

In the case that $\underline{\mathbf{e}}$-list contains a *complete* configurational specification of *N* orbitals (denoted $\underline{\mathbf{e}}_K$), corresponding to *particular* determinant $D_K^{(I)}$, we can similarly define the *N*-electron "configuration population" $P(\underline{\mathbf{e}}_K)$ as

(6) $P(\underline{\mathbf{e}}_K) = \sum_I |c_I|^2 |d_K^{(I)}|^2$

The NPEPA module allows evaluation of few-electron $P(\underline{\mathbf{h}}/\underline{\mathbf{e}})$ or *N*-electron ("resonance structure") $P(\underline{\mathbf{e}}_K)$ populations for quite general choices of localized or delocalized basis orbitals.

B.24.2 NPEPA Keywords and the $NPEPA Keylist

NPEPA is requested by the user through a keyword of the form "NPEPA=*basis,threshold*" in the $NBO keylist, where *basis* and *threshold* are optional. Allowed basis set choices are the orthogonal NAO, NHO, NBO, NLMO, NO, or MO sets, and the desired level of print detail is set by *threshold*. By default, NPEPA is performed in the NBO basis with a print threshold of 0.001 (determinants of probability exceeding 0.1% are reported).

In addition, the user can provide a $NPEPA keylist specifying a succession of desired poly-electron occupation patterns (in bracket-list format) whose "populations" (occupation probabilities) are to be evaluated. The program automatically analyzes 1e-excitation probabilities for the leading donor-acceptor delocalizations in the NBO basis and reports these in a form similar to the 2nd-order perturbation theory (E2PERT) table.

Each bracket-list entry of the $NPEPA keylist describes a specific "hole/electron" pattern of interest, i.e., a listing of unoccupied ("hole") and occupied ("electron") spin-orbitals whose occurrence in the wavefunction (Born probability = sum of squared coefficients for determinantal contributions with the specified pattern) is to be quantified. Spin-orbitals of each hole/electron list are identified by their integer order in the chosen basis set, with affixed "a" for alpha spin and "b" for beta spin. If NBOs are the chosen basis, for example, "17a" and "34b" would specify alpha NBO 17 and beta NBO 34, respectively, in the standard NBO numbering. Integer values without a spin label, such as "17", refer to the pair of spin-orbitals, 17a and 17b in this case. All input in the $NPEPA keylist is case-insensitive and free-format.

For partial hole/electron patterns (i.e., those leaving many details of the *N*-electron determinant to be "averaged over" in the probability summation), a simple bracket-list of the form

```
<h1 h2 … hn/e1 e2 … em>
```

is convenient to specify the *n* holes and *m* electrons of the target **h**/**e** pattern. For example, the bracket-list `<3a 3b/11a 11b>` (or `<3/11>`) could be used to specify the manifold of determinants in which NBOs 3a and 3b are vacant (having served as electronic "donors" from a starting reference configuration) and NBOs 11a, 11b are occupied ("acceptor" orbitals that were formerly vacant in the reference configuration), corresponding to doubly-excited (NBO 3)^2 $\rightarrow$ (NBO 11)^2 contributions to the wavefunction [e.g., $(n_N)^2$

$\rightarrow (\sigma^*_{CH})^2$ delocalizations in CH_3NH_2]. Similarly, the bracket-list `</11a 11b>` requests the probability that NBO 11 is doubly occupied, regardless of which other spin-orbitals are occupied or vacant, and `<3a 3b/>` requests the probability that NBOs 3a and 3b are both vacant.

Alternatively, for resonance-type applications in which it is desirable to specify the *full N*-electron pattern (full "resonance structure"), one can employ *labeled* bracket lists of the form

```
<L o1 o2 … >
```

where "L" is a label ("R", "C", "I", "B", "S", "X1", "X2", etc.) and "o1", "o2",… are spin-orbital identifiers as above.

"R" and "X*k*" labeled listings must begin with a reference ("R") listing of *all* occupied spin-orbitals in a starting "reference" determinant,

```
<R o1 o2 … oN>
```

Excitations ("X") of chosen order *k* ("X*k*", *k* = 1, 2, …) can then be specified by the **h**/**e** entries in a bracket-list of the form

```
<Xk h1 h2 … hk/e1 e2 … ek>
```

Generic forms of sequential labeled bracket-lists are illustrated below:

`<R 1a 1b 2a 2b …>`	("reference" configuration)
`<X1 h1/e1>`	(single excitation)
`<X2 h1 h2/e1 e2>`	(double excitation)
`<X3 h1 h2 h3/e1 e2 e3>`	(triple excitation)

and so forth. In the reference "R" configuration listing, spin-orbitals may be specified in any desired order and continued on as many lines as needed. Dashes can be used to specify ranges of spin-orbitals, so that

```
<R 1a 2a 3a 1b 2b 3b>
```

is more compactly expressed by

```
<R 1a-3a 1b-3b>
```
or
```
<R 1-3>
```

Each excitation type "X*k*" must contain the same number (*k*) of occupied (`ei`) and vacant (`hi`) spin-orbitals (to preserve overall order of the *N*-electron determinant) but the order of spin-orbital entries within each **h** or **e** listing is immaterial. Specifying the excitation level "*k*" is optional, so that "`<X1 h1/e1>`" and "`<X h1/e1>`" are equivalent single excitation bracket-lists. Each new "`<R o1 o2 … >`" bracket-list resets the reference configuration to which subsequent "`<X`*k* `h1 h2 … h`*k*`/e1 e2 … e`*k*`>`" bracket-lists refer.

For example, the ground ("Lewis") NBO configuration of CH_3NH_2 (18-e) can be explicitly specified as

```
<R la lb 2a 2b 3a 3b 4a 4b 5a 5b 6a 6b 7a 7b 8a 8b 9a 9b>
```

The 1-e excitation from lone pair NBO 3 to antibonding NBO 11 could then be specified as the single excitation

```
<X1 3a/11a>
```

Other entries of the 2nd-order interaction energy (E2PERT) table or the associated NRT resonance weightings could be rigorously evaluated at the Born-probabilistic NPEPA level.

For the cases NPEPA=NAO or NPEPA=NHO, three special labeled bracket-lists are recognized for covalent ("C"), ionic ("I"), and bond order ("B") 2-e patterns, namely,

```
<C ol o2>
<I o1/o2>
<B ol o2>
```

where the orbital numbers are given *without* subsidiary "a" or "b" spin labels. The first is equivalent to the sum of the two unlabeled contributions

```
<o1b o2a/o1a o2b> + <o1a o2b/o1b o2a>
```

for the idealized "covalent" Heitler-London function formed from `o1`, `o2`, whereas the second is equivalent to the unlabeled contribution

```
<o1a o1b/o2a o2b>
```

of the "ionic" Heitler-London form, with `o2` completely occupied and `o1` completely vacant. The third is equivalent to the sum of the covalent and ionic patterns, i.e.,

```
<B o1 o2> = <C o1 o2> + <I o1/o2> + <I o2/o1>
```

and can be considered a measure of the total bond order arising from coupling of orbitals `o1` and `o2`. These special forms are convenient for isolating the probabilities of Heitler-London-type valence bond (VB) components.

Finally, the "S" labeled bracket-list requests the calculation of Born probabilities for all occupation patterns (of holes and electrons) for a set of spin-orbitals, and the evaluation of their sum, which must equal one for a normalized wavefunction. For example, for a single spin-orbital such as `3a`, the "S" bracket-list

```
<S 3a> = </3a> + <3a/>
```

is the sum of probabilities for an electron occupying the spin orbital (`</3a>`) and the spin-orbital being empty (`<3a/>`). The total probability that an electron occupies the spin-orbital or not is clearly equal to one.

B.24.3 Sample Input and Output

A simple example of NPEPA=NBO input for RHF/3-21G CH_3NH_2 is shown below:

```
$NBO NPEPA=NBO $END
$NPEPA
  <R 1a 2a 3a 4a 5a 6a 7a 8a 9a
     1b 2b 3b 4b 5b 6b 7b 8b 9b>  !reference psi(L)
  <X1 3a/11a>                     !1e: 3a→11a
  <X1 3a/12a>                     !1e: 3a→12a
  <X1 3a/13a>                     !1e: 3a→13a
  <X2 3a 3b/11a 11b>              !2e: (3)²→(11)²
$END
```

The resulting output is:

```
NATURAL POLY-ELECTRON POPULATION ANALYSIS

     Born
 Probability   Determinant(s)                    Donor(h)        Acceptor(e)
================================================================================
   0.953020    <R 1a-9a 1b-9b>
   0.014224    <X1 3a/11a> + <X1 3b/11b>        3.  N 2(lp)     11.  C 1- H 3*
   0.003918    <X1 9a/13a> + <X1 9b/13b>        9.  N 2- H 7    13.  C 1- H 5*
   0.003918    <X1 8a/12a> + <X1 8b/12b>        8.  N 2- H 6    12.  C 1- H 4*
   0.003902    <X1 6a/14a> + <X1 6b/14b>        6.  C 1- H 4    14.  N 2- H 6*
   0.003902    <X1 7a/15a> + <X1 7b/15b>        7.  C 1- H 5    15.  N 2- H 7*
   0.002563    <X1 3a/13a> + <X1 3b/13b>        3.  N 2(lp)     13.  C 1- H 5*
   0.002563    <X1 3a/12a> + <X1 3b/12b>        3.  N 2(lp)     12.  C 1- H 4*
--------------------------------------------------------------------------------

     Born
 Probability   User-selected Configuration(s) (NBO basis functions)
================================================================================
   0.953020    <R 1a-9a 1b-9b>
   0.007112    <X1 3a/11a>
   0.001282    <X1 3a/12a>
   0.001282    <X1 3a/13a>
   0.000053    <X2 3a 3b/11a 11b>
```

The output includes two tables. The first of these tables is printed by default. It lists the Born probabilities of the reference determinant (the determinant of Lewis NBOs) and of the principal 1e-excitations into the non-Lewis NBOs (analogous to the donor-acceptor delocalizations of the 2nd-order perturbation theory table of default NBO output). The reference determinant (probability=0.953020) clearly dominates the description of the B3LYP density, and the leading corrections are the 1e-excitations of the alpha and beta electrons from NBO 3 (the lone pair of N2) into NBO 11 (the antiperiplanar

C1-H3 antibond). These two excitations (probability sum=0.014224) account for the largest fraction of the NBO 11 occupancy (0.01531, reported elsewhere in NBO output).

The second table reports the reference determinant and individual excitations requested by the user, which in this case largely reproduces information already reported in the first (default) table. The only new information in the second table is that the 2e-excitation from NBOs 3 to 11 has a probability that is about two orders of magnitude smaller than the corresponding 1e-excitations. In other words, the small, but significant, occupancy of NBO 11 arises principally from single excitations, not double.

As a second example, the following NPEPA=NAO input could be used to probe NAO **h**/**e**-patterns in LiH (B3LYP/6-311++G**). In this analysis, NAO 2 is the valence Li 2s and NAO 23 is the valence H 1s:

```
$NBO  NPEPA=NAO  $END
$NPEPA
 </23a>                        ! 1e occupancy of H 1s
 <23a/>                        ! 1h occupancy of H 1s
 </23a 23b>                    ! 2e occupancy of H 1s
 </2a 23a>                     ! 2c/2e Fermi probability
 <C 2 23>                      ! H-L covalent probability
 <2a 23b/2b 23a>               ! 1st component of <c 2 23>
 <2b 23a/2a 23b>               ! 2nd component of <c 2 23>
 <I 2/23>                      ! ionic Li+H- probability
 <2a 2b/23a 23b>               ! same as <I 2/23>
 <I 23/2>                      ! ionic Li-H+ probability
 <23a 23b/2a 2b>               ! same as <I 23/2>
 <B 2 23>                      ! sum of <C> and <I>
$END
```

NPEPA yields the following output:

```
NATURAL POLY-ELECTRON POPULATION ANALYSIS

      Born
  Probability   Determinant(s)                    Donor(h)        Acceptor(e)
================================================================================
    0.999886    <R 1a 2a 1b 2b>
--------------------------------------------------------------------------------

      Born
  Probability   User-selected Configurations (NAO basis functions)
================================================================================
    0.899870    </23a>
    0.100130    <23a/>
    0.809766    </23a 23b>
    0.000000    </2a 23a>
    0.150206    <C 2 23>
    0.075103    <2a 23b/23a 2b>
    0.075103    <23a 2b/2a 23b>
    0.809765    <I 2/23>
    0.809765    <2a 2b/23a 23b>
    0.006966    <I 23/2>
    0.006966    <23a 23b/2a 2b>
    0.150206    <C 2 23>
    0.006966    <I 23/2>
    0.809765    <I 2/23>
    0.966937    <B 2 23>
```

NPEPA produces two tables. The first is the default analysis in the NBO basis, and the second is the analysis in the NAO basis requested by the user via $NPEPA input. The default analysis shows that the LiH reference description dominates the B3LYP density—there are no significant 1e-excitations (delocalizations) to report.

The first four entries of the second table describe electron and hole occupancies of the NAOs. The first two of these are the 1e-occupancy (0.899870) and 1h-occupancy (0.100130) of the H 1s NAO. These occupancies sum to unity, as required by Eq. (2b). Note also that the 1e-occupancy is equivalent to half of the NAO 23 occupancy (1.79974) reported in the natural population analysis (elsewhere in NBO output). The third table entry reports the probability (0.809766) that the H 1s is simultaneously occupied by alpha and beta electrons. The fourth entry shows that it is unlikely to find alpha electrons simultaneously in the Li 2s (NAO 2) and H 1s (NAO 23).

The last eleven table entries explore the Heitler-London covalent and ionic character of the LiH bond formed from the Li 2s and H 1s NAOs. The bond is principally of $Li^{+}H^{-}$ ionic character (~81%) but does reveal some covalency (~15%). Note that the “B” bracket-list entry results in four probabilities being reported, including the covalent probability, the two ionic probabilities, and their sum. The coupling of the Li 2s and H 1s NAOs yields the “NPEPA bond order” of 0.967.

As a final example, we use NPEPA=NHO to examine the nature of a carbonyl pi bond in NiCO by evaluating the Born probabilities for all electron/hole patterns involving a pair of 2p hybrids. The calculation was performed at the B3LYP/6-311++G** level with $NBO and $NPEPA input

```
$NBO  NPEPA=NHO  $END
$NPEPA  <S 20 21>  $END
```

where NHOs 20 and 21 are respectively the C 2p and O 2p hybrids of one of the CO pi bonds. In this case, NPEPA calculates all possible configurations generated from the four spin-orbitals 20a, 20b, 21a, and 21b, producing the following output:

```
      Born
  Probability   User-selected Configuration(s) (NHO basis functions)
================================================================================
    0.009105    </20a 21a 20b 21b>
    0.065297    <20a/21a 20b 21b>
    0.021010    <21a/20a 20b 21b>
    0.000009    <20a 21a/20b 21b>
    0.065297    <20b/20a 21a 21b>
    0.468271    <20a 20b/21a 21b>
    0.150669    <21a 20b/20a 21b>
    0.000066    <20a 21a 20b/21b>
    0.021010    <21b/20a 21a 20b>
    0.150669    <20a 21b/21a 20b>
    0.048479    <21a 21b/20a 20b>
    0.000021    <20a 21a 21b/20b>
    0.000009    <20b 21b/20a 21a>
    0.000066    <20a 20b 21b/21a>
    0.000021    <21a 20b 21b/20a>
    0.000000    <20a 21a 20b 21b/>
    1.000000    <S 20a 21a 20b 21b>
```

Sixteen configurations arise from all possible arrangements of electrons and holes in four spin-orbitals. NPEPA reports the probabilities for each (the first sixteen entries in the table) and then the sum of the probabilities (which must equal one). The first configuration listed corresponds to four electrons in four spin-orbitals, and the last (16^{th}) configuration corresponds to four holes.

The leading configurations are the 2e ionic C^+O^- form (probability=0.468) and covalent forms (0.301 = 2×0.151). The ionic C^-O^+ form has considerably lower probability (0.048). Apparent 1e donation from Ni ($3d\rightarrow\pi^*$) is responsible for the 3e forms CO^- (0.131 = 2×0.065) and C^-O (0.042 = 2×0.021). These eight configurations (of the 16 total) account for 99% of the CO pi bonding character of NiCO.

B.25. 2nd-ORDER REDUCED DENSITY MATRIX ELEMENTS (RDM2)

References:
[1] F. Weinhold and E. B. Wilson, Jr., *J. Chem. Phys.* **46**, 2752-2758 (1967).
[2] E. D. Glendening and F. Weinhold, "Density matrix representability criteria..."

Coming soon…

B.25.1 Introduction to 2nd-order reduced density matrix description of electron correlation effects in Ψ

Let the N-electron wavefunction Ψ be expressed in configuration interaction (CI) form as a linear combination of the complete set of Slater determinants D_K built from a chosen complete orthonormal set of spin-orbitals $\{\varphi_i\}$

$$(1)\quad \Psi(1,2,...,N) = \sum_K c_K D_K(1,2,...,N)$$

with coefficients (probability amplitudes) c_K. It can be shown that *all possible* 1- or 2-electron properties of the N-electron total system can be evaluated from the information contained in the 2nd-order reduced density operator $\boldsymbol{\Gamma}^{(2)}(1,2|1',2')$, whose kernel is defined as

$$(2)\quad \boldsymbol{\Gamma}^{(2)}(1,2|1',2') = \tfrac{1}{2}N(N-1)\int \Psi(1,2,3,...,N)\,\Psi^*(1',2',3,...,N)\,d\tau_3...d\tau_N$$

The $d\tau_3...d\tau_N$ integrations are taken over the complete space-spin variables of the $N-2$ "averaged-out" electrons 3,...,N.

Matrix elements $\boldsymbol{\Gamma}^{(2)}_{ij;kl}$ of the 2-electron integral operator (2) can be evaluated in a basis of 2-electron Slater determinants D_{ij}, D_{kl}

$$(3)\quad \boldsymbol{\Gamma}^{(2)}_{ij;kl} = \int D_{ij(}{}^{*}(1,2)\boldsymbol{\Gamma}^{(2)}(1,2|1',2')\,D_{kl}(1',2')\,d\tau_1 d\tau_2 d\tau_{1'} d\tau_{2'}$$

where, e.g.,

$$(4)\quad D_{ij(}(1,2) = 2^{-1/2}[\varphi_i^{\uparrow}(1)\varphi_j^{\downarrow}(2) - \varphi_j^{\uparrow}(1)\varphi_i^{\downarrow}(2)]$$

in a chosen set of basis orbitals φ_i, φ_j, φ_k, φ_l. Just as the orthonormal NBOs (or other available orbital sets) $\{\varphi_i\}$ span the 1-electron basis space to provide matrix representations of any 1-electron operator (such as kinetic energy, nuclear-electron potential energy, dipole moment, electron density, etc.), so do

the 2-electron $\{D_{ij}\}$ Slater determinants provide the corresponding "geminal" basis set for matrix representations of $\boldsymbol{\mathcal{H}}$ or other 2-electron properties.

In particular, for the non-relativistic Hamiltonian $\boldsymbol{\mathcal{H}}$ or other 2-electron operator $\boldsymbol{\mathcal{F}}^{(2e)} = \sum_{i\le j} \boldsymbol{f}^{(2e)}(i,j)$, the exact N-electron expectation value $\langle\Psi|\boldsymbol{\mathcal{F}}|\Psi\rangle$ can be evaluated as the 2-electron integral

(5a) $$\langle\Psi|\boldsymbol{\mathcal{F}}^{(2e)}|\Psi\rangle = \int[\boldsymbol{f}^{(2e)}(1,2)\boldsymbol{\Gamma}^{(2)}(1,2|1',2')]_{1'\to1,2'\to2}\, d\tau_1 d\tau_2$$

or more compactly, in matrix trace notation, as

(5b) $$\langle\Psi|\boldsymbol{\mathcal{F}}^{(2e)}|\Psi\rangle = \mathrm{Tr}\{\boldsymbol{f}^{(2e)}\,\boldsymbol{\Gamma}^{(2)}\}$$

In single-determinant Hartree-Fock (HF) or density functional description, where electron correlation effects are absent, all electronic properties can be described by the still simpler *first*-order reduced density operator $\boldsymbol{\Gamma}^{(1)}(1|1')$ that results from further reduction of $\boldsymbol{\Gamma}^{(2)}(1,2|1',2')$, viz.,

(6) $$\boldsymbol{\Gamma}^{(1)}(1|1') = 2/(N-1)\int \boldsymbol{\Gamma}^{(2)}(1,2|1',2)\, d\tau_2$$

At HF level, $\boldsymbol{\Gamma}^{(2)}$ contains no new information beyond that in $\boldsymbol{\Gamma}^{(1)}$, because the former can be expressed in terms of the latter by the relationship,

(8) $$\boldsymbol{\Gamma}^{(2)}(1,2|1',2') = \tfrac{1}{2}[\boldsymbol{\Gamma}^{(1)}(1|1')\,\boldsymbol{\Gamma}^{(1)}(2|2') - \boldsymbol{\Gamma}^{(1)}(1|2')\,\boldsymbol{\Gamma}^{(1)}(2|1')] \quad \text{(HF level)}$$

At post-HF (multi-configuration) levels, however, non-zero *differences* between the terms on each side of Eq. (8) lead to a non-vanishing "cumulant" ($\boldsymbol{\Xi}$) operator

(9) $$\boldsymbol{\Xi}^{(2)}(1,2|1',2') \equiv \boldsymbol{\Gamma}^{(2)}(1,2|1',2') - \tfrac{1}{2}[\boldsymbol{\Gamma}^{(1)}(1|1')\boldsymbol{\Gamma}^{(1)}(2|2') - \boldsymbol{\Gamma}^{(1)}(1|2')\boldsymbol{\Gamma}^{(1)}(2|1')] \quad \text{(post-HF)}$$

Matrix elements of the cumulant $\boldsymbol{\Xi}^{(2)}(1,2|1',2')$ therefore provide useful quantitative descriptors of electron correlation effects that are beyond description by $\boldsymbol{\Gamma}^{(1)}$-based analysis methods.

To express Eq. (9) in more familiar terms, we can obtain matrix representations of the operators in the basis of NBOs φ_i, φ_j (for $\boldsymbol{\Gamma}^{(1)}$) or the associated geminals D_{ij} (for $\boldsymbol{\Gamma}^{(2)}$ and $\boldsymbol{\Xi}^{(2)}$). Key matrix elements of these operators can then be written in simplified Dirac notation as

(10a) $\lambda_i = \langle\varphi_i|\boldsymbol{\Gamma}^{(1)}|\varphi_i\rangle$

(10b) $\lambda_{ij} = \langle\varphi_i|\boldsymbol{\Gamma}^{(1)}|\varphi_j\rangle$

(10c) $\Lambda_{ij} = \langle D_{ij}\,|\boldsymbol{\Gamma}^{(2)}|D_{ij}\rangle$

(10d) $\xi_{ij} = \langle D_{ij}|\boldsymbol{\Xi}^{(2)}|D_{ij}\rangle$

In this notation [1], λ_i and λ_{ij} refer respectively to diagonal (NBO population) and off-diagonal (NBO coupling) elements of $\boldsymbol{\Gamma}^{(1)}$, whereas (10c,d) provide unique information pertaining to correlated aspects of the multi-configuration Ψ. Note also that RDM2 usage is intrinsically tied to multi-configuration $WF keylist input (Sec. B.7.7) which describes such electron correlation effects.

In the notation of Eqs. (10c,d), Eq. (9) requires that the cumulant matrix elements ξ_{ij} satisfy

(11) $\xi_{ij} = \Lambda_{ij} - (\lambda_i\,\lambda_j - \lambda_{ij}^2)$

It can also be shown [2] that the Pauli exclusion principle imposes a variety of upper and lower bounds on the possible ξ_{ij} values. Two simple examples are shown as the inequalities of (12a,b):

(12a) $\lambda_{ij}^2 + \lambda_i\,(1-\lambda_j) \geq \xi_{ij} \geq \lambda_{ij}^2 - (1-\lambda_i)(1-\lambda_j)$

(12b) $\lambda_{ij}^2 + (\lambda_i\,\lambda_j)^{1/2}[1-(\lambda_i\,\lambda_j)^{1/2}] \geq \xi_{ij} \geq \lambda_{ij}^2 - \lambda_i\,\lambda_j$

Each upper and lower bound in (12a,b) involves only the (λ_i, λ_j, λ_{ij}) quantities obtainable from $\boldsymbol{\Gamma}^{(1)}$.

In summary, the `RMD2` keyword provides a variety of raw $\boldsymbol{\Gamma}^{(2)}{}_{ij;kl}$ and cumulant ξ_{ij} matrix elements [as well as associated Pauli-type upper and lower bounds (12a,b)] for NBOs or other basis choices, allowing detailed quantification of electron correlation effects in multi-configuration wavefunctions. For single-configuration Hartree-Fock or density functional calculations, the `RDM2` keyword provides no information that is not otherwise obtainable from earlier $\boldsymbol{\Gamma}^{(1)}$-based NBO analysis methods.

B.25.2 RDM2 Keyword and Sample Output

Default RDM2 output is obtained by simply including the `RDM2` keyword in the $NBO keylist. The output consists of diagonal $\boldsymbol{\Gamma}^{(2)}_{ii;ii}$ ("G2" type) and cumulant $\boldsymbol{\Xi}^{(2)}_{ii;ii}$ ("X2" type) pair-population values for doubly-occupied D_{ii} Slater determinants of all Lewis-type NBOs φ_i, including best available Pauli-type upper and lower bounds for $\boldsymbol{\Xi}^{(2)}_{ii;ii} = \xi_{ii}$ from inequalities (12a,b).

Other matrix elements of the 2nd-order reduced density matrix $\boldsymbol{\Gamma}^{(2)}$ are requested by the user through a keyword of the form

`RDM2=`*`basis < i1 j1 k1 l1 / i2 j2 k2 l2 /...>`*

in the $NBO keylist. Here, *basis* [default *NBO*] is an orthonormal orbital basis set of NAO, NHO, NBO, NLMO, NO, or MO type, and each "*i j k l*" entry of the bracket-list identifies the 2-electron Slater determinants D_{ij}, D_{kl} of basis orbitals φ_i, φ_j, φ_k, φ_l, that enter evaluation of $\boldsymbol{\Gamma}^{(2)}_{ij;kl}$ matrix elements, Eq. (3), and associated cumulant $\boldsymbol{\Xi}^{(2)}_{ij;kl}$ values, Eq. (9). Note that each "*i j k l*" listing specifies *spin*-orbital labels that must include "a" (alpha) or "b" (beta) along with the ordinal NBO number in the specified spin set. Note also that any non-NBO *basis* choice must be accompanied by a bracket-list of user-requested matrix elements, since no default RDM2 output is provided in such cases.

For the simple example of methylamine, sample RDM2 input might be chosen as follows:

```
$NBO file=methylamine
RDM2 <11a 11b 11a 11b/3a 3b 11a 11b>
$END
```

This first entry "`11a 11b 11a 11b`" of the bracket-list requests the diagonal (pair-population) value for non-Lewis NBO 11, supplementing the Lewis-type pair populations that are included by default. The second entry of the bracket list requests the off-diagonal "`3a 3b 11a 11b`" element between electron pairs in NBO 3 (the nitrogen lone pair) and NBO 11 (the antiperiplanar σ_{CH}* antibond). Corresponding output for the requested values is shown below:

B.25. 2ND-ORDER REDUCED DENSITY MATRIX ELEMENTS (RDM2)

RDM2: SECOND-ORDER REDUCED DENSITY MATRIX (G2) AND CUMULANT (X2) ELEMENTS

Orbital basis: NBO {Oi}
Geminal basis: Dij(1,2) = Norm*[Oi(1)*Oj(2) - Oj(1)*Oi(2)]

NBO				RDM2	Cumulant Value and Bounds		
i	j	k	l	G2(i,j;k,l)	X2(i,j;k,l)	X2(l.b.)	X2(u.b.)
3a	3b	3a	3b	0.96553	0.00218	0.00000	0.16552*
4a	4b	4a	4b	0.99216	-0.00031	-0.03333	0.21664*
5a	5b	5a	5b	0.98994	0.00006	0.00000*	0.00816
6a	6b	6a	6b	0.99448	0.00000	-0.03159	0.11111
7a	7b	7a	7b	0.99774	-0.00001	.	.
8a	8b	8a	8b	0.98996	-0.00012	.	.
9a	9b	9a	9b	0.99545	0.00004	.	.
User requested:							
11a	11b	11a	11b	0.01625	0.00022		
3a	3b	11a	11b	-0.03442	-0.00117		

*Ineq(12b), otherwise Ineq. (12a); NBO7 Manual, p. B-??.

B.26. RESONANCE NATURAL BOND ORBITALS (RNBO)

References: E. D. Glendening and F. Weinhold, "Resonance Natural Bond Orbitals: Efficient Semi-Localized Orbitals for Computing and Visualizing Reactive Chemical Processes," *J. Comput. Chem.,* **15**, 916-921 (2019).

B.26.1 Introduction

For a stable equilibrium molecule, principal theoretical interest focuses on the Lewis-structural bonding pattern and associated orbitals that are optimal for its description. For a chemical reaction, however, the primary focus turns to bond *shifts* between reactant and product species and the corresponding dynamical *transformations* of orbital form and location along a reactive pathway on the potential energy surface (PES). By construction, the natural bond orbitals $\{\Theta_i\}$ satisfy the first of these *desiderata*, but cannot continuously transition from one distinct resonance-structural bonding pattern to another. To meet the latter need, the RNBO ("resonance" or "reaction" NBO) algorithm combines NRT-based description of continuously variable weightings and bond orders with $CHOOSE-type NBO optimizations for each contributing resonance structure to generate "shifting" RNBO orbitals (allowed to have strong multi-center character) that can aptly depict mechanistic details of "curly arrow" delocalization when viewed in animated sequences (see e.g. <http://nbo7.chem.wisc.edu/claisen.ppsx>).

In the near-equilibrium region of a stable reactant species with natural Lewis structure $NLS^{(R)}$, the localized NBOs $\{\Theta_i^{(R)}\}$ and NLMOs $\{\widetilde{\Theta}_i^{(R)}\}$ can deform somewhat with nuclear displacements, but must "switch" abruptly (unphysically) between bonding patterns at some point along the reaction path to the NBOs $\{\Theta_i^{(P)}\}$ and NLMOs $\{\widetilde{\Theta}_i^{(R)}\}$ of the product $NLS^{(P)}$. However, we can envision a continuously varying set of NBO-based "resonance-averaged" orbitals $\{\Omega_i\}$ that smoothly interpolate between those ($\{\widetilde{\Theta}_i^{(R)}\}$, $\{\widetilde{\Theta}_i^{(P)}\}$ of limiting reactant and product structures (possibly augmented with intermediate resonance contributions $\{\widetilde{\Theta}_i^{(I)}\}$), all expressible in NRT-averaged form as

$$(1) \quad \{\Omega_i\} = w^{(R)}\{\widetilde{\Theta}_i^{(R)}\} + w^{(P)}\{\widetilde{\Theta}_i^{(P)}\} + \sum_I w^{(I)}\{\widetilde{\Theta}_i^{(I)}\}$$

with non-negative weighting factors ($w^{(R)}$, $w^{(P)}$, $w^{(I)}$,...) summing to unity. The RNBO resonance hybrid (1) is constructed from the NLMOs $\{\widetilde{\Theta}_i^{(R)}\}$, $\{\widetilde{\Theta}_i^{(P)}\}$, $\{\widetilde{\Theta}_i^{(I)}\}$ of resonance structures of the NRT expansion. The RNBOs are normalized and symmetrically orthogonalized.

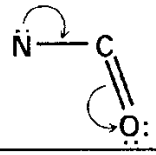
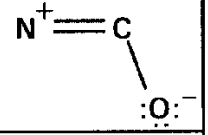
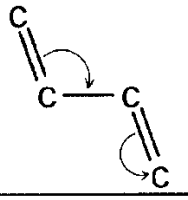
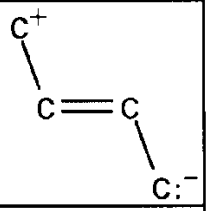
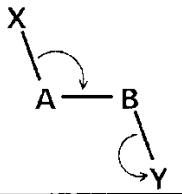
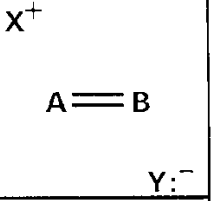
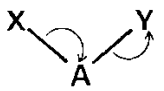
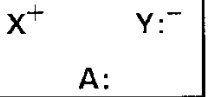
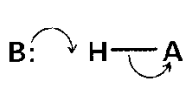
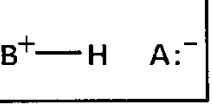
B.26. RESONANCE NATURAL BOND ORBITALS (RNBO)

RNBO orbitals $\{\Omega_i\}$ are generally developed for dynamic animation purposes. The chemically active RNBOs are expected to exhibit significant multi-center character, but are required to maintain high occupancy and strong visual continuity with respect to localized NBO precursors. The detailed interpolative forms of RNBOs are generally dependent on user-selected path along the PES, as well as the structures selected for resonance averaging.

The user is advised to employ a $NRTSTR keylist to guide the construction of RNBOs along a reaction pathway. The keylist should include:

- the reactant and product structures;
- any intermediate structure having direct donor-acceptor connection to either (or both) the reactant or product structure.

"Direct donor-acceptor connection" means that a 2-electron promotion from donor NBO to acceptor NBO of a parent resonance structure can be rewritten as the "connected" resonance structure. The table below shows the curly-arrow association of resonance structures with donor-acceptor interactions for some common cases. The principal such structures can be taken from leading donor-acceptor interactions of the E(2) perturbation output.

NBO	parent NLS	CT resonance
amide $n_N \rightarrow \pi^*_{CO}$		
vicinal $\pi_{CC} \cdot \pi^*_{CC}$		
vicinal $\sigma_{AX} \rightarrow \sigma^*_{BY}$		
geminal $\sigma_{AX} \rightarrow \sigma^*_{AY}$		
H-bond $n_B \rightarrow \sigma^*_{AH}$		

B.26.2 RNBO and PRNBO Keywords

Default RNBO output is obtained by including the `RNBO` keyword in the $NBO keylist and an optional $NRTSTR keylist specifying the structures for resonance averaging. As described above, the resonance structures included in the $NRTSTR keylist should be selected on the basis of exploratory single-point NRT calculations along the chosen reaction pathway.

RNBO averaging is performed over resonance structures having weights greater than 1%, or one-tenth of the leading weight, whichever is smaller. Thus, if the weight of the dominant structure is 50%, all structures of weight greater than 1% will contribute to the averaging (1% < 0.1×50%), whereas if the leading weight is 5%, all structures of weight greater than 0.5% (0.1×5%) will contribute. The user can set the weight threshold to a value other than 1%. For example, "`RNBO=25`" performs averaging over resonance structures having weights greater than 25%.

The keyword `AORNBO=W` writes the AO-RNBO transformation matrix to an external "`jobname.`*nn*" file (default: *nn* = 44) for subsequent visualization. The user may optionally use the keyword "`AORNBO=W`*nn*" to request an alternate integer extension for this file. Only the *N*/2 occupied RNBOs are written to external file; there is no provision for calculating virtual RNBOs. Separate alpha and beta transformations are generated for open-shell systems.

Pre-orthogonalized RNBOs, which neglect the interatomic PNAO-NAO orthogonalization step, can be requested using the `PRNBO` keyword in the $NBO keylist. Like the PNBOs and PNLMOs, the PRNBOs lack orthogonalization tails and, likely, yield renderings that are more pleasing to the eye. The keyword `AOPRNBO=W`*nn* writes the AO-PRNBO transformation matrix to an external "`jobname.`*nn*" file (default: *nn* = 43).

The combination of `PLOT` and `NRT` keywords in the $NBO keylist automatically triggers the calculation of the RNBOs and the writing of the AO-PRNBO and AO-RNBO transformations to external files.

B.26.3 RNBO Output

The NBO program prints a table summarizing the character of the occupied RNBOs. The RNBOs for RHF/3-21G methylamine (cf. Section A.3) are shown below:

```
 RESONANCE NATURAL BOND ORBITAL (RNBO) ANALYSIS:

 Resonance-averaged NLMOs for 6 leading structures using 1% weight threshold

 Hybridization/Polarization Analysis of RNBOs in NAO Basis:
 RNBO / Occupancy / Atomic Hybrid Contributions
 ------------------------------------------------------------------------------
   1. (2.00000)  CR ( 1)  C  1
                          99.993%  C  1 s(100.00%)
   2. (2.00000)  CR ( 1)  N  2
                          99.996%  N  2 s(100.00%)
   3. (2.00000)  LP ( 1)  N  2
                           0.482%  C  1 s(  0.84%)p99.99( 99.16%)
                          98.918%  N  2 s( 18.28%)p 4.47( 81.72%)
                           0.434%  H  3 s(100.00%)
                           0.082%  H  4 s(100.00%)
                           0.082%  H  5 s(100.00%)
   4. (2.00000)  BD ( 1)  C  1- N  2
                          40.027%  C  1 s( 21.86%)p 3.57( 78.14%)
                          59.894%  N  2 s( 30.44%)p 2.29( 69.56%)
                           0.017%  H  3 s(100.00%)
                           0.023%  H  6 s(100.00%)
                           0.023%  H  7 s(100.00%)
   5. (2.00000)  BD ( 1)  C  1- H  3
                          59.711%  C  1 s( 25.19%)p 2.97( 74.81%)
                           0.048%  N  2 s(  1.76%)p55.67( 98.24%)
                          40.216%  H  3 s(100.00%)
   6. (2.00000)  BD ( 1)  C  1- H  4
                          60.875%  C  1 s( 25.51%)p 2.92( 74.49%)
                           0.056%  N  2 s( 12.35%)p 7.10( 87.65%)
                           0.015%  H  3 s(100.00%)
                          38.824%  H  4 s(100.00%)
                           0.016%  H  5 s(100.00%)
                           0.204%  H  6 s(100.00%)
   7. (2.00000)  BD ( 1)  C  1- H  5
                          60.875%  C  1 s( 25.51%)p 2.92( 74.49%)
                           0.056%  N  2 s( 12.35%)p 7.10( 87.65%)
                           0.015%  H  3 s(100.00%)
                           0.016%  H  4 s(100.00%)
                          38.824%  H  5 s(100.00%)
                           0.204%  H  7 s(100.00%)
   8. (2.00000)  BD ( 1)  N  2- H  6
                           0.165%  C  1 s(  8.45%)p10.83( 91.55%)
                          67.978%  N  2 s( 25.89%)p 2.86( 74.11%)
                           0.096%  H  4 s(100.00%)
                           0.014%  H  5 s(100.00%)
                          31.733%  H  6 s(100.00%)
   9. (2.00000)  BD ( 1)  N  2- H  7
                           0.165%  C  1 s(  8.45%)p10.83( 91.55%)
                          67.978%  N  2 s( 25.89%)p 2.86( 74.11%)
                           0.014%  H  4 s(100.00%)
                           0.096%  H  5 s(100.00%)
                          31.733%  H  7 s(100.00%)
```

The structure of the RNBO table is identical to that of the NLMO table (cf. Section B.6.2).