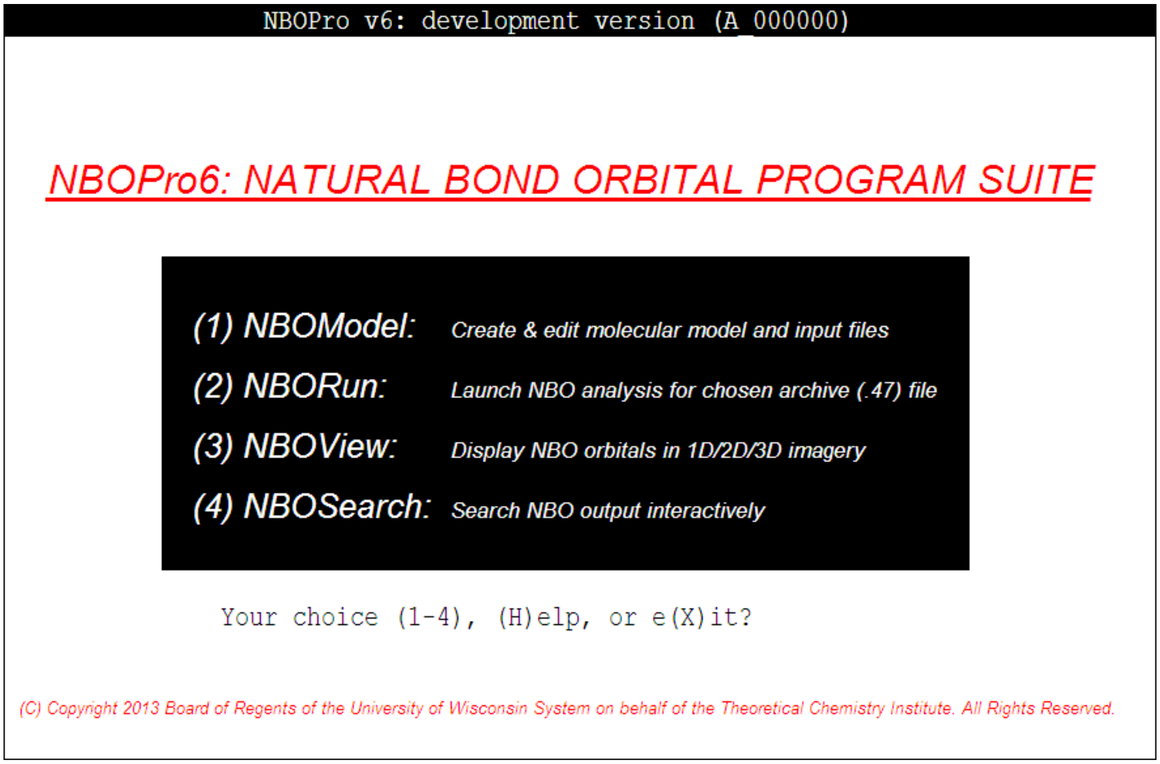
This is the legacy manual for original (keyboard-oriented) *NBOPro* program, which lacks many features of *NBOPro@Jmol*. However, the numerous illustrative examples and additional documentation of the raytracing optical model (p. 48ff) may provide a useful supplement to the HELP buttons that serve as "Manual" for current *NBOPro@Jmol.*

***NBOPro v.6*: NBO Program Suite**

What Does The *NBOPro* Program Do?

NBOPro v.6 is a suite of four separate but interacting utility programs that facilitate the analysis of modern electronic structure wavefunctions with Natural Bond Orbital (NBO) methods, all consistent with *NBO 6.0* program level and output. Your general entry to *NBOPro* modules is through the main program screen:



NBOPro v6: development version (A_000000)

NBOPro6: NATURAL BOND ORBITAL PROGRAM SUITE

(1) NBOModel:	*Create & edit molecular model and input files*
(2) NBORun:	*Launch NBO analysis for chosen archive (.47) file*
(3) NBOView:	*Display NBO orbitals in 1D/2D/3D imagery*
(4) NBOSearch:	*Search NBO output interactively*

```
Your choice (1-4), (H)elp, or e(X)it?
```

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These modules provide support from beginning to end of your computational chemistry project, as described below:

- ***Creating the starting model and input file.*** With the ***NBOModel*** "molecular design editor" module, you can show the full 3-dimensional z-matrix input for a normal-valent (Lewis-like) molecular or supramolecular species by merely typing a suitable line-structure formula! Alternatively, you can use generic forms of many file types for model input [including Gaussian input or log files, NBO archive (.47) files, or other standard cartesian or internal coordinate data formats] or choose from an extensive library of pre-formed coordinating ligands and other chemical and biochemical species. Starting from such line-formula, file, or internal input, you can freely `mutate` substituents, `alter` structural details, `unify` molecular units into supramolecular complexes, request overall `symmetry` or the `value` of any desired geometrical feature, and edit the model geometry in any desired manner. Finally, you can `draw` the model in ORTEP and other popular graphical file formats and save the model to basic input files for Gaussian, GAMESS, Orca, Jaguar, ADF and other popular programs. The intuitive command syntax (`show, use, mutate, alter,`...) allows you to conveniently manage and visualize all aspects of input preparation and output analysis for the electronic structure system (ESS) of your choice.

- ***Performing NBO analysis.*** With the ***NBORun*** "analyzer" module, you can conveniently perform the NBO analysis of the archive (.47) wavefunction file from a chosen ESS calculation at your desktop. *NBORun* is your entry to the workhorse *GenNBO* program of NBO analysis, allowing you to request new NBO keyword options without the usual edit-manipulations of the archive (.47) file. Repeat the analysis for as many alternative options as you wish, *without* re-calculating the wavefunction! [Alternatively, *NBORun* can also perform wavefunction calculations with a chosen ESS program that is specified in a user-supplied ESS.BAT batch file. This option allows all aspects of input file preparation, wavefunction caculation, and NBO analysis to be performed within the *NBOPro* environment.]

- ***Visualizing NBOs and other orbitals.*** With the ***NBOView*** "orbital viewer" module. you can conveniently visualize donor-acceptor orbital interactions in a variety of 1D (profile), 2D (contour), and 3D (surface) image forms, using PLOT files generated by *NBORun* from your archive (.47) wavefunction file. A highly sophisticated optical ray-tracing model allows you to achieve stunning "photograph-like" graphical images for a wide variety of localized (NAO, NHO, NBO, NLMO, or pre-orthogonal counterparts) and delocalized (CMO) orbital types.

- ***Interactively searching final NBO output.*** With the ***NBOSearch*** "data miner" module, you can obtain selected output NBO descriptor values, scan output for extremal entries, and prepare graphical displays of orbitals, resonance structures, or composite visualizations of various NBO-based wavefunction descriptors, all without seeing an actual NBO output file! *NBOSearch* receives your query and, if necessary, performs a new analysis (with help from *NBORun*) or prepares requested orbital and molecule imagery (with help from *NBOView* and *NBOModel*) to retrieve the requested information "on the fly." *NBOSearch* also makes it simple to do side-by-side comparisons of NBO descriptors from different jobs, or to prepare journal-quality graphical displays summarizing data combed from printed output. You may never need to re-generate, visually scan, or print an output file again!

In short, it's possible to conduct your entire computational project in *NBOPro* (except for job submission to a chosen ESS host) without concerns for details of input, archive, output files and the like. *NBOPro* keeps the focus on "getting to the chemistry" rather than managing I/O flow through the multiple steps of a computational chemistry investigation.

General Overview of *NBOPro* Usage

NBOPro is generally driven by keyboard commands and menu selections. Each *NBOPro* module appears as a "window in a window," with its own command set (as listed near the top of the screen), syntax, and command options, as well as its own HELP utilities. The mouse can be used for screen capture (see below) and to exit the program, but is otherwise ignored.

NBOPro maintains several background files that record session details or provide temporary storage for graphical images that the user may wish to use subsequently. The four principal files are:

- `NBOLOG$$.DAT`, a text file that stores a printed record of *NBOModel* commands and replies, preserving a more permanent record of the scrolling screen dialog;
- `NBOERR$$.DAT`, a text file that stores a list of warnings or error conditions that occur during the *NBOPro* session, possibly enabling the user to understand further details of severe errors that interrupt

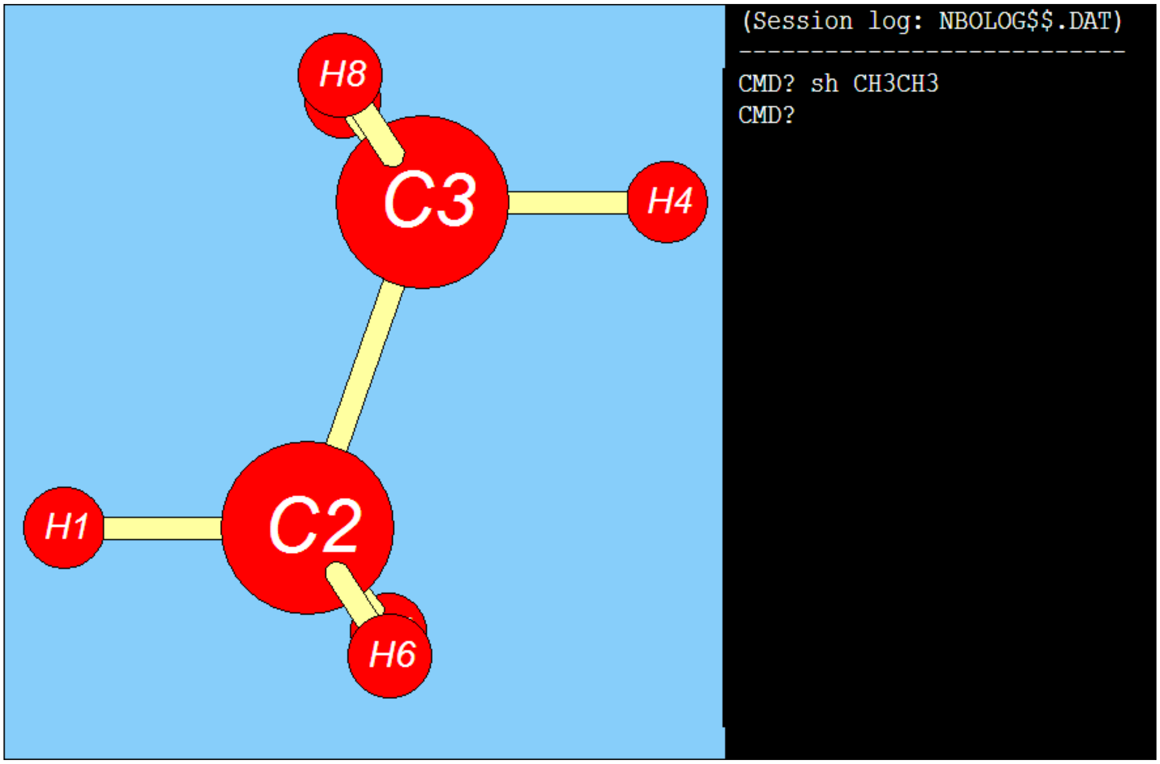
program execution (used mainly by program developers for debugging purposes);

- `NBOPIC$$.BMP`, a graphics bitmap file that temporarily stores the orbital image displayed in the graphics region (left) of the current screen (as indicated in the caption below the image). You can copy or rename this file to a safe location (from a DOS command prompt or Windows Explorer screen) before proceeding to overwrite the current image with a new command.
- `NBOSCR$$.BMP`, a graphics bitmap file that captures a full-screen image when the current screen is (left)double-clicked with the mouse. This allows you save a full-screen snapshot for subsequent editing, before it is overwritten by another double-click.

***NBOModel*: NBO Molecular Design Editor**

What Does The *NBOModel* Program Do?

The *NBOModel* program creates 3D molecular and supramolecular models that can be edited and used as input to standard electronic structure systems (ESS). *NBOModel* offers a uniquely simple way of creating ordinary (Lewis-compliant) molecular and supramolecular species by simply typing a line-structure formula. For example, typing the command “show CH3CH3” creates the molecular model for ethane, as shown below:

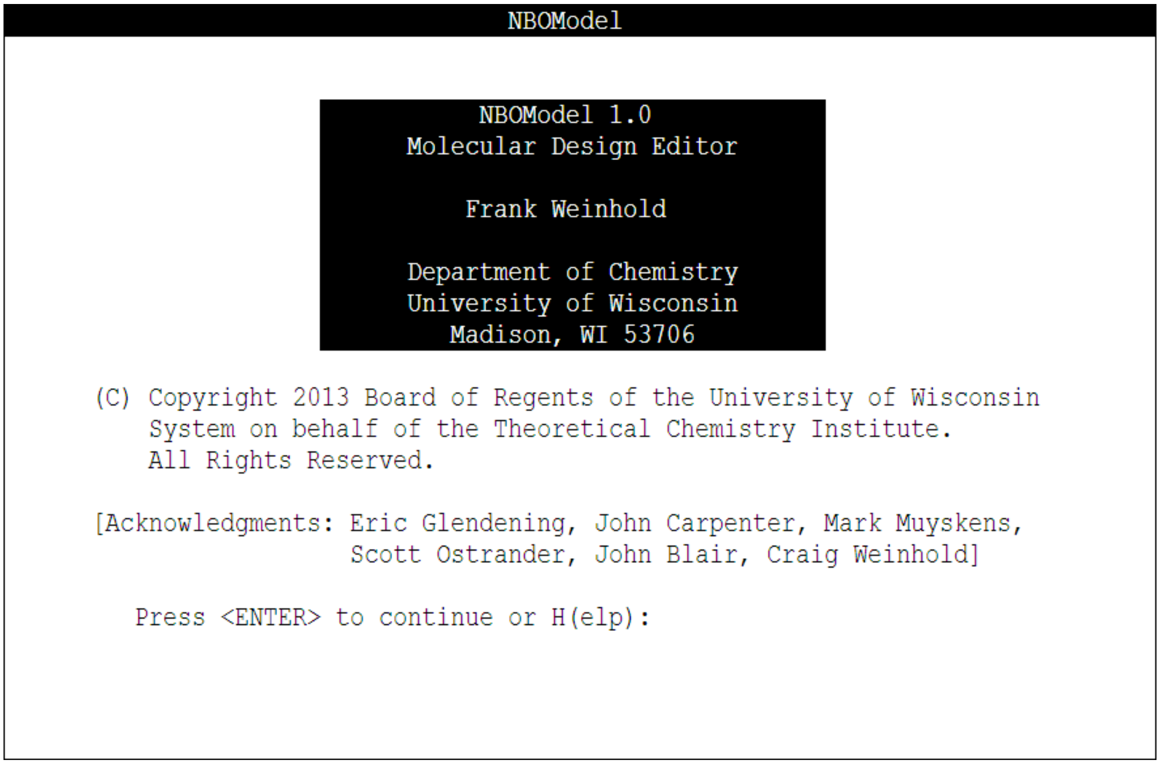


```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh CH3CH3
CMD?
```

NBOModel can also import model geometry from a variety of ESS files (such as Gaussian or GAMESS input files, or Gaussian log files) or other popular file formats (see the ***save.t*** and ***use.t*** entries in the table of ***NBOModel* Commands** below for a full listing). For more complex bonding motifs, *NBOModel* also stores an extensive library of preformed molecular models for polycyclic saturated and unsaturated hydrocarbons, peptides, nucleic acids, and chelating ligands. All such models — whether from formula, file, or internal library input — can be edited with a powerful set of commands (`alter`, `clip`, `draw`, `fuse`,..., as shown in the listing near the top of the screen and further illustrated below). The edited model can then be saved in a variety of valid input file formats for Gaussian, GAMESS, and other popular ESS programs. *NBOModel* can also draw journal-quality ORTEP diagrams of the model geometry. In effect, *NBOModel* serves as a general model creator, editor, file-conversion, and display utility, useful at many stages of a computational chemistry project.

Getting Started

Launch the *NBOModel* program (by selection from the *NBOPro* main menu) to see the program title page as displayed below:



```
                              NBOModel

                          NBOModel 1.0
                     Molecular Design Editor

                         Frank Weinhold

                     Department of Chemistry
                     University of Wisconsin
                        Madison, WI 53706

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        System on behalf of the Theoretical Chemistry Institute.
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    [Acknowledgments: Eric Glendening, John Carpenter, Mark Muyskens,
                      Scott Ostrander, John Blair, Craig Weinhold]

       Press <ENTER> to continue or H(elp):
```
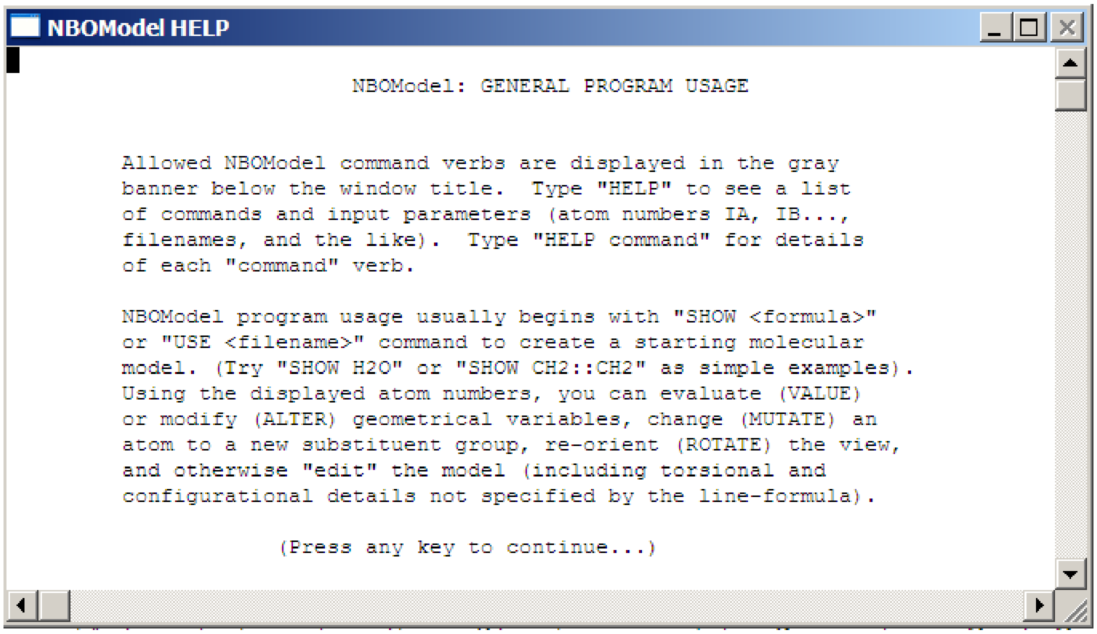
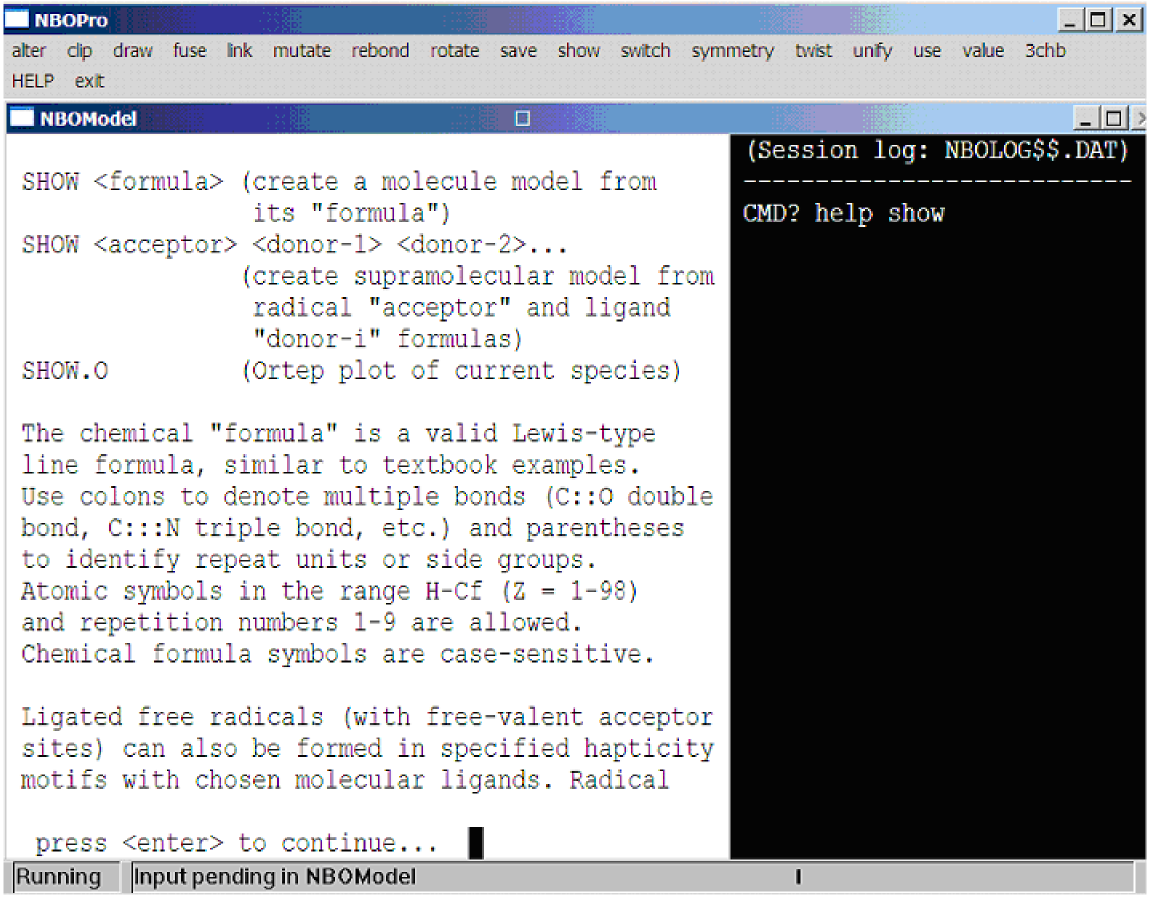

At this point, you can press “H” to see the first screen page of general HELP, as shown below:



```
                    NBOModel: GENERAL PROGRAM USAGE


      Allowed NBOModel command verbs are displayed in the gray
      banner below the window title.  Type "HELP" to see a list
      of commands and input parameters (atom numbers IA, IB...,
      filenames, and the like).  Type "HELP command" for details
      of each "command" verb.

      NBOModel program usage usually begins with "SHOW <formula>"
      or "USE <filename>" command to create a starting molecular
      model. (Try "SHOW H2O" or "SHOW CH2::CH2" as simple examples).
      Using the displayed atom numbers, you can evaluate (VALUE)
      or modify (ALTER) geometrical variables, change (MUTATE) an
      atom to a new substituent group, re-orient (ROTATE) the view,
      and otherwise "edit" the model (including torsional and
      configurational details not specified by the line-formula).

                  (Press any key to continue...)
```

If this is your first time using the program, you may wish to request specific help for individual commands (`help alter`, `help clip,...`), as illustrated below for the first page of "`help show`":



```
SHOW <formula> (create a molecule model from
                its "formula")
SHOW <acceptor> <donor-1> <donor-2>...
               (create supramolecular model from
                radical "acceptor" and ligand
                "donor-i" formulas)
SHOW.O         (Ortep plot of current species)

The chemical "formula" is a valid Lewis-type
line formula, similar to textbook examples.
Use colons to denote multiple bonds (C::O double
bond, C:::N triple bond, etc.) and parentheses
to identify repeat units or side groups.
Atomic symbols in the range H-Cf (Z = 1-98)
and repetition numbers 1-9 are allowed.
Chemical formula symbols are case-sensitive.

Ligated free radicals (with free-valent acceptor
sites) can also be formed in specified hapticity
motifs with chosen molecular ligands. Radical

 press <enter> to continue...
```

```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? help show
```

The “show” command is usually the starting point for *NBOModel* sessions, so you’ll want to study the seven pages of this help screen carefully before trying out formula input (“`show <line-formula>`”) on your own. A wide variety of molecular and supramolecular species can be modeled with the concise command syntax of formula input.

Molecular Covalent Bonding

Follow chemical intuition in typing molecular line formulas from the keyboard:

- Use parentheses as necessary to set off side groups
- Repetition numbers 1-9 can follow atom symbols or parentheses
- Specify multiple bonds by the appropriate number of colon “:” symbols

Try out some simple things first, such as “`show CH4`” or the “`show CH3CH3`” example illustrated above, adding parenthesized side-groups [such as “`show C(CH3)4`”] for variety. Then try a few examples with multiple-bonds (multiple-colons), such as “`show H2C::O`” (formaldehyde), “`show HC::OOH`” (acetic acid), or “`show HC:::CH`” (acetylene), emulating how the formula might be written in a freshman textbook with bond-strokes instead of colons.

For more complex chemical and biochemical species, you can also draw from a library of pre-formed species abbreviations, such as “`Bz`” for benzene or “R6C” for chair-cyclohexane (try “`show Bz`” or “`show R6C`“). The library also includes common inorganic ligands whose mode of complexation can be specified by an appropriate colon-list (denticity) prefix (::lig for bidentate, :::lig for tridentate, etc.). The table of available library species and associated abbreviations and allowed denticity specifications is given below:

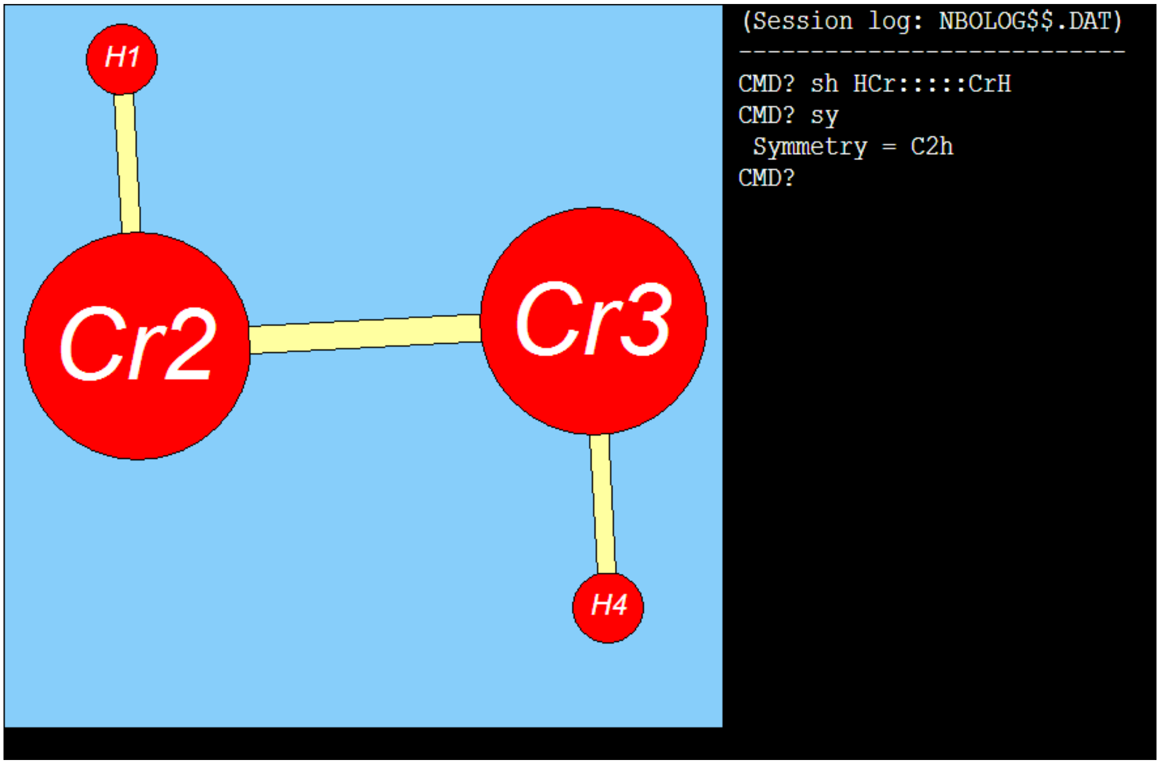
Table of NBOModel Abbreviations

abbrev.	***denticity***	***species***
		Common inorganic ligands
acac	2	acetylacetonate anion
bipy	2	2,2'-bipyridine
cp	1-3	cyclopentadieny anion
dien	3	diethylenetriamine
dppe	2	1,2-bis(diphenylphosphino)ethane
edta	6	ethylenediaminetetraacetic acid
en	2	ethylenediamine

phen	2	1,10-phenanthroline	
tren	4	tris(2-aminoethyl)amine	
trien	4	triethylenetetramine	
		Common cyclic aromatic species	
Bz	1-3	benzene (C_6H_6)	
A10R2L	NA	naphthalene ($C_{10}H_8$)	
A14R3L	NA	anthracene ($C_{14}H_{12}$)	
A18R4L	NA	tetracene ($C_{18}H_{14}$)	
A22R5L	NA	pentacene ($C_{22}H_{20}$)	
A14R3	NA	phenanthrene ($C_{14}H_{10}$	
A14R4	NA	chrysene ($C_{14}H_{12}$)	
A16R4	NA	pyrene ($C_{16}H_{10}$)	
A18R4	NA	triphenylene ($C_{18}H_{12}$)	
A20R5	NA	benzopyrene ($C_{20}H_{12}$)	
A20R6	NA	corannulene ($C_{20}H_6$)	
A21R7	NA	sumanene ($C_{21}H_{12}$)	
A32R10	NA	ovalene ($C_{32}H_{14}$)	
		Common cyclic saturated species	
R6C	NA	cyclohexane (C_6H_{12}, chair)	
R6B	NA	cyclohexane (C_6H_{12}, boat)	
R6T	NA	cyclohexane (C_6H_{12}, twist-boat)	
R5	NA	cyclopentane (C_5H_{10})	
R4	NA	cyclobutane (C_4H_8)	
R3	NA	cyclopropane (C_3H_6)	
RB222	NA	[2,2,2]bicyclooctane	
RB221	NA	[2,2,1]bicycloheptane (norbornane)	
RB211	NA	[2,1,1]bicyclohexane	
RB222	NA	[1,1,1]bicyclopentane (propellane)	
R5S	NA	spiropentane	
RAD	NA	adamantane	
		Peptide fragments (RCH_2NHCHO)	
GLY	NA	glycine	R = H
ALA	NA	alanine	R = CH_3
VAL	NA	valine	R = $CH(CH_3)_2$
LEU	NA	leucine	R = $CH_2CH(CH_3)_2$
ILE	NA	isoleucine	R = $CHCH_3C_2H_5$
PRO	NA	proline	R = C_3NH_7
PHE	NA	phenylalanine	R = $CH_2C_6H_5$
TYR	NA	tyrosine	R = $CH_2C_6H_4OH$
TRP	NA	tryptophan	R = $CH_2C_8NH_6$
SER	NA	serine	R = CH_2OH
THR	NA	threonine	R = $CHOHCH_3$
CYS	NA	cysteine	R = CH_2SH
MET	NA	methionine	R = $CH_2CH_2SCH_3$
ASN	NA	asparagine	R = CH_2CONH_2
GLN	NA	glutamine	R = $CH_2CH_2CONH_2$
ASP	NA	aspartate	R = CH_2COOH^-
GLU	NA	glutamate	R = $CH_2CH_2COOH^-$
LYS	NA	lysine	R = $CH_2CH_2CH_2CH_2NH_3^+$
ARG	NA	argenine	R = $CH_2CH_2CH_2NHC(NH_2)_2^+$
HIS	NA	histidine	R = $CH_2C_3N_2H_3$
		Nucleic acid fragments	
NA_G	NA	guanine	

NA_C	NA	cytosine
NA_A	NA	adenine
NA_T	NA	thymine
NA_U	NA	uracil
NA_R	NA	ribose backbone fragment
	Higher-symmetry skeletal motifs	
D3H	NA	trigonal bipyramid (SF_5)
D4H	NA	octahedral (SF_6)

When you are more ambitious, try some corresponding Lewis-compliant (12e-rule) structures for transition metal species, such as "show `WH6`" (tungsten hexahydride) or quintuple-bonded "show `HCr:::::CrH`" (dichromiumdihydride), as illustrated below:



```
(Session log: NBOLOG$$.DAT)
----------------------------
CMD? sh HCr:::::CrH
CMD? sy
 Symmetry = C2h
CMD?
```

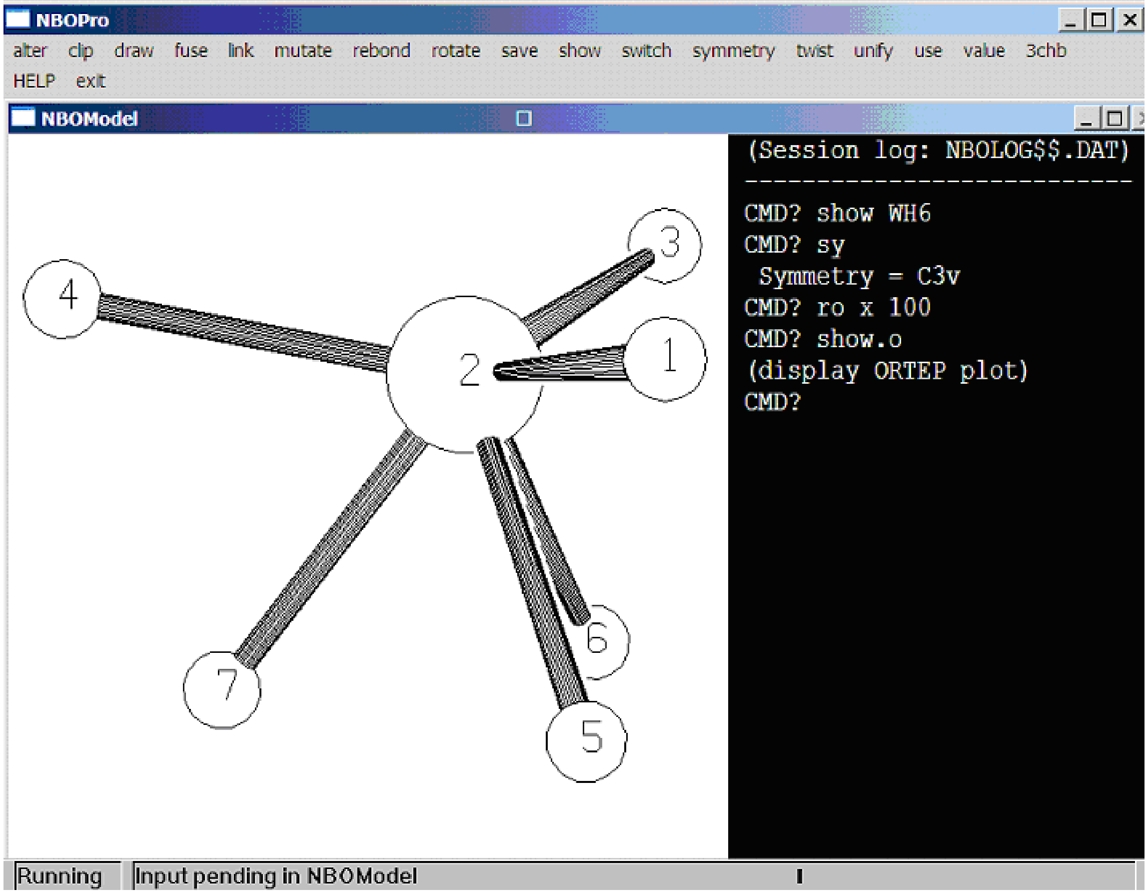
For those unacquainted with the usefulness of simple Lewis-like concepts in predicting the strangely un-VSEPR-like geometries of such species, the uncanny accuracy of the results may appear quite surprising!

The above screen also illustrates some other points of general interest:

- Although *NBOModel* commands are generally case-insensitive (and can be abbreviated to shortest unique form, e.g., `SHOW =`

`show` = `SH` = `sh`), chemical formulas are case-sensitive (e.g., `CrH ≠ CRh`) and must correspond to normal-valent species (satisfing the 8e- or 12e-rule for main- or transition-group atoms, respectively) to be recognized by *NBOModel*. All abbreviations for pre-formed library species are also case-sensitive.

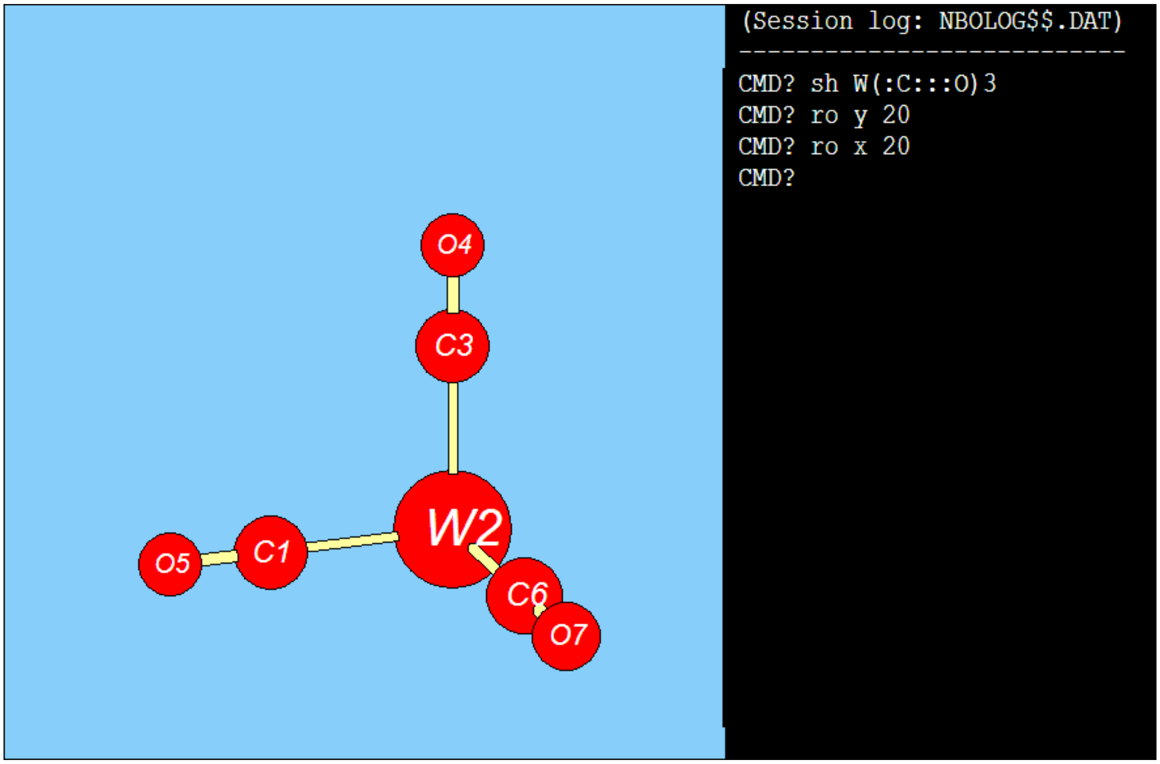
- In general, a “bond-stick” carries no connotation of formal “bond order,” but is only a visual guide to 3D geometry (cf. “`clip`” and “`link`” commands, which add or remove bond-sticks without regard to chemical sensibility).
- The “`symmetry`” command can be used at any point to determine the nuclear point-group symmetry of the current model (C_{2h} in this case). The model is then automatically re-oriented to point the principal symmetry element (a two-fold C_2 rotation axis in this case) toward the viewer.
- Successive commands (and responses) scroll upwards when the command bar at the right is filled, so you can always see the most recent 20 or so entries. [As noted above, the entire *NBOModel* dialog is stored in the NBOLOG$$.DAT file for later reference.]
- The parameterized “`show.o`” command specifies the alternative ORTEP graphical representation, as shown in the example below for WH_6:



```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? show WH6
CMD? sy
 Symmetry = C3v
CMD? ro x 100
CMD? show.o
(display ORTEP plot)
CMD?
```

- [The “`rotate x 100`” command rotates the model by 100° about the horizontal x axis to better show the “squashed” C_{3v} geometry that is found in experimental representatives of this bonding motif.] Tapping the <ENTER> key after a rotate command causes the command to be repeated, and holding down the <ENTER> command after rotation by a small angle (e.g., “`rotate x 5`”) will cause the model to continue rotating in a somewhat continuous fashion about the chosen axis.

Although input line-structure formulas must usually correspond to normal-valent Lewis bonding patterns with no formal charge, one can also specify formulas for simple cases of organometallic coordination (dative) bonding with monodentate ligands. This is done by identifying the ligand coordinating site (the first atom of the <:ligand> formula) with a precursor “:” and enclosing the <:ligand> formula in parentheses. For example, an idealized tungsten tricarbonyl [$W(CO)_3$] coordination complex can be created with the “show `W(:C:::O)3`” command (rotated for improved perspective), as illustrated below:



```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh W(:C:::O)3
CMD? ro y 20
CMD? ro x 20
CMD?
```

Supramolecular Donor-Acceptor Bonding

NBOModel can also create a variety of radical-type supramolecular complexes based on simple NBO donor-acceptor concepts. For such species, one starts from a chosen <acceptor> radical monomer, as specified by a chemical formula or previously saved `acc.cfi` filename. The acceptor can then be surrounded by one or more Lewis-compliant donor monomers, each specified by formula or filename ("<donor-i>") and prefxed by a stoichiometric coefficient ("n_i"; optional) and "colon list" ("$[:]_1$") in a general command of the form

```
show <acceptor> n1[:]1<donor-1> n2[:]2<donor-2> ...
```

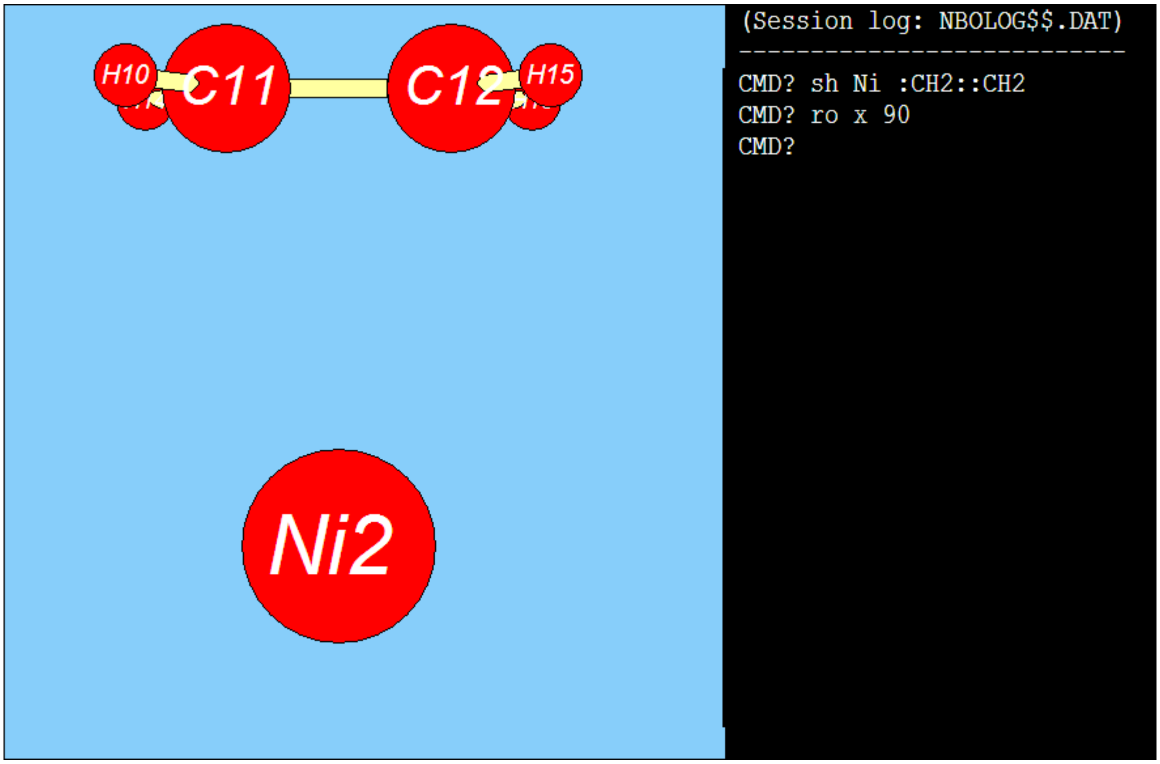
As usual, stoichiometric coefficients ($n_i \geq 2$) dictate the number of *i*-type ligands to be included in the final complex. The colon list "$[:]_i$" consists of one or more colon (:) symbols that specify the number of formal 2e donor sites (either lone pair or pi-bond) of the desired coordination motif (viz., ":<donor-i>" for a 2e donor, "::<donor-i>" for a 4e donor, and so forth). This "$[:]_i$" list effectively specifies the desired denticity or hapticity of ligand attachment (with contributions η_1 for a lone pair site or η_2 for a pi-bond site).

Monomers may be entered in any order, but each donor or acceptor monomer must be separated by commas or spaces from other monomers. Each donor monomer must be a Lewis-compliant molecular species, but the acceptor monomer can be an organometallic radical or other Lewis-deficient (hypovalent) species, considered to be in a state of highest allowed spin multiplicity. *NBOModel* will attempt to formulate a model of the ligated radical so long as the requested number of active 2e donor ligand sites (as implied by the sum of $n_i[:]_i$ symbols) remains less than or equal to the remaining free valencies of the acceptor radical. The idealized radical model takes no account of monomer relaxation, alternative radical hybridization motifs (see REBOND), spin reorganization, or configurational and conformational isomerism about donor-acceptor bonds, so can only be considered a crude initial guess of the envisioned radical spin state geometry, ready for subsequent editing and optimization.

As a simple example, a naked Ni atom can be complexed to an ethylene ligand (formal 2e donor) with the command

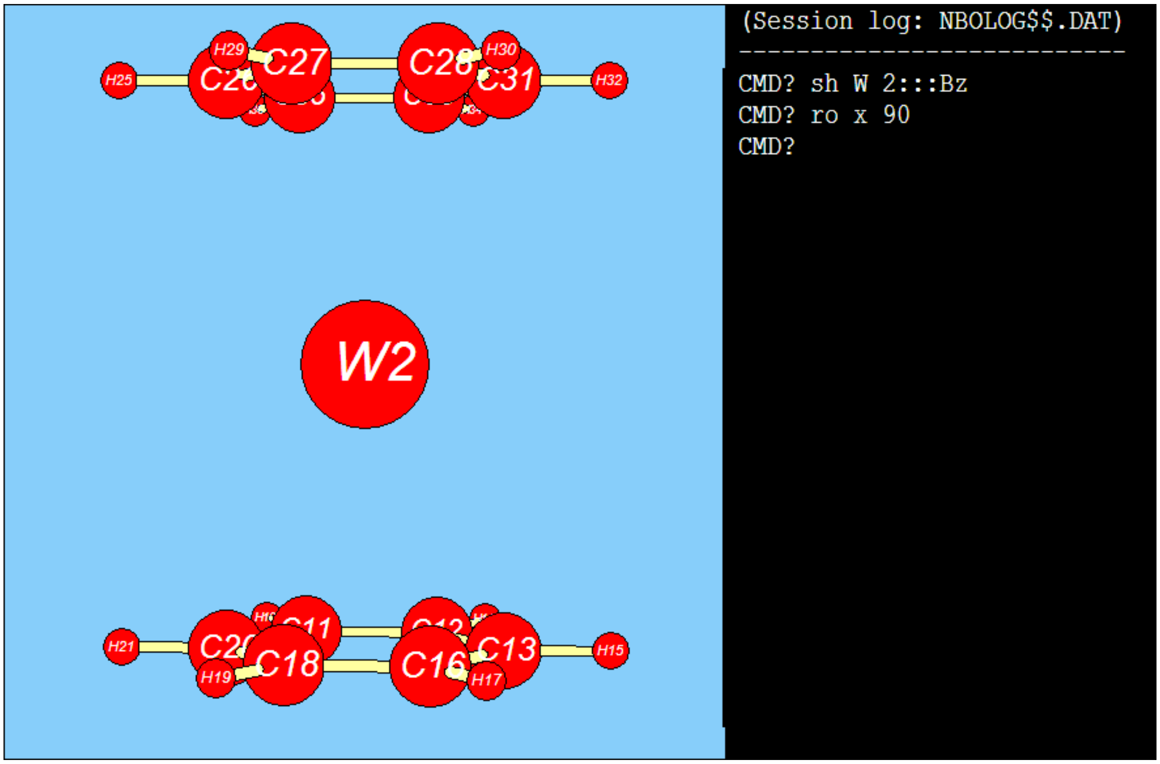
```
show Ni :CH2::CH2
```

as shown below:



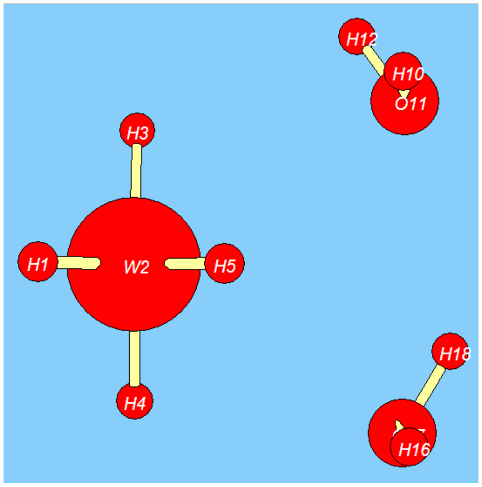
```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh Ni :CH2::CH2
CMD? ro x 90
CMD?
```

Similarly, a polyvalent $^5WH_2$ radical (formally, 8e short of duodectet compliance) can be complexed to any combination of 8e (or fewer) donor ligands in combinations such as “`show WH2 4:NH3`”, “`show WH2 3:H2O :NH3`”, “`show WH2 :::Bz :NH3`”, and so forth. (Note however that realistic polyvalent radicals often undergo radical transfer reactions with simple monodendate ligands, so the idealized *NBOModel* geometry is only a possible starting point for further numerical investigations.) Coordination patterns of higher hapticity are also achievable, as in the “`show W 2:::Bz`” dibenzene “sandwich” complex displayed below:

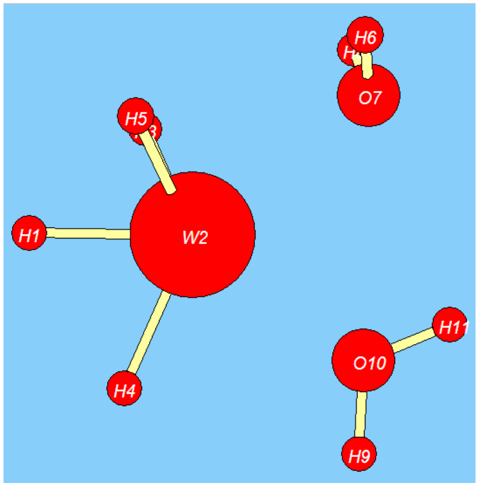


```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh W 2:::Bz
CMD? ro x 90
CMD?
```

Because donor-acceptor bonds are typically weaker than ordinary covalent bonds, the idealized *NBOModel* supramolecular geometry is generally less accurate than the Lewis-like covalent geometry of molecule formation. For example, the diaquo complex of triplet WH_4 (“`show WH4 2:H2O`”) leads to the idealized *NBOModel* geometry shown in the left panel below, which can be compared with the fully optimized B3LYP/LANL2DZ geometry in the right panel:



ideal



B3LYP/LANL2DZ

The local geometry of both radical and ligand species is seen to be significantly altered in the final optimized structure. Nevertheless, the acute intermolecular O-W-O angular disposition (63.4° ideal vs. 74.6° optimized, both differing sharply from naive VSEPR-type expectations) is reasonably well represented in the idealized model, sufficient to serve as input for an optimization job.

Study the instructions and examples in each “`help <command>`” screen, then try the command in simple applications to gradually expand your repertoire. As you progress, try using the internal library of pre-formed cyclic hydrocarbon molecules and radicals — such as benzene (“`show Bz`″) or cyclohexane in chair (“`show R6C`”), boat (“`show R6B`”), or twist-boat (“`show R6T`”) conformations. Common polydentate inorganic ligands (e.g., acetylacetonate, ::acac, or ethylenediaminetetraacetic acid, ::::::edta) can also be visualized in uncomplexed (e.g., “`show acac`”) or complexed forms (with appropriate denticity colons, e.g., “`show Cr 3::acac`”). More complex polypeptide and ribonucleic acid chains can also be formed from the internal library, then `twisted` into proper conformation, `switched` into proper absolute configuration, or otherwise edited (`mutate, 3chb, alter,...`) for biochemical applications. You can also use existing files of various types (“`use.t`”) to initialize your model, such as a Gaussian input file (“`use.g myjob.g09`”), Gaussian log file (“`use.l myjob.log`”), or NBO archive file (“`use.a myjob.47`”). The initial model from any of these starting points can then be fine-tuned with other *NBOModel* editing tools, as introduced and illustrated below.

Valid *NBOModel* Commands

The full list of *NBOModel* commands, unique abbreviations, command arguments (if any), and requested action is summarized in the table below:

NBOModel Commands

Command	Argument(s)	Action
Alter	*I (J K L) value*	Alter the *I (J K L)* variable [as identified by the specified atom number(s)] to the specified numerical *value*: "*I*" = nuclear charge of atom *I*; "*I J*" = bond length R_{IJ}; "*I J K*" = Θ_{IJK} bond angle; "*I J K L*" = Φ_{IJKL} dihedral angle.
CLip	*I J*	Erase the bond-stick between atoms *I* and *J* (*clip* is the opposite of *link*).
Draw(.t)	*filename*	Draw an ORTEP-style picture of the current model [with characteristics specified by parameter(s) ".t"] to an external file *filename*. Allowed ".t" parameters are: ".a" = (a)djust picture size; ".n" = (n)o numbers; ".g" = (g)raphics bitmap (.bmp) file [default] ".p" = (p)ostscript (.ps) file ".t" = (t)echset bitmap (.tsb) file ".v" = techset (v)ector (.tsv) file
Fuse	*I J*	Delete monovalent atoms *I, J* and replace with a new bond-stick between atoms to which *I* and *J* were formerly attached.
Link	*I J*	Draw a bond-stick between atoms *I* and *J* (*link* is the opposite of *clip).*
Mutate	*I <group>*	Replace atom *I* by a new substituent-group (of equal valency) as specified by the "*<group>*" line-structure formula.

REbond	*I symtype*	Change the bonding symmetry around transition atom *I* to a desired *symtype* [see “`help rebond`” for allowed *symtype* codes for various ML_n (n = 4,5,6) metal centers].
ROtate	*axis angle*	Rotate the model clockwise about the chosen *axis* (x = horizontal, y = vertical; z = toward viewer) by the specified *angle*. (Pressing <ENTER> repeats the command for stepwise rotation about the chosen axis.)
SAve.t	*filename*	Save the current model to external file *filename*, with “.t”-type format: “.adf” = ADF (.adf) input file “.c” = cartesian coordinate CFILE (.cfi) “.g” = Gaussian (.gau) input file “.gms” = GAMESS (.gms) input file “.jag” = Jaguar (.jag) input file “.mm” = MM2-type (.mm2) input file “.mnd”= MINDO/AM1 (.mnd) input file “.mp” = Molpro (.mp) input file “.nw” = NWChem (.nw) input file “.orc” = Orca (.orc) input file “.pqs” = PQS (.pqs) input file “.qc” = Q-Chem (.qc) input file “.v” = valence coordinate VFILE (.vfi)
SHow	*<formula>*	Create a geometrical model [Pople-Gordon idealized geometry: J.A. Pople, M.S. Gordon, *J. Am. Chem. Soc.* **87**, 4253 (1967)] for the Lewis-structural line *<formula>* (see “`help show`” and examples above for valid “*<formula>*” syntax).
SWitch	*I J*	Switch the bond-linkages that connect atoms *I* and *J* (and all attached atoms) to a common stereocenter, thus changing absolute configuration at that center.
SYmmetry		Determine the nuclear point-group symmetry of the current model.
TRanslate	*axis shift*	Translate the model along the chosen *axis*

		(x = horizontal, y = vertical; z = toward viewer) by the specified *shift*. (Pressing <ENTER> repeats the command for stepwise panning along the chosen axis.)
TWist	*I J K L value*	Perform a rigid torsional twist about the *J-K* bond that brings the *I-J-K-L* dihedral angle to a chosen final *value* (with all other atoms of torsional groups connected by the *J-K* bond twisted accordingly).
UNify	*cfile1 cfile2* *I J K L dist*	A complex command that aligns two existing models (specified in cartesian CFILE format as *cfile1, cfile2*) in linear *I-J-K-L* arrangement (with *I, J* in *cfile1*; *K,L* in *cfile2*), separated by R_{IL} = *dist*.
USe.t	*filename*	Read external file *filename* (of ".t" format type) to create a new model. Allowed format types include: ".a" = NBO archive (.47) file ".adf" = ADF (.adf) input file ".c" = cartesian coordinate CFILE (.cfi) ".g" = Gaussian (.gau) input file ".gms" = GAMESS (.gms) input file ".jag" = Jaguar (.jag) input file ".l" = Gaussian (.log) log file ".mp" = Molpro (.mp) input file ".nw" = NWChem (.nw) input file ".orc" = Orca (.orc) input file ".pqs" = PQS (.pqs) input file ".qc" = Q-Chem (.qc) input file ".v" = valence coordinate VFILE (.vfi)
Value	*I (J K L)*	Return current value of model property specified by "*I*" (nuclear charge of atom *I*), "*I J*" (R_{IJ} bond length), "*I J K*" (Θ_{IJK} bond angle), or "*I J K L*" (Φ_{IJKL} dihedral angle).
3chb	*I J <:ligand>*	Create a linear 3-center/4-electron (3c/4e) "hyperbonded" linkage between covalently bonded atoms *I* and *J* of the current model and the first atom of the *<:ligand>* formula [identified as a

		coordinating ligand by the preceding ":" ("electron pair") symbol].
Help	*command*	Provide a brief on-screen summary of syntax, parameters, and function of the specified *command*, with illustrative examples.
Exit		Normal exit from the program (return to *NBOPro* main menu).

Multiple arguments may be separated by commas or spaces. In general, input is case-insensitive (except for chemical symbols) and commands may be abbreviated by their leading unique characters (as shown by caps in the table above). Thus, the command "SWITCH 1,2" could be entered as "switch 1 2", "sw 1 2", etc. Further details of the dialog associated with individual commands are given in following sections.

Editing a Starting Model

NBOModel offers a variety of tools for editing an initial model, including (1) altering details of geometry; (2) changing substituent groups; or (3) combining two or more starting monomers into a composite oligimer or supramolecular complex.

Geometry Alterations

Current values of geometrical parameters can be requested with the "`value <atom list>`" command, where the requested parameter depends on the specified list of atom numbers: one (*I*) for nuclear charge Z_I; two (*I J*) for bond length R_{IJ}; three (*I J K*) for bond angle Θ_{IJK}; and four (*I J K L*) for dihedral angle Φ_{IJKL}. The values (Å for distances, ° for angles) are returned whether the atoms appear bonded or not in the displayed model.

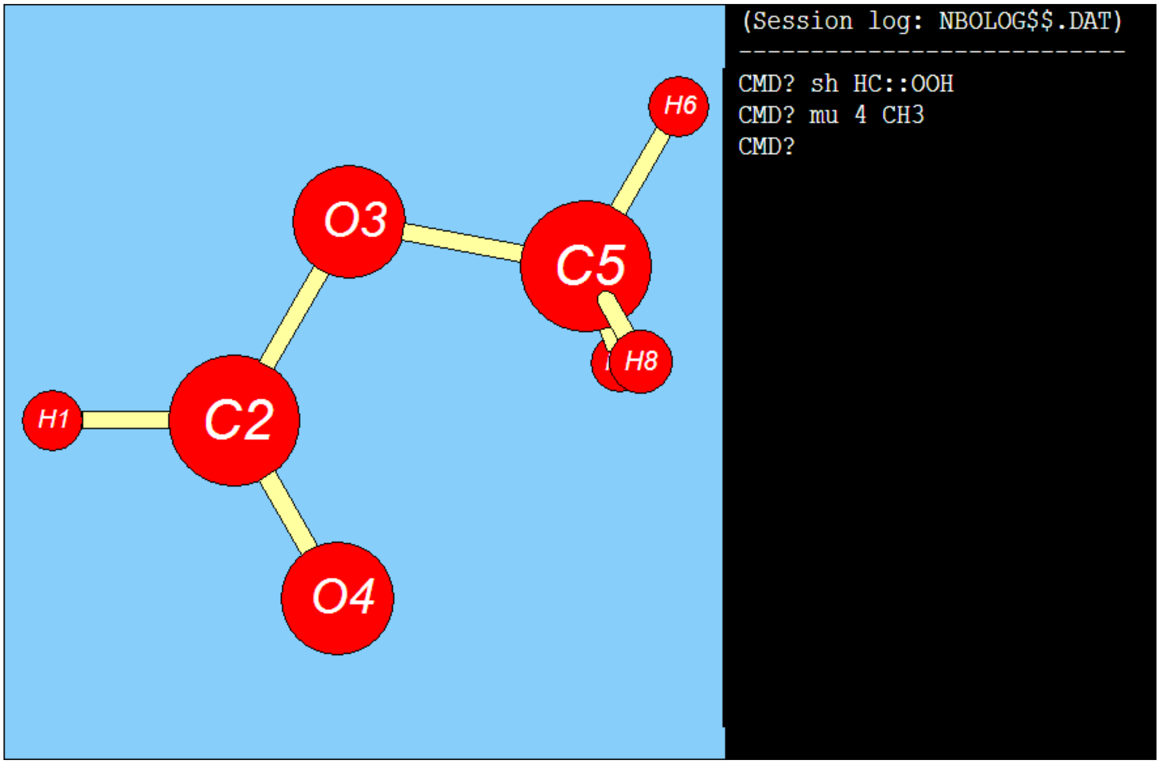
The "`alter <atom list> value`" command is similarly used to alter the corresponding Z_I, R_{IJ}, Θ_{IJK}, or Φ_{IJKL} parameter to a chosen `value`. [This assumes the variable is one of the independent valence coordinates in current usage, as can be determined by examining the model VFILE (myjob.vfi file) with *Notepad* or other text editor.] Note that the alteration is applied to the model whether it makes chemical sense or not.

Torsional twisting about a *J*-*K* single bond is better accomplished with the `twist` command. This takes the form “`twist I J K L value`”, where atoms *I*-*J*-*K*-*L* are covalently linked around the *J*-*K* torsional bond and `value` is the final Φ_{IJKL} dihedral angle. The command is ignored if the bonding pattern doesn’t conform to the expected *J*-*K* single bond.

[A correct chemical bonding pattern is also required for the “`switch I J`” command, which exchanges the *I*-based and *J*-based groups attached to a common stereocenter to reverse absolute configuration.]

Substituent Changes

Although “`alter I newZ`” can change the identity of an atomic substituent (whether or not it makes chemical sense), a more reasonable choice is the “`mutate I <formula>`” command, where *I* is the atom (often H) to be replaced by a substituent of specified `<formula>`. For example, if formic acid was created with “`HC::OOH`”, one can “mutate” the acid to its methyl ester [convert acid proton H(4) to a methyl group] with the command “`mutate 4 CH3`”, as shown in the screen below:

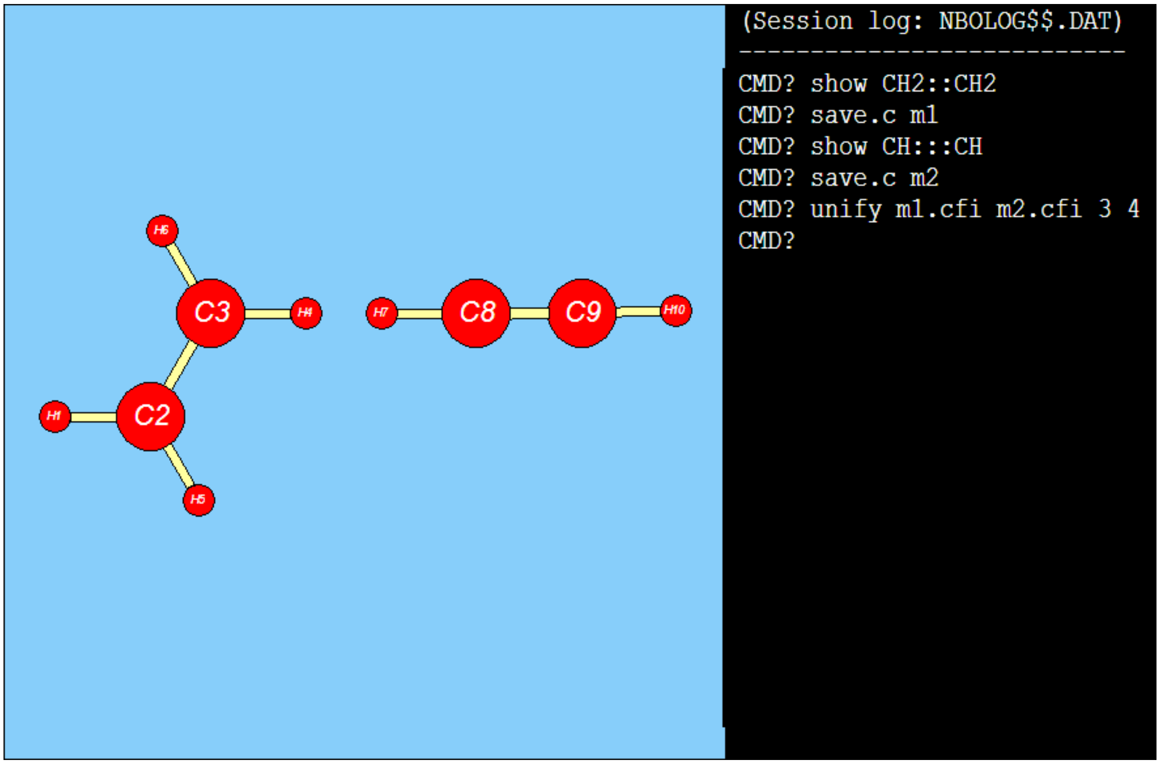


```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh HC::OOH
CMD? mu 4 CH3
CMD?
```

Building Composite Models from Monomeric Units

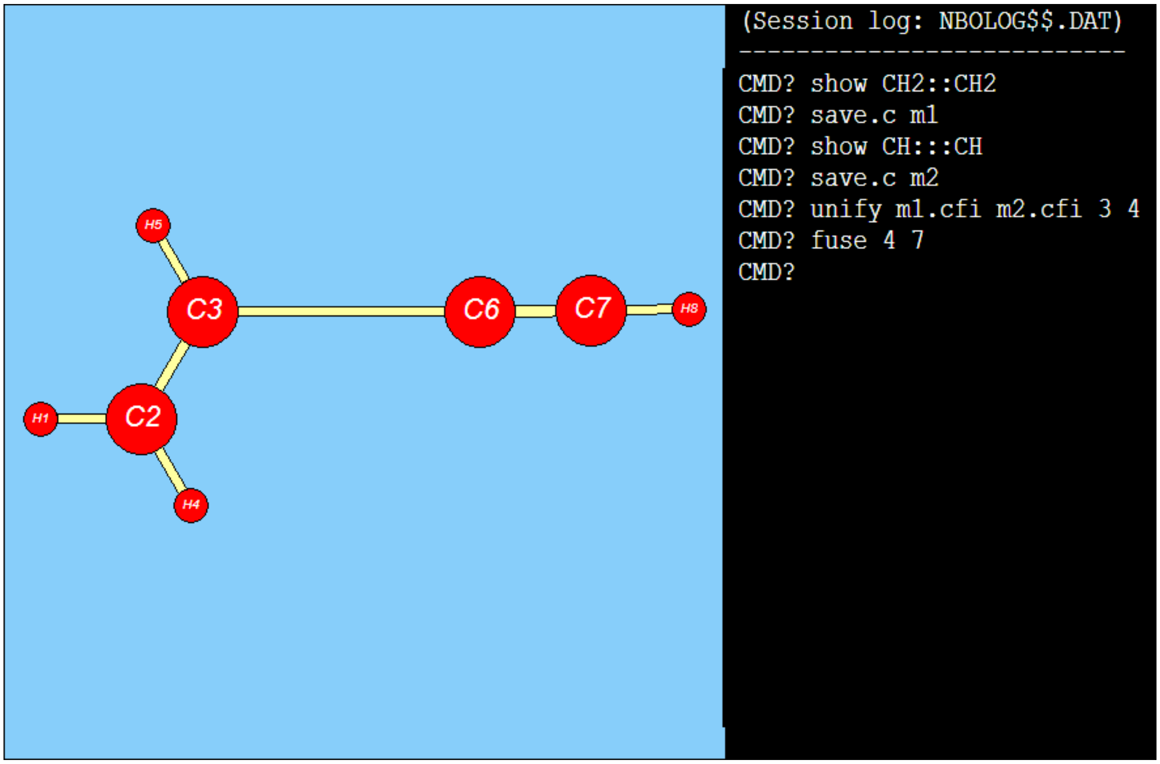
As mentioned above, coordinative show commands can be used to create certain metal ligand complexes. For example, "show `NiC:::O`" is not recognized as a valid Lewis structure, but "show `Ni(:C:::O)`" [or "show `Ni:C:::O`"] produces the expected nickel carbonyl species. Combinations of `mutate` and `alter` commands can also create more complex oligomeric species. However, two other *NBOModel* commands (`unify`,`3chb`) are more specifically designed to build composite structures from starting monomeric units

The `unify` command requires that starting monomers were previously saved in CFILE format (with "`save.c filename`"), say, as files *m1.cfi* and *m2.cfi*. One then chooses atoms *I, J* in model1 and *K, L* in model2 which are to be linearly oriented in the composite, with chosen *I*-*L* distance that will become the R_{IL} bond length after the *J,K* atoms are "fused" to complete the composite model. The first step of the composite task is accomplished by giving the "`unify m1.cfi m2.cfi I J K L distance`" command, as illustrated in the screen below for the simple example of unifying ethylene and acetylene molecules at R_{CC} = 3Å distance (with a portion of the actual command "`unify m1.cfi m2.cfi 3 4 1 2 3.0`" extending beyond the visible region of the command bar):



```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? show CH2::CH2
CMD? save.c m1
CMD? show CH:::CH
CMD? save.c m2
CMD? unify m1.cfi m2.cfi 3 4
CMD?
```

(Note that original atoms 1, 2 of the acetylene model were renumbered to 7, 8 by `unify`.) Now use the "`fuse 4 7`" command to eliminate H(4), H(7), giving the resulting vinylacetylene model (and partial atom renumbering) as shown below:

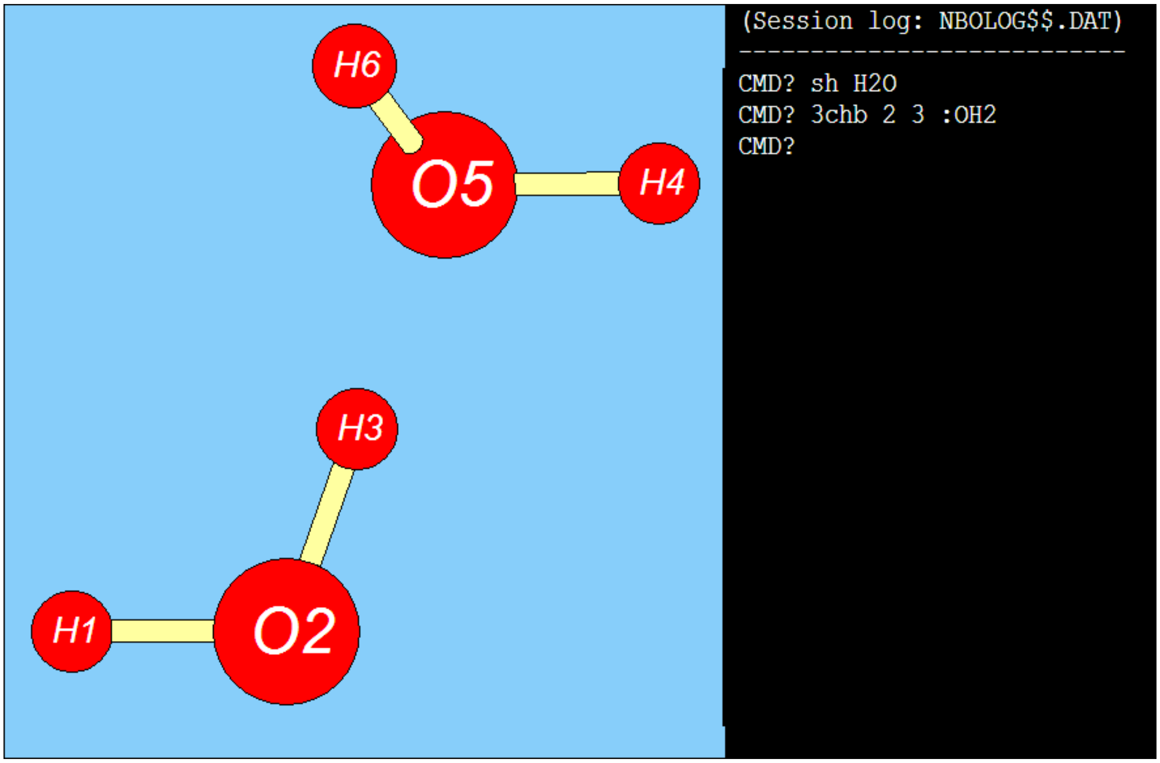


```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? show CH2::CH2
CMD? save.c m1
CMD? show CH:::CH
CMD? save.c m2
CMD? unify m1.cfi m2.cfi 3 4
CMD? fuse 4 7
CMD?
```

The originally requested distance (R_{CC} = 3Å) for the renumbered C(3)-C(6) atoms (or other features of model geometry) can now be `altered` as desired. (Of course, an improved vinylacetylene model could be obtained more directly by the "`show CH2::CHC:::CH`" command in this simple case, but the `unify`/`fuse` commands offer inherently greater flexibility for more complex composites.)

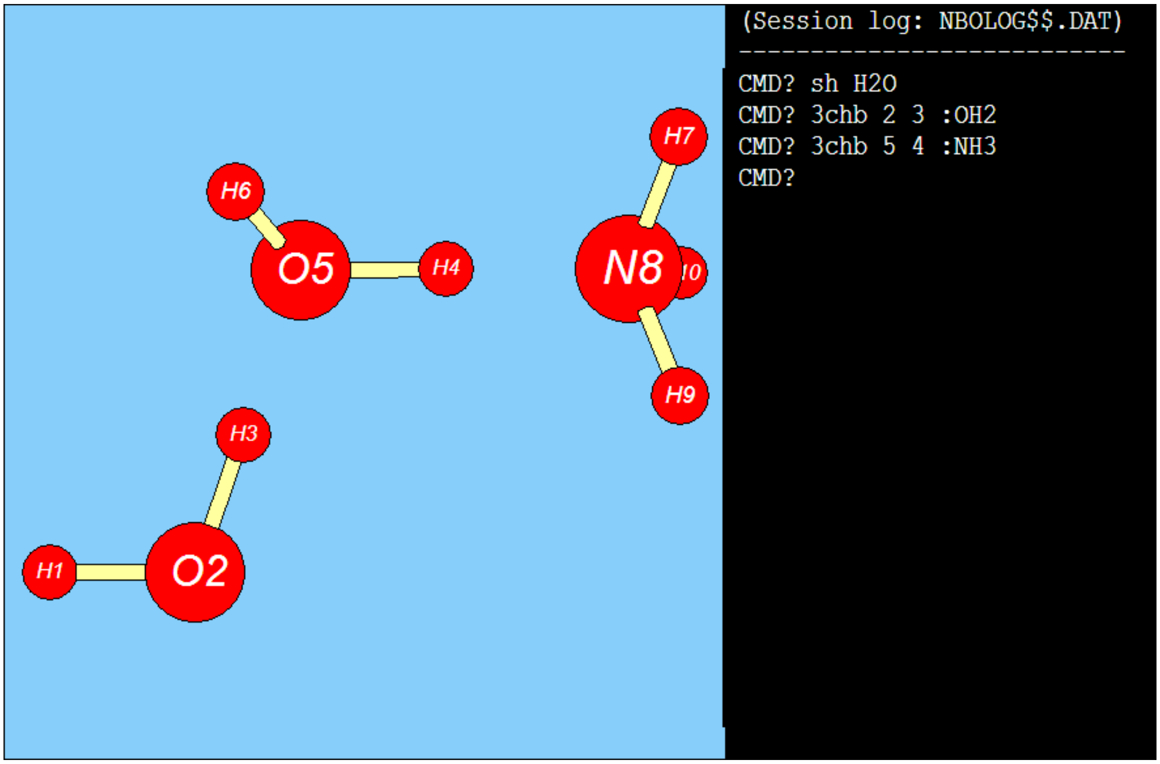
For the important class of 3-center/4-electron (3c/4e) "hyperbonding" donor-acceptor interactions (including H-bonding interactions), *NBOModel* offers the general "`3chb I J <:ligand>`" command. Starting from a monomer with expected strong Lewis acid (acceptor) character at atoms *I, J* (e.g., the σ^*_{IJ} NBO), one can use `3chb` to coordinate the *I-J* acceptor site with the principal Lewis base (donor) site of a chosen `<:ligand>` formula. The "`<:ligand>`" formula should start with a colon (":" electron-pair) symbol preceding the initial donor atom, but can otherwise follow the ordinary rules for Lewis-compliant `<formula>` input.

For example, if one starts with a water monomer and chooses the $\sigma^*_{O(2)H(3)}$ acceptor OH site (atoms 2, 3) for H-bonding, the “`3chb 2 3 :OH2`″ command leads to a respectable model of the H-bonded water dimer, as shown in the screen below:



```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh H2O
CMD? 3chb 2 3 :OH2
CMD?
```

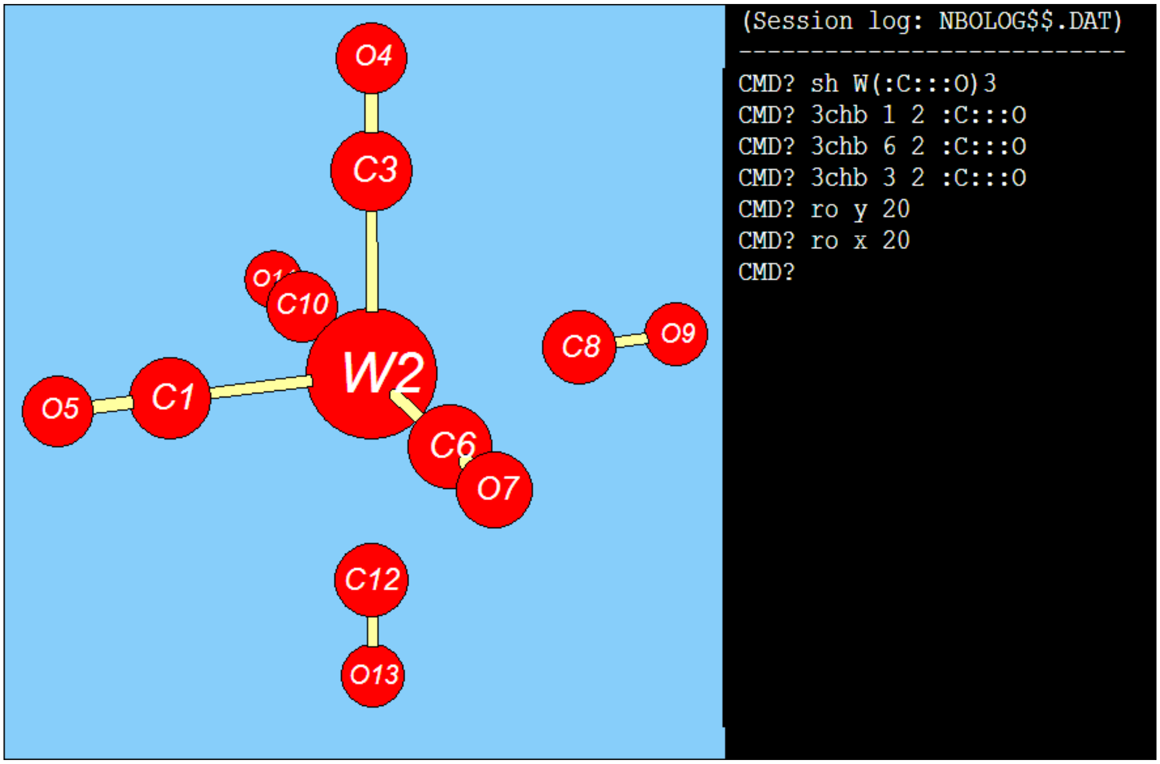
The “`3chb 5 4 :NH3`” command could then be used to coordinate this water dimer to an ammonia molecule, as shown below:



```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh H2O
CMD? 3chb 2 3 :OH2
CMD? 3chb 5 4 :NH3
CMD?
```

The examples suggest how 3chb can facilitate preparation of initial models for a wide variety of H-bonded species of chemical and biochemical interest.

One can similarly prepare the hyperbonded derivatives of many Lewis-like (12e) organometallic parent species, up to the “saturated” 18e limit. This is illustrated below for successive hyperbonded carbonyl additions from parent 12e $W(CO)_3$ to final 18e $W(CO)_6$ (with slight rotations to improve the view of the final 3D geometry):



```
(Session log: NBOLOG$$.DAT)
---------------------------
CMD? sh W(:C:::O)3
CMD? 3chb 1 2 :C:::O
CMD? 3chb 6 2 :C:::O
CMD? 3chb 3 2 :C:::O
CMD? ro y 20
CMD? ro x 20
CMD?
```

The examples illustrate how judicious combinations of `3chb`, `unify`, `alter`, and other *NBOModel* commands can be used to create reasonable starting geometries for a wide variety of composite supramolecular species, beyond those accessible to show and `mutate` commands.

Saving and Using the Edited Model

The usual final step of *NBOModel* model-building is to save the model geometry in some type ("`.t`") of file format for permanent storage and later usage under a chosen `filename`. This is requested by the corresponding "`save.t filename`" command, where the type "`.t`" parameter can be selected from the following options:

- `.c` = cartesian coordinate (.cfi) CFILE format
- `.v` = valence coordinate (.vfi) VFILE format
- `.g` = Gaussian input file (.gau)
- `.gms` = GAMESS input file (.gms)
- `.jag` = Jauar input file (.jag)
- `.mm` = MM2-type molecular mechanics input file (.mm2)
- `.mnd` = Dewar-stype AM1/MINDO input file (.mnd)
- `.mp` = Molpro input file (.mp)

- `.nw` = NWChem input file (.nw)
- `.orc` = Orca input file (.orc)
- `.pqs` = PQS input file (.pqs)
- `.qc` = Q-Chem input file (.qc)

The CFILE (cartesian coordinate) and VFILE (valence coordinate) files are internal files maintained by *NBOModel*. The CFILE format can be used to save all features of the current screen view (e.g., “`save.c myjob`”) for future usage in another session (“`use.c myjob`”).

Samples of some of these formats are shown below for CH_3NH_2 (methylamine):

CFILE (.cfi)

```
*** CH3NH2
    8    7
    1    1     -1.1237016      0.4631468     -0.8899809
    2    6     -0.7136726     -0.0142525      0.0000000
    3    7      0.7498174      0.1239404      0.0000000
    4    1      1.1297526     -0.3184206      0.8246615
    5    1     -0.9787876     -1.0715199     -0.0000007
    6    1     -1.1237016      0.4631459      0.8899817
    7    1      1.1297525     -0.3184197     -0.8246618
    8    0      0.9930423      1.0939105      0.0000005
    1    2    2    3    2    5    2    6    3    4    3    7    3    8
 1 1 1 1 1 1 1
```

VFILE (.vfi)

```
*** CH3NH2
**
   0   0   0   1  1  0.0000   0    0.00   0    0.00   0   2
   0   0   1   2  6  1.0900   1    0.00   0    0.00   0   1   3   5   6
   0   1   2   3  7  1.4700   2  109.47   3    0.00   0   2   4   7   8
   1   2   3   4  1  1.0100   4  109.47   5  180.00   6   3
   4   3   2   5  1  1.0900   7  109.47   8  300.01   9   2
   4   3   2   6  1  1.0900  10  109.47  11   60.00  12   2
   1   2   3   7  1  1.0100  13  109.47  14  300.00  15   3
   1   2   3   8  0  1.0000  16  109.47  17   60.01  18   3

  N =  0 D =    0.0000
 **
```

Gaussian input file (.gau)

```
 %mem=1GB
 #N B3LYP/6-311++G** POP=NBORead
```

```
CH3NH2

  0  1
 H
 C     1   1.0900
 N     2   1.4700    1    109.4712
 H     3   1.0100    2    109.4712    1    180.0000
 H     3   1.0100    2    109.4712    1    300.0000
 H     2   1.0900    3    109.4712    5    180.0000
 H     2   1.0900    3    109.4712    4    300.0000

$NBO file=ch3nh2 archive $END
```

GAMESS input file (.gms)

```
!
! GAMESS input generated by NBOPro
!
                               ! CH3NH2
!
$CONTRL  SCFTYP=RHF  RUNTYP=ENERGY  $END
$BASIS  GBASIS=N31  NGAUSS=6  NDFUNC=1  $END
$DATA
 CH3NH2
 C1
 H   1.    -1.123702     0.463147    -0.889981
 C   6.    -0.713673    -0.014253     0.000000
 N   7.     0.749817     0.123940     0.000000
 H   1.     1.129753    -0.318421     0.824661
 H   1.    -0.978788    -1.071520    -0.000001
 H   1.    -1.123702     0.463146     0.889982
 H   1.     1.129753    -0.318420    -0.824662
$END
$NBO file=test archive $END
```

Dewar-style MINDO/AM1 input file (.mnd)

```
   AM1

CH3NH2
   H      0.000000  0    0.000000  0    0.000000  0   0  0  0
   C      1.090000  0    0.000000  0    0.000000  0   1  0  0
   N      1.470000  0  109.471214  0    0.000000  0   2  1  0
   H      1.010000  0  109.471214  0  179.999985  0   3  2  1
   H      1.090000  0  109.471222  0  300.005585  0   2  3  4
   H      1.090000  0  109.471207  0   60.000000  0   2  3  4
   H      1.010000  0  109.471214  0  299.999969  0   3  2  1
   XX     1.000000  0  109.471230  0   60.006065  0   3  2  1
```

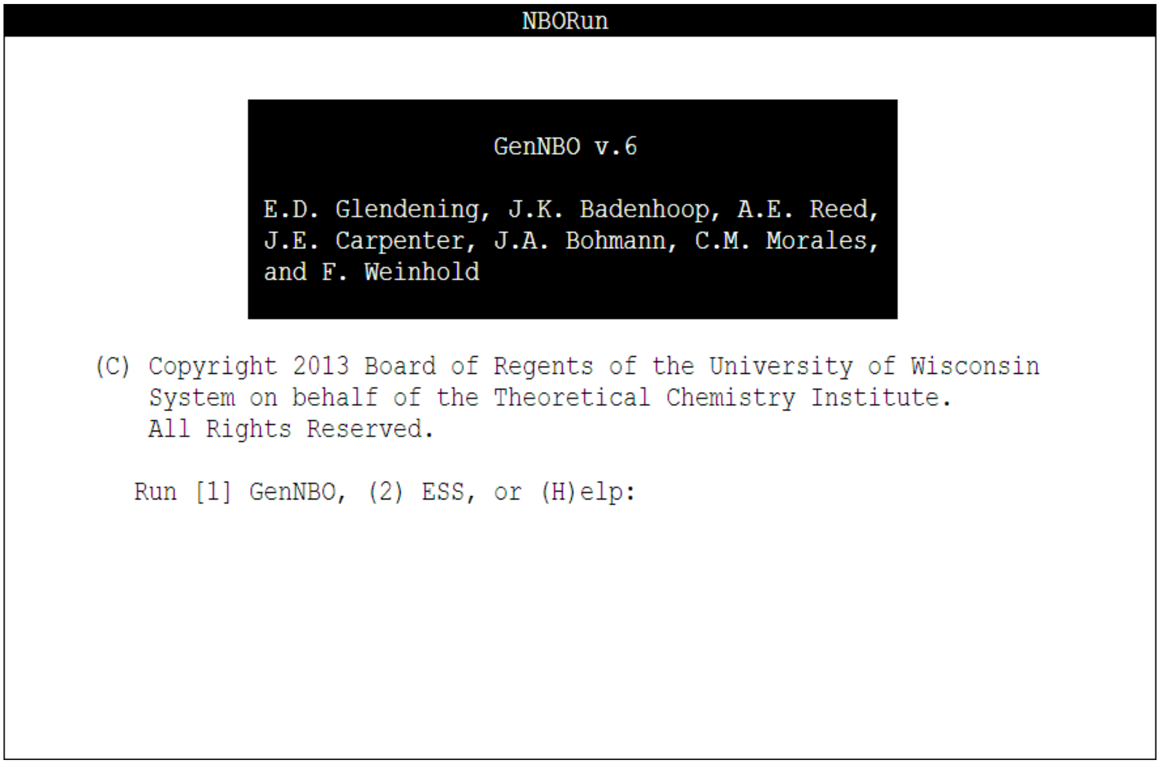
ESS input files are prepared with arbitrary default options (e.g., 6-311++G** basis for Gaussian jobs, 6-31G* for other ESS jobs) and should be edited as desired before actual usage.

NBORun: GenNBO Analysis Program

What Does The *NBORun* Program Do?

The principal function of the *NBORun* program is to perform NBO analysis (stand-alone GenNBO v. 6) on a selected input archive (.47) JOB file. *NBORun* performs desired NBO analysis options either in direct response to a user request or in indirect response to background requests from other program modules. [Optionally, *NBORun* can also calculate the wavefunction with a chosen ESS program, if a suitable user-supplied "ESS.BAT" file is included in the default directory; see further details at the end of this section.]

Launch *NBORun* (by selecting it from the *NBOPro* main menu) to see the program entry screen as shown below:



```
                    GenNBO v.6

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J.E. Carpenter, J.A. Bohmann, C.M. Morales,
and F. Weinhold

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    System on behalf of the Theoretical Chemistry Institute.
    All Rights Reserved.

   Run [1] GenNBO, (2) ESS, or (H)elp:
```
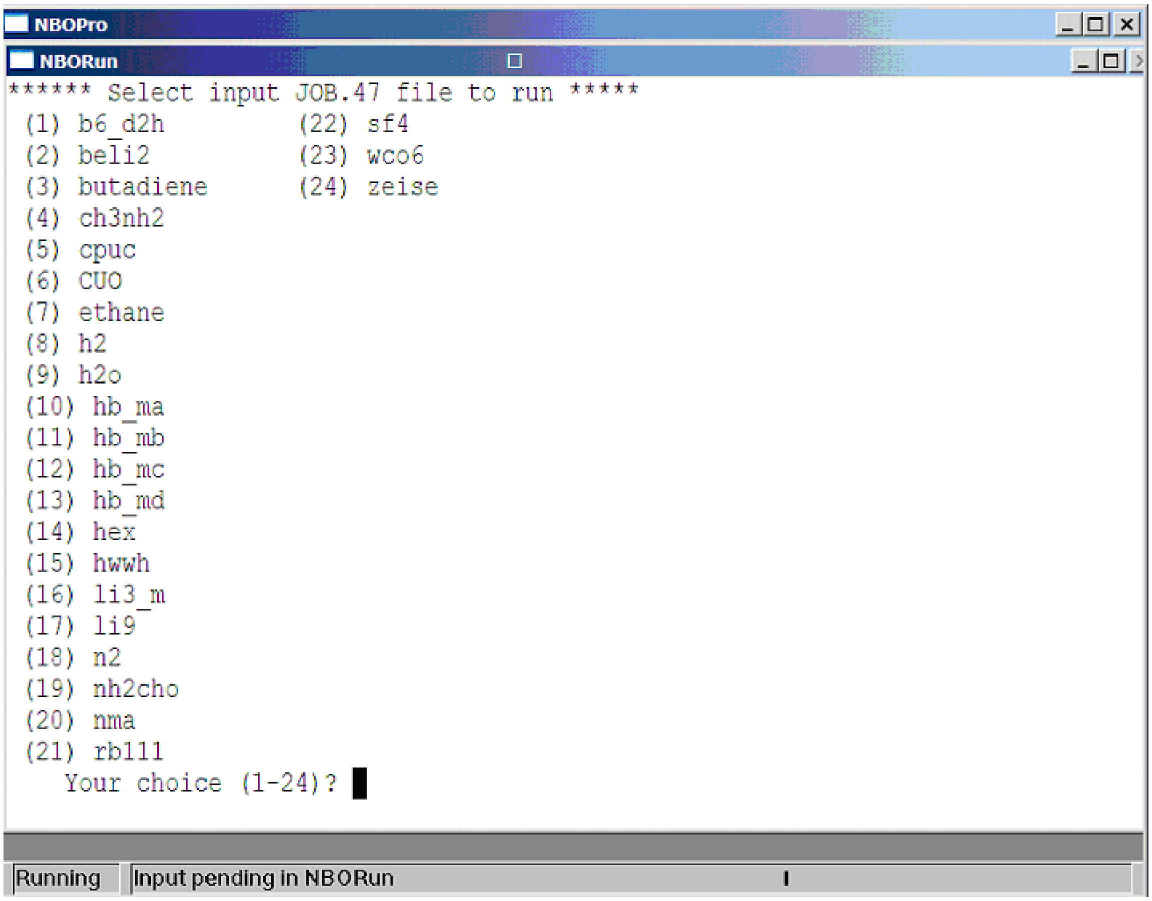
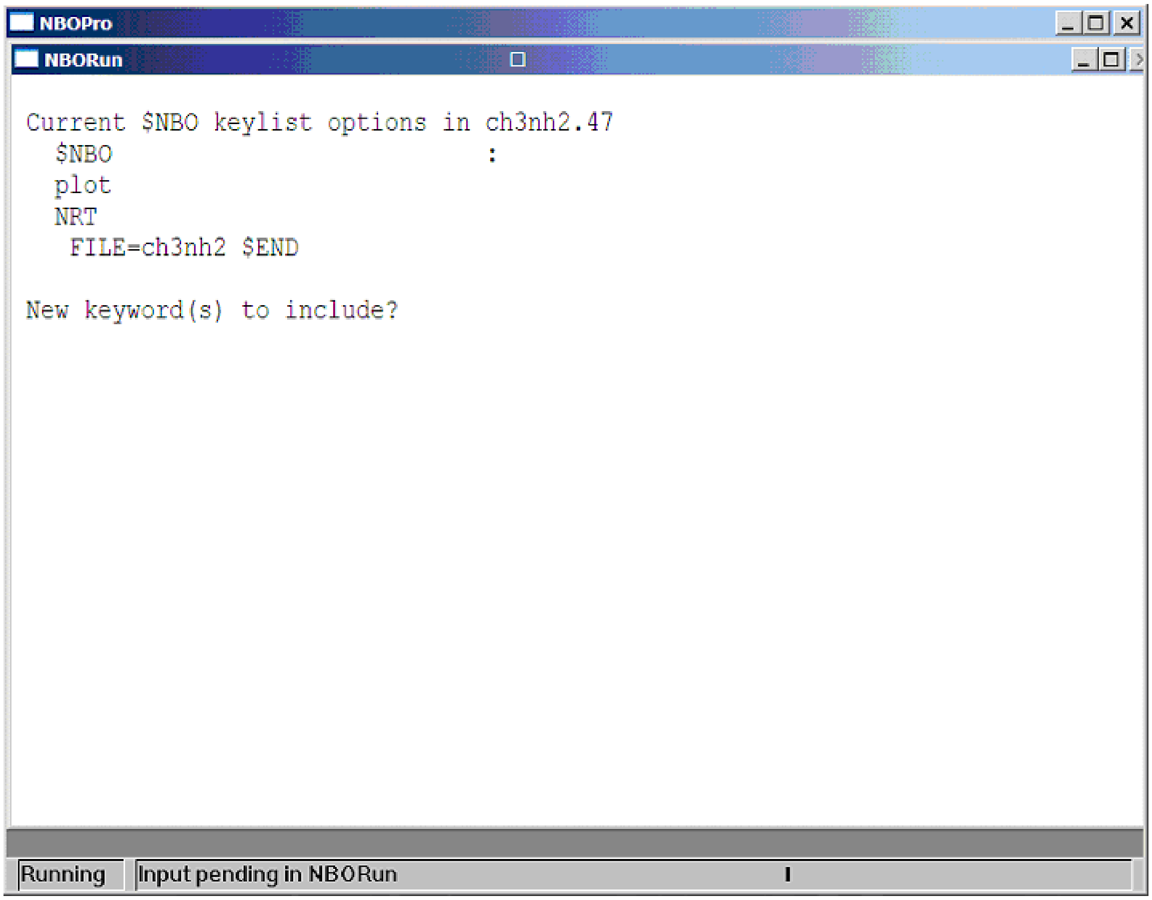

For default *GenNBO* mode, press “1” (or <ENTER>) to enter the JOB selection screen, as illustrated below:



```
****** Select input JOB.47 file to run *****
 (1) b6_d2h          (22) sf4
 (2) beli2           (23) wco6
 (3) butadiene       (24) zeise
 (4) ch3nh2
 (5) cpuc
 (6) CUO
 (7) ethane
 (8) h2
 (9) h2o
 (10) hb_ma
 (11) hb_mb
 (12) hb_mc
 (13) hb_md
 (14) hex
 (15) hwwh
 (16) li3_m
 (17) li9
 (18) n2
 (19) nh2cho
 (20) nma
 (21) rb111
    Your choice (1-24)?
```

In this case, 24 archive (“JOB.47”) files were found in the current directory. (If your own selection list is empty, copy some available JOB.47 files into the *NBOPro* directory, or re-run your favorite ESS program with the $NBO keylist “`$NBO file=JOB archive $END`” to generate the necessary starting JOB.47 file.)

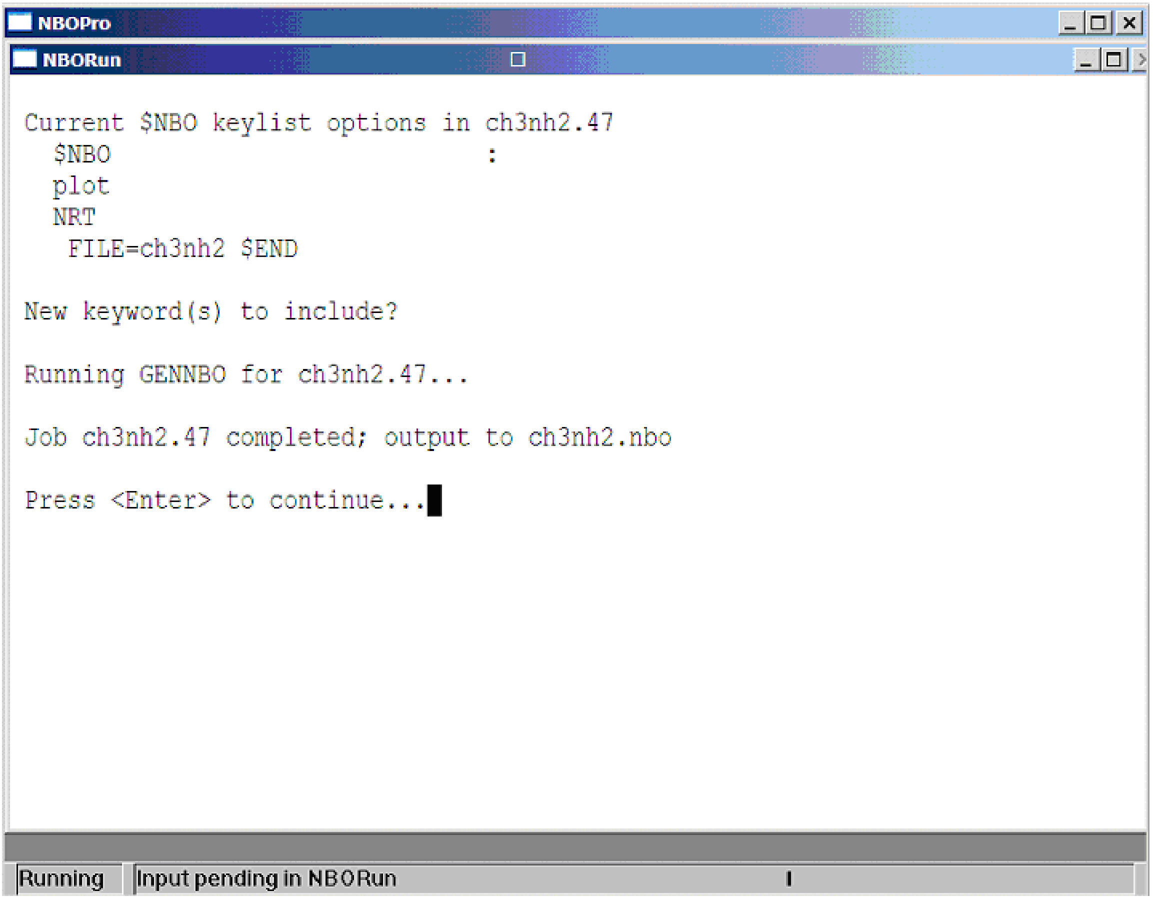
Suppose you select entry (4), the “ch3nh2” job. This leads to a screen such as that illustrated below, with keyword entries (`plot NRT ...`) that were included when the job was last run:



```
Current $NBO keylist options in ch3nh2.47
  $NBO                        :
  plot
  NRT
   FILE=ch3nh2 $END

New keyword(s) to include?
```

Enter new NBO analysis keywords, if you wish, or simply hit <ENTER> to submit the job for *GenNBO* processing.

A blank command-screen will appear as *GenNBO* is working, then the original screen will return to announce that the job is completed, as shown below:



```
Current $NBO keylist options in ch3nh2.47
  $NBO                              :
  plot
  NRT
   FILE=ch3nh2 $END

New keyword(s) to include?

Running GENNBO for ch3nh2.47...

Job ch3nh2.47 completed; output to ch3nh2.nbo

Press <Enter> to continue...
```

This announces that your job is complete, with output stored in the "ch3nh2.nbo" file, ready to be searched with *NBOSearch* or to be read in its entirety with a text editor.

Press <ENTER> to return control to the *NBOPro* main menu.

[*NBORun* can also be used in ESS mode -- option (2) on the entry menu -- to perform wavefunction calculations with a chosen ESS program. This option requires that the current directory contains a corresponding "ESS.BAT" DOS batch file (e.g., "GAMESS.BAT" for the GAMESS program) that summons an ESS program stored elsewhere on your system. *NBORun* will then display the available list of "JOB.ESS" input files for selection, insert requested NBO keylist options, and perform the requested wavefunction calculation (equivalent to issuing the "ESS JOB.ESS" batch-file command). This option permits *all* steps of a computational chemistry project to be performed within the *NBOPro* program environment, but requires previous installation of the suitably prepared ESS.BAT batch file(s). Ask your system manager whether one or more such ESS options are available on your system.]

***NBOView*: NBO Orbital Graphics Plotter**

What Does The *NBOView* Program Do?

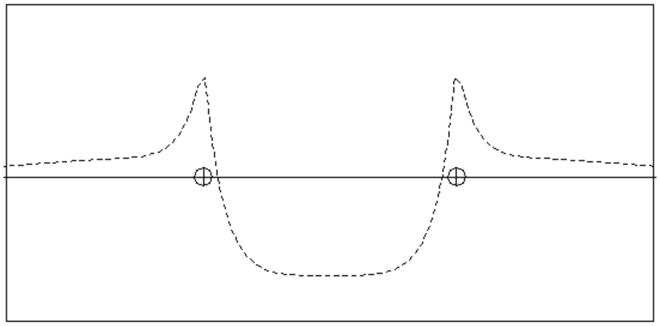
The *NBOView* program creates graphical 1D/2D/3D images of electronic orbitals produced by the Natural Bond Orbital (NBO) program (see *NBORun* module). Your NBO job should first include the PLOT keyword as an option in the input $NBO keylist (say for ethane, C_2H_6),

```
     $NBO PLOT FILE=ethane $END
```

The NBO program produces a series of "plot files" (say, ethane.31, ethane.32, ..., ethane.46) that can be read by *NBOView* to produce graphical localized and delocalized images for the chosen molecule.

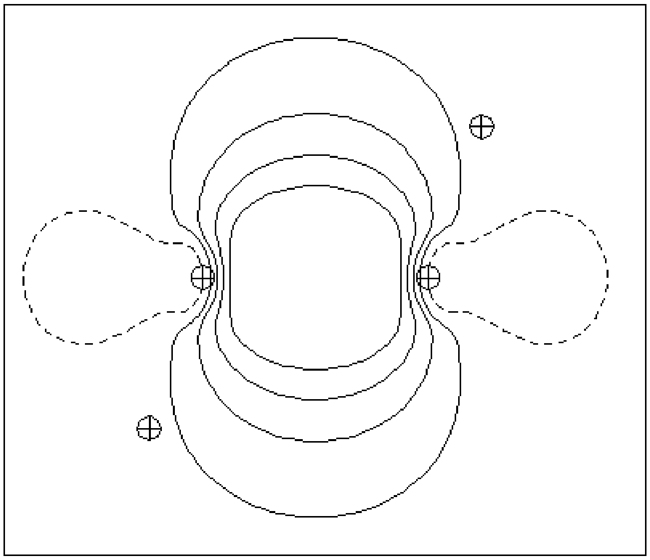
NBOView can provide a variety of 1-, 2-, and 3-dimensional graphical images of electronic orbitals (or total electron density) in individual or composite forms, using a variety of file formats suitable for viewing or printing:

- ***1-D Profile Images***



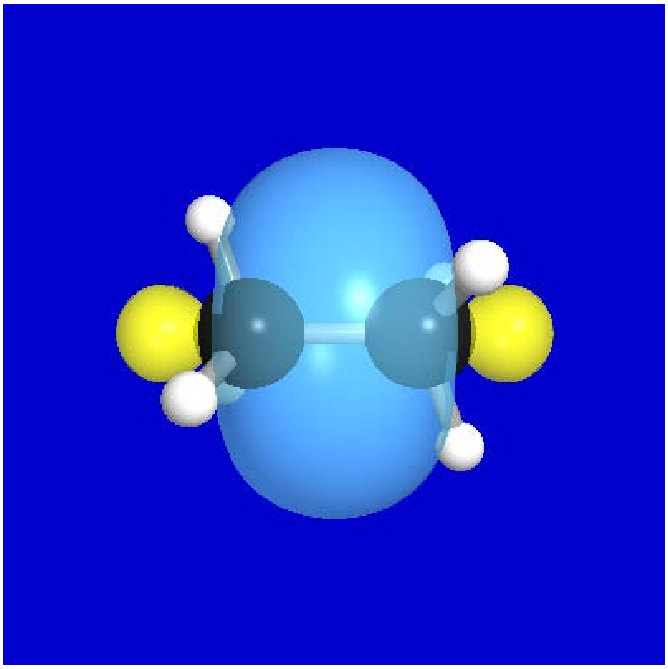
displaying a profile of the orbital amplitude (or electron density) along a chosen axis through the molecule;

- ***2-D Contour Images***



displaying contours of the orbital amplitude (or electron density) in a chosen plane within the molecule, analogous to a topographical map of the "elevations" (positive phase) and "depressions" (negative phase) of the undulating orbital waveform;

- ***3-D Rendered Images***



displaying photograph-like images of the translucent orbital lobes (blue for positive phase, yellow for negative phase) and the underlying ball-and-stick framework of the molecular skeleton, in a chosen camera and lighting model;

- ***Composite Images,*** displaying overlays of two or more individual orbital images, effective in depicting the bonding or antibonding *overlap* of the orbitals and hence the strength of their mutual interactions;

- ***Viewing, Printing, and File Storage Options,*** allowing images to be stored in bitmap (.bmp) form for convenient display or file conversion by general graphical utilities (Paint, Adobe Photoshop, etc.), as well as in scalable PostScript, native HP LaserJet bitmap, or TechSet bitmap formats for high-resolution printer output.

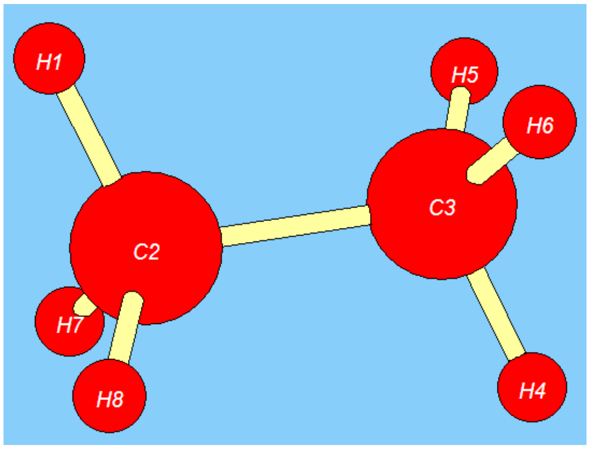
NBOView can accept input plot files from a variety of installed ESS/NBO configurations or from the *NBORun* module.

Getting Started

Prior to running *NBOView*, you must generate the required PLOT files by including the “PLOT” keyword in a chosen species (e.g., analyzed with *NBORun*). We shall suppose that the PLOT files ethane.31, ethane.32, ... for the ethane molecule (CH_3CH_3) were created with the z-matrix coordinates (e.g., using show `CH3CH3` in *NBOModel*),

```
  1    -0.8899816    -0.5138308     1.1333330
  6     0.0000000     0.0000000     0.7700000
  6     0.0000000     0.0000000    -0.7700000
  1     0.8899816     0.5138308    -1.1333330
  1     0.8899812    -0.5138308     1.1333330
  1     0.0000004     1.0276617     1.1333330
  1    -0.0000004    -1.0276617    -1.1333330
  1    -0.8899812     0.5138308    -1.1333330
```

leading to the geometry and atom numbering shown below:



Note that all orbital numbering and basis labels used by *NBOView* conform to those of the NBO output.

Launch the *NBOView* program (by selection from the *NBOPro* main menu) to see the program title page as displayed below:

```
                NBOView 2.0: NBO Orbital Graphics

                NBOView 2.0: NBO Orbital Graphics

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                     Department of Chemistry
                     University of Wisconsin
                        Madison, WI 53706

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        System on behalf of the Theoretical Chemistry Institute.
        All Rights Reserved.

    [Acknowledgments: Eric Glendening, John Carpenter, Mark Muyskens,
                      Scott Ostrander, Zdenek Havlas, Dave Anderson]

       Press <ENTER> to select JOB (plot files) or H(elp):
```
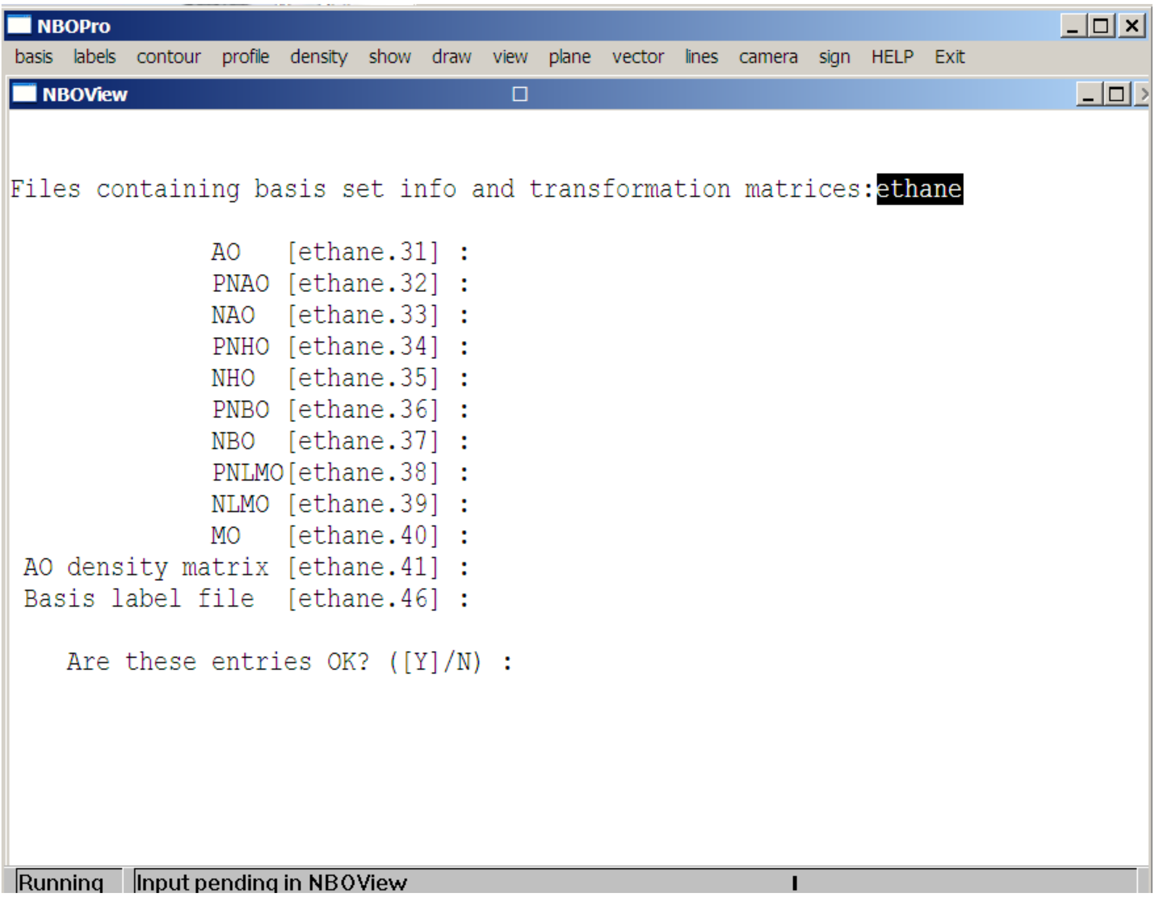
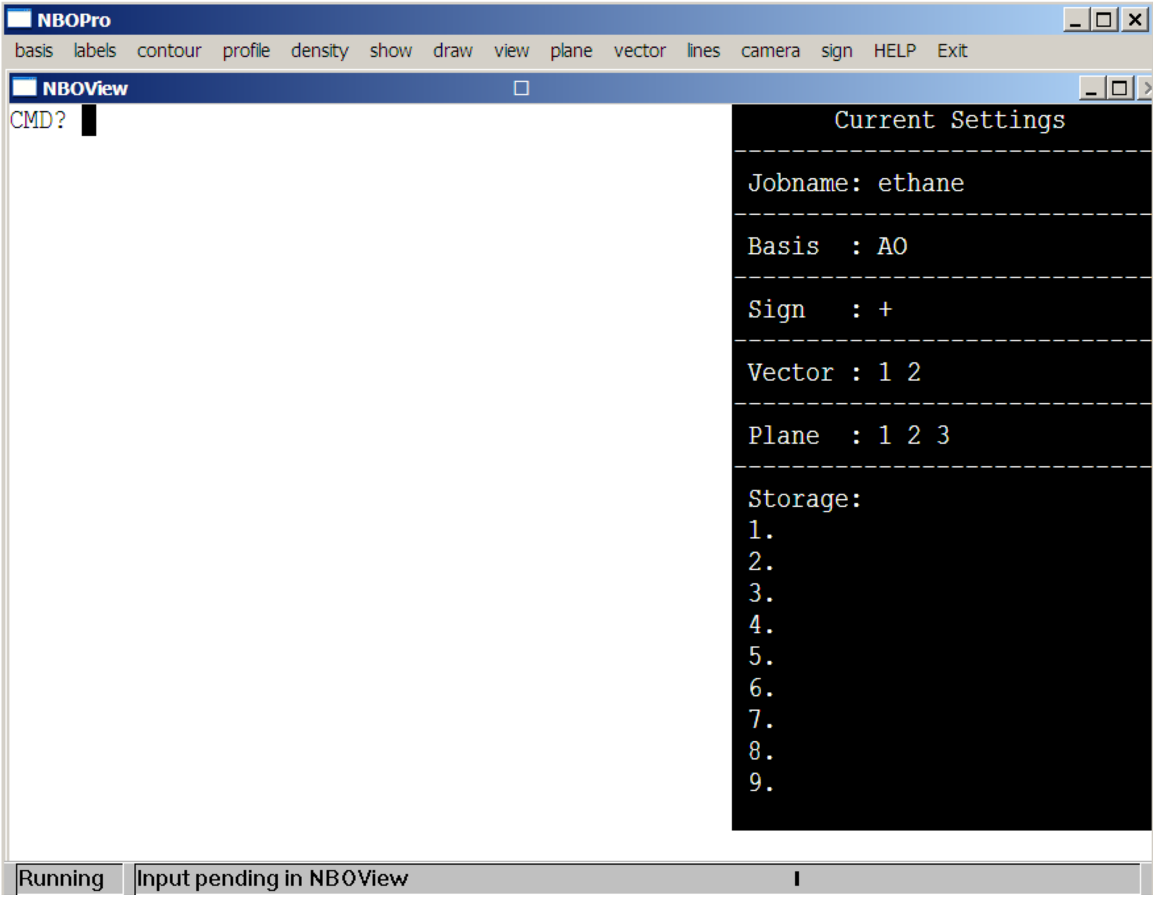

Press the ENTER (carriage return) key to continue to the PLOT input page. *NBOView* first asks for the stem-name of the molecule PLOT files; choose "ethane". You should see a list of basis sets and the associated filenames found in the directory, as shown below:



```
Files containing basis set info and transformation matrices:ethane

              AO    [ethane.31] :
              PNAO  [ethane.32] :
              NAO   [ethane.33] :
              PNHO  [ethane.34] :
              NHO   [ethane.35] :
              PNBO  [ethane.36] :
              NBO   [ethane.37] :
              PNLMO [ethane.38] :
              NLMO  [ethane.39] :
              MO    [ethane.40] :
 AO density matrix  [ethane.41] :
 Basis label file   [ethane.46] :

    Are these entries OK? ([Y]/N) :
```

In response to "Are these entries OK?", press the ENTER key to accept the default "Y" (yes) response. Throughout the program, you can simply press ENTER to accept any displayed [*default*] value enclosed in brackets. By responding "N" (or "n", "No", etc.), you can also enter a new basis filename, if you have altered a default NBO filename, or type "N" if a basis file is unavailable. Note that the AO basis info .31 file *must* be available, as well as the file for any basis set selected with the BASIS command.

After this initial program setup, the main *NBOView* command page and "Command:" prompt appears:

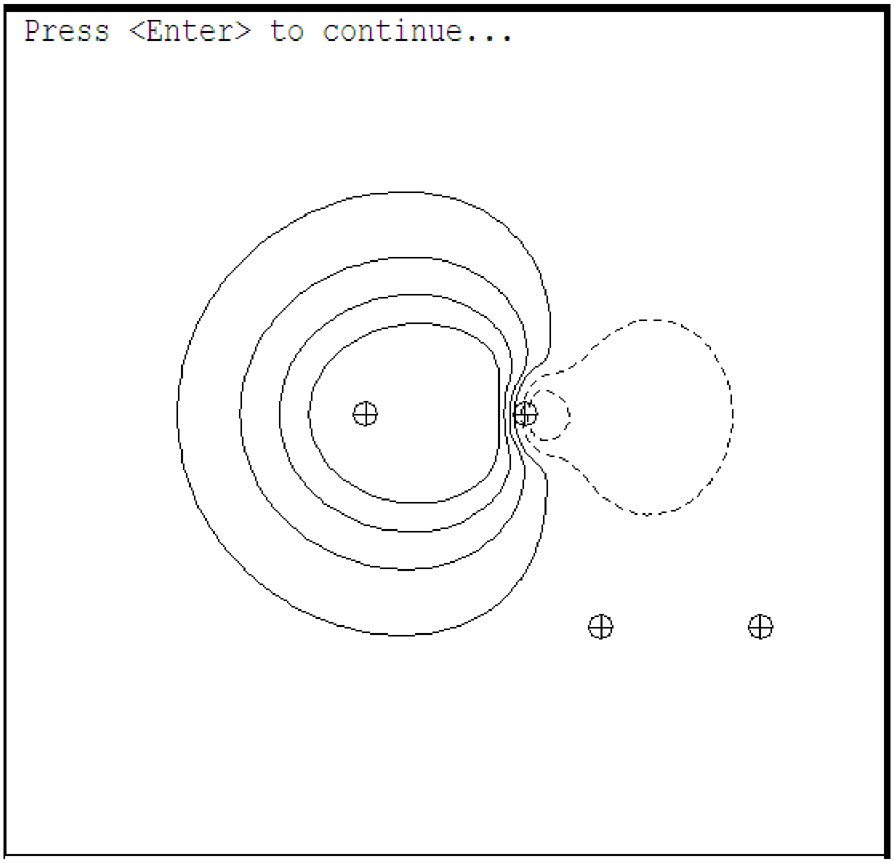


```
CMD?
```

```
       Current Settings
-----------------------------
 Jobname: ethane
-----------------------------
 Basis  : AO
-----------------------------
 Sign   : +
-----------------------------
 Vector : 1 2
-----------------------------
 Plane  : 1 2 3
-----------------------------
 Storage:
 1.
 2.
 3.
 4.
 5.
 6.
 7.
 8.
 9.
```

Running | Input pending in NBOView

The list along the top of the page gives valid commands that may be entered, as a full name or unique abbreviation. For example, type "BASIS PNBO" to select the pre-orthogonal PNBO basis set and "CONTOUR 1" to draw contours of PNBO 1 on the terminal screen. Continue pressing ENTER to accept the default parameters until the orbital image appears on the screen, as shown below:



```
Press <Enter> to continue...
```

The orbital image is also saved in location 1 of the nine available storage locations, as shown by the "[C 1] PNBO H1-C2" entry in the status bar at the right edge of the screen. The status bar summarizes the current contents of the nine storage locations *s1*, *s2*, ..., *s9*, as well as the current JOBNAME, BASIS, SIGN, VECTOR axis, and contour PLANE settings.

Now type "CONTOUR 84" to similarly display PNBO 84, which will be stored in location 2 ("[C 84] PNBO C3-H4*"). Then type "SHOW 1 2" to show an overlay of the plots stored in locations 1, 2 (i.e., an overlay of PNBOs 1 and 84, the C1-H2 bond and C3-H4* antibond). You can similarly type "PROFILE 1" to see a comparison 1D plot of the C1-H2 bond amplitude. Type "EXIT" when you wish to end the session.

These examples briefly illustrate the command-line interaction with the program. More complete specifications of available commands, syntax, and status bar entries will now be given.

Valid *NBOView* Commands

The full list of *NBOView* commands, unique abbreviations, command arguments (if any), and requested action is summarized in the table below:

NBOView Commands

Command	Argument(s)	Action
BAsis	*type*	Selects the current basis set. For example, "BASIS PNBO" selects the pre-NBO basis. For open-shell systems, the command "BASIS a" (alpha) or "BASIS b" (beta) selects a particular spin set of the current basis.
COntour	*i*	Displays 2D contours for selected orbital *i* of the current basis set in the current contour plane (see PLANE) on the terminal screen. For example, "CONTOUR 24" displays contours of orbital 24.
PRofile	*i*	Displays a 1D orbital amplitude profile for a selected orbital *i* of the current basis set along the current vector axis (see VECTOR) on the terminal screen. For example, "PROFILE 24" displays the amplitude profile of orbital 24.
DEnsity		Displays contours of total electron density in the current contour plane (see PLANE) on the terminal screen. The current basis set must be orthonormal.
SHow	*s1, s2,...*	Displays the contents of current storage locations *s1*, *s2*, ... on the terminal screen. For example, "SHOW 2,4" displays the current contents of storage locations 2 and 4 in an overlaid image on the terminal screen.
DRaw	*s1, s2,...*	Similar to SHOW, but creates a file suitable for printing on a laser printer. You will be prompted for the desired format:

		PostScript (.ps), graphics bitmap (.bmp), HP LaserJet bitmap (.hpb) , or TechSet bitmap (.tsb). For example, "DRAW 2,4" prepares an overlaid image of storage locations 2 and 4 for hardcopy output.
VIew	*s1, s2,...*	Creates a 3D rendered photo-like view of the orbital objects in storage locations *s1*, *s2*, ... and stores it in a bitmap (.bmp) file of chosen name, size, and resolution. For example, "VIEW 2,4" prepares a rendered .bmp file showing 3D images of the orbitals in storage locations 2 and 4.
PLane		Allows user to specify the contour plane for CONTOUR and DENSITY plots. Full details of requested input are described below. The default contour plane contains the first three atoms of the molecule, with the origin (screen center) midway between the first two atoms.
VEctor		Allows user to specify the vector axis for PROFILE plots. Full details of requested input are described below. The default profile axis passes through the first two atoms of the molecule, with the origin (screen center) midway between these atoms.
LIne		Allows user to specify the number and types of the contour lines (outermost contour, contour interval, maximum number of contours) as well as details (length, spacing) of the dashed lines for contours of negative phase. Initial defaults are provided for all parameters. The default outermost contour (0.0316 a.u.) corresponds roughly to the empirical van der Waals radius [see Bader and coworkers, J. Chem. Phys. **46**, 3341 (1967)].
CAmera		Allows user to specify details of the camera and lighting model for fully

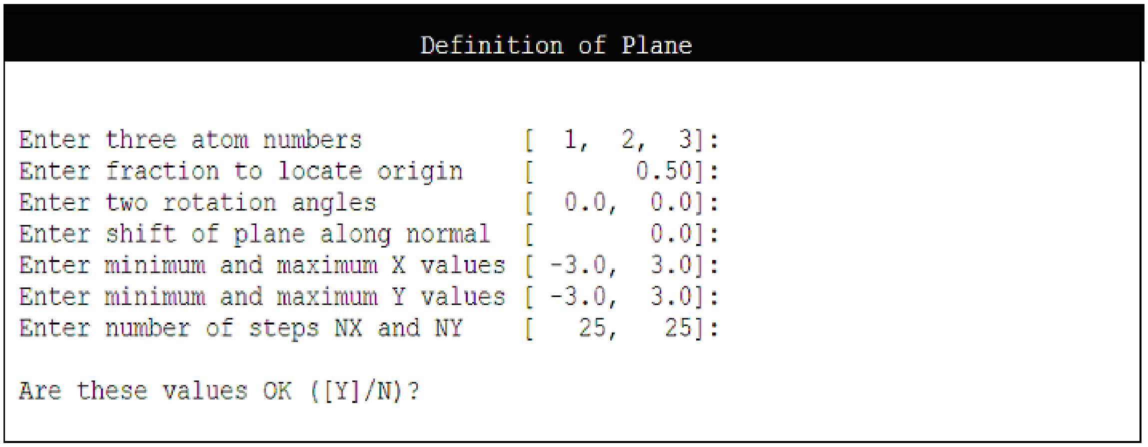
		rendered 3D images, including many details of viewing angle and light sources as well as color, translucency, and surface reflectivity of orbitals, atoms, and bonds. Full details of requested input parameters are described below, with recommended defaults provided for all parameters.
SIgn		Reverses the overall sign (phase) of orbitals, interchanging positive (blue) and negative (yellow) lobes of subsequent CONTOUR or PROFILE plots. The SIGN command toggles between the two possible overall signs (+ or -), as shown in the status bar.
LAbel		Displays a list of orbital labels for the current basis set. The numbers and labels correspond to those used in NBO output.
Help	*command*	Provides a brief on-screen summary of command syntax, parameters, abbreviation, and function for each command. For example, the command "HELP DRAW" displays help for the DRAW command.
Exit		Normal exit from the program (return to *NBOPro* main menu).

Multiple arguments may be separated by commas or spaces. In general, all input is case-insensitive and commands may be abbreviated by their leading unique characters. Thus, the command "DRAW 1 2" could be entered as "draw 1 2", "dr 1 2", etc. Further details of the dialog associated with individual commands are given in following sections.

Defining a Contour Plane

Before computing a 2D contour diagram, a contour plane must be specified. This plane can be defined to pass through three atoms of the molecule, or may be rotated by a chosen angle about either bond axis connecting these atoms. Full specification of the viewing plane also includes specifiying its center (the origin of a cartesian *X,Y* axis system that describes any position in the plane) and the outermost limits in the *X* and *Y* directions. Dialog to define the plane is initiated whenever you give the PLANE command, or upon first use of a CONTOUR or DENSITY command.

The dialog to define a contour plane is illustrated below:



```
                         Definition of Plane


Enter three atom numbers          [  1,  2,  3]:
Enter fraction to locate origin   [        0.50]:
Enter two rotation angles         [  0.0,   0.0]:
Enter shift of plane along normal [         0.0]:
Enter minimum and maximum X values [ -3.0,   3.0]:
Enter minimum and maximum Y values [ -3.0,   3.0]:
Enter number of steps NX and NY   [   25,    25]:

Are these values OK ([Y]/N)?
```

The bracketed default values may be accepted by pressing the ENTER key at every prompt. Otherwise, you may type in altered values, as shown for the first prompt. Entries may be separated by commas or spaces.

The following algorithm is used to determine the plane from the prompted input:

- ***"Enter three atom numbers"*** AXIS 1 coincides with the line of nuclear centers between the first and second atoms, directed from the first toward the second. AXIS 2 is orthogonal to AXIS 1 and lies in the plane that contains all three atoms. (Pad the list of 3 atoms with zeros if the plot is for an atom or diatomic molecule.)

- ***"Enter fraction to locate origin"*** The value 0.0 places the origin on the first atom, and the value 1.0 places the origin on the second. Other values locate the origin accordingly, with AXIS 1 and AXIS 2 intersecting at the origin. The default value 0.5 puts the origin midway between the first two atoms.

- ***"Enter two rotation angles"*** AXIS 2 is first rotated about AXIS 1 by the first rotation angle (in degrees). Then, AXIS 1 is rotated about AXIS 2 by the second rotation angle (in degrees).

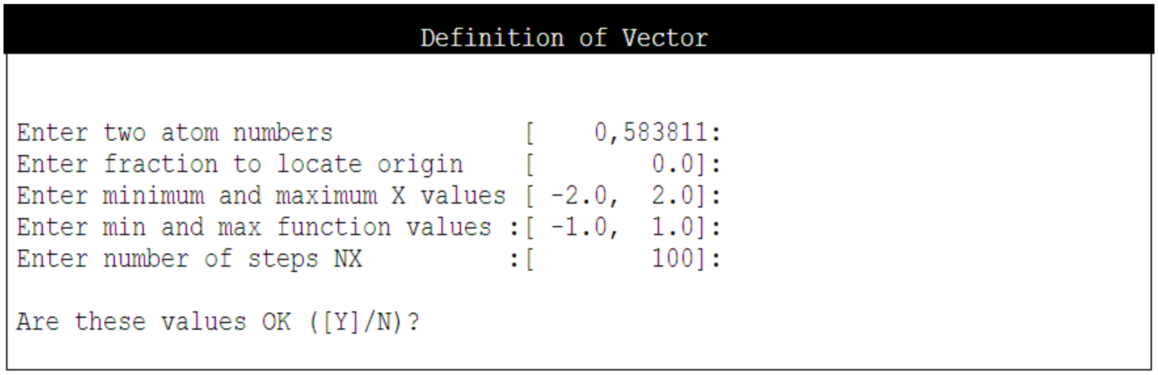
- ***"Enter shift along normal"*** The plane defined by AXIS 1 and AXIS 2 is shifted by a specified number of angstroms togward the viewer.

This completes the selection of a plane. The *X* (horizontal) axis coincides with AXIS 1 and the *Y* (vertical) axis with AXIS 2. Note that by suitable choices of these seven input parameters you can specify *amy possible* choice of the contour plane. Usually the plane will be chosen to pass through three atoms, and in this case the final three parameters (two rotation angles and a normal shift, with default values 0.0) can be ignored. However, by setting either of the rotation angles to 90 degrees, one can view contours in the plane of pi-bonding with respect to each pair of atoms. Similarly, by setting a non-zero normal shift one can select cross-sections through a pi-bond above or below the nodal plane. Thus, the input parameters are usually convenient to orient the contour plane with respect to any desired chemical features.

The three remaining dialog prompts are used to select a viewing window and density of grid points on this plane. The maximum and minimum *X*, *Y* values are in angstroms. A 25 x 25 grid is generally sufficient for contour diagrams of first-row compounds, but enhanced resolution (say, 50 x 50) may be necessary when the image has ornate nodal features.

Defining a Profile Vector Axis

The dialog to select a vector axis for orbital profile diagrams is similar. This dialog is initiated whenever you give the VECTOR command, or upon first use of a PROFILE command:



```
                    Definition of Vector


Enter two atom numbers              [    0,583811:
Enter fraction to locate origin     [         0.0]:
Enter minimum and maximum X values  [ -2.0,  2.0]:
Enter min and max function values  :[ -1.0,  1.0]:
Enter number of steps NX           :[        100]:

Are these values OK ([Y]/N)?
```

The vector coincides with the line of nuclear centers between the two atoms specified, directed from the first toward the second. The fraction

0.0 places the origin on the first atom and 1.0 on the second atom, with other values shifting the origin accordingly. Note that the maximum and minimum *X* values (distance along a bond axis) are in angstrom units, but the maximum and minimum *Y* values (orbital amplitude) are in atomic units.

Graphical Image STORAGE

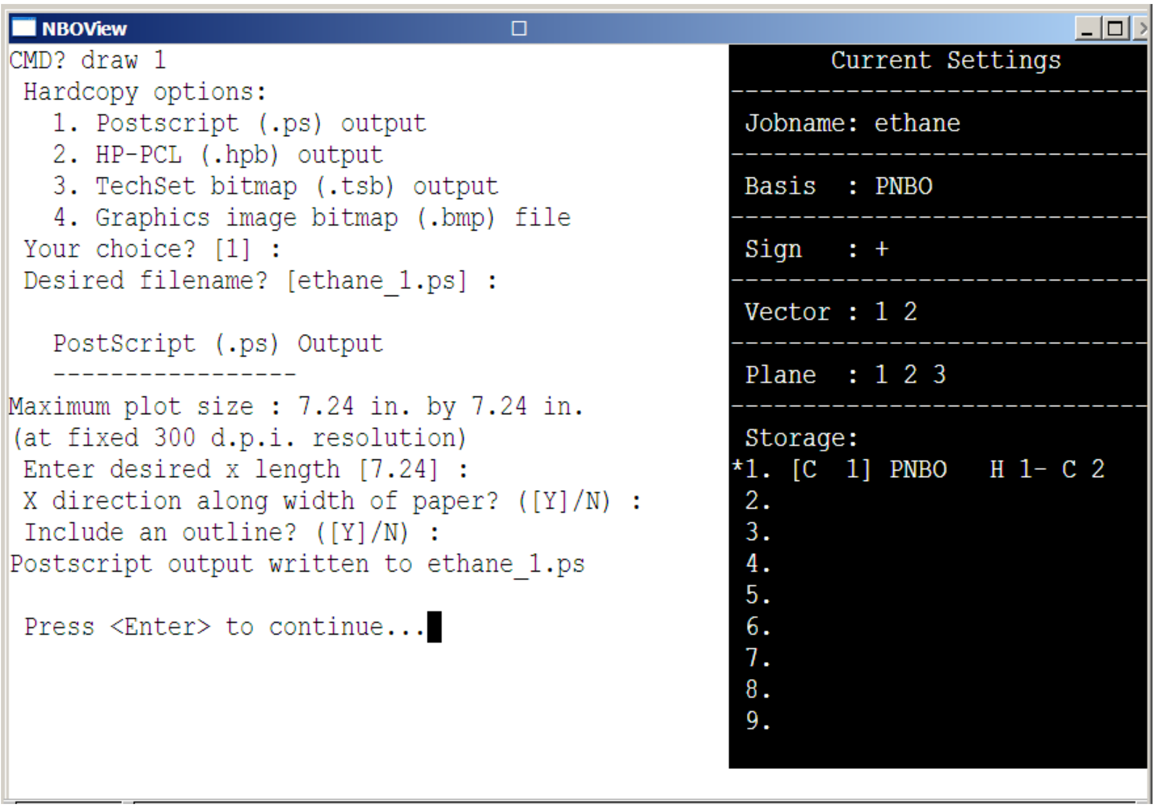
NBOView stores up to nine graphical images in memory. Each time a PROFILE, CONTOUR, or DENSITY command is given, the computed image is stored, the first image in location 1, the second in location 2, and so on. When all nine memory locations are filled, *NBOView* begins writing new images over old ones, so that the tenth image in written to location 1, the eleventh to location 2, and so on. The most recent entry is marked with an asterisk (*) in the "current settings" status bar area at the right edge of the screen.

DRAWing Stored Images to a Hardcopy Device

Like SHOW or VIEW, the DRAW command refers to images that have already been created and stored with CONTOUR or PROFILE commands:

```
     DRAW s1, s2, ...
```

The DRAW command leads to dialog for desired output options as shown below for default Postscript output:



```
CMD? draw 1
 Hardcopy options:
   1. Postscript (.ps) output
   2. HP-PCL (.hpb) output
   3. TechSet bitmap (.tsb) output
   4. Graphics image bitmap (.bmp) file
 Your choice? [1] :
 Desired filename? [ethane_1.ps] :

   PostScript (.ps) Output
   -----------------
Maximum plot size : 7.24 in. by 7.24 in.
(at fixed 300 d.p.i. resolution)
 Enter desired x length [7.24] :
 X direction along width of paper? ([Y]/N) :
 Include an outline? ([Y]/N) :
Postscript output written to ethane_1.ps

 Press <Enter> to continue...
```

```
        Current Settings
-----------------------------
 Jobname: ethane
-----------------------------
 Basis  : PNBO
-----------------------------
 Sign   : +
-----------------------------
 Vector : 1 2
-----------------------------
 Plane  : 1 2 3
-----------------------------
 Storage:
*1. [C  1] PNBO   H 1- C 2
 2.
 3.
 4.
 5.
 6.
 7.
 8.
 9.
```

Accept the displayed [default] options by pressing the ENTER key at each prompt, or select alternatives of your choice. The default Postscript (.ps) option employs vector graphics instructions that are easily re-scaled to any desired plotsize, whereas the remaining options produce 300 dpi bitmap files that are best printed at the selected size. The HP-PCL (.hp) bitmap is of native PCL (printer control language) form that can be printed directly on any HP LaserJet-compatible laser printer. The TechSet (.tsb) bitmap can be printed with the TechSet system. The graphics image bitmap (.bmp) can be displayed or printed with many browsers or screen utilities.

Creating a 3D Rendered VIEW of Stored Orbital Images

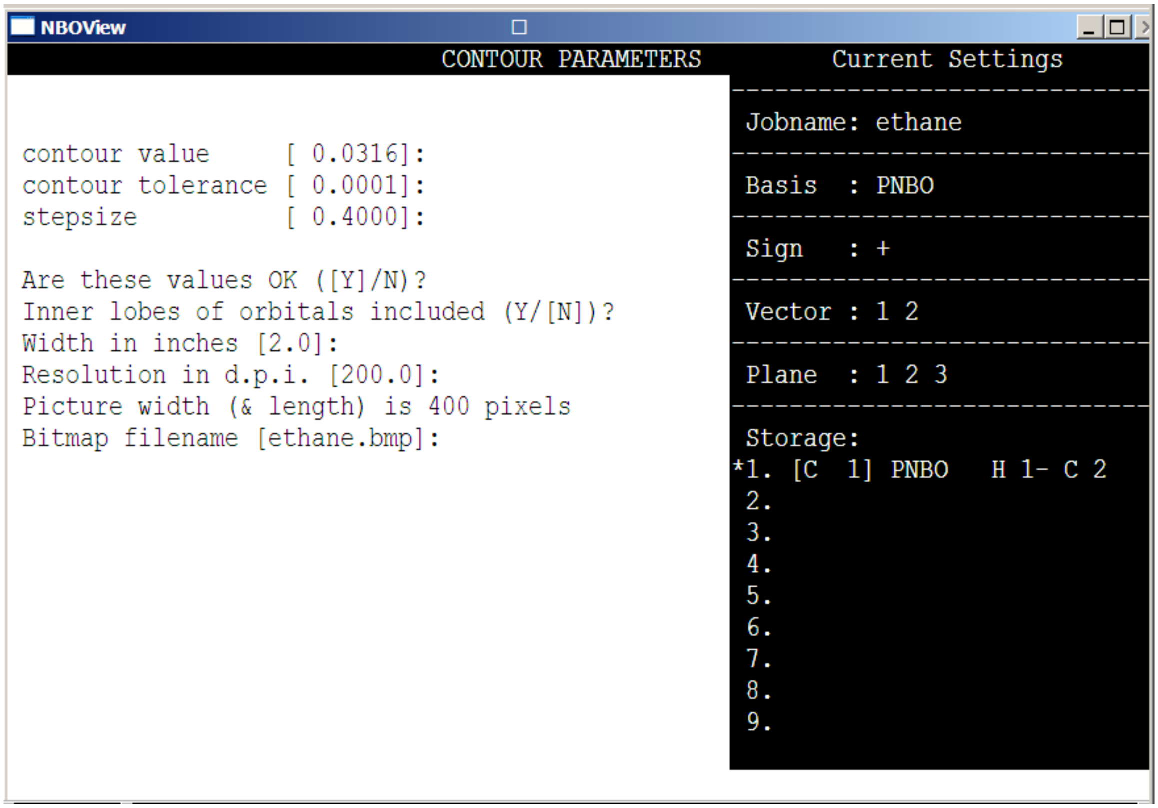
One or more orbitals that have previously been displayed and stored in memory with a PROFILE or CONTOUR command can be converted to fully rendered form as a 3-dimensional photograph-like bitmap (.bmp) image. The syntax for conversion to a 3-dimensional VIEW is similar to that for SHOW or DRAW commands, viz.,

```
    VIEW s1, s2, ...
```

where *s1*, *s2*, ... are valid storage locations (1-9) containing the orbitals to be rendered. Like the DRAW command, VIEW produces a .bmp (bitmap) file for external usage, rather than for display within *NBOView* itself. You can produce any number of VIEW bitmap files within a single *NBOView* session.

If this is your first VIEW command, you will be prompted for the input associated with the CAMERA command, which determines details of orbital optical properties, camera placement, lighting, and the like. A full description of the input dialog is given below. Initially, you can simply accept the default parameters by pressing the ENTER key in response to each prompt.

Following the CAMERA dialog, you will be prompted for lobe detail, image size, resolution, and bitmap filename as shown below:

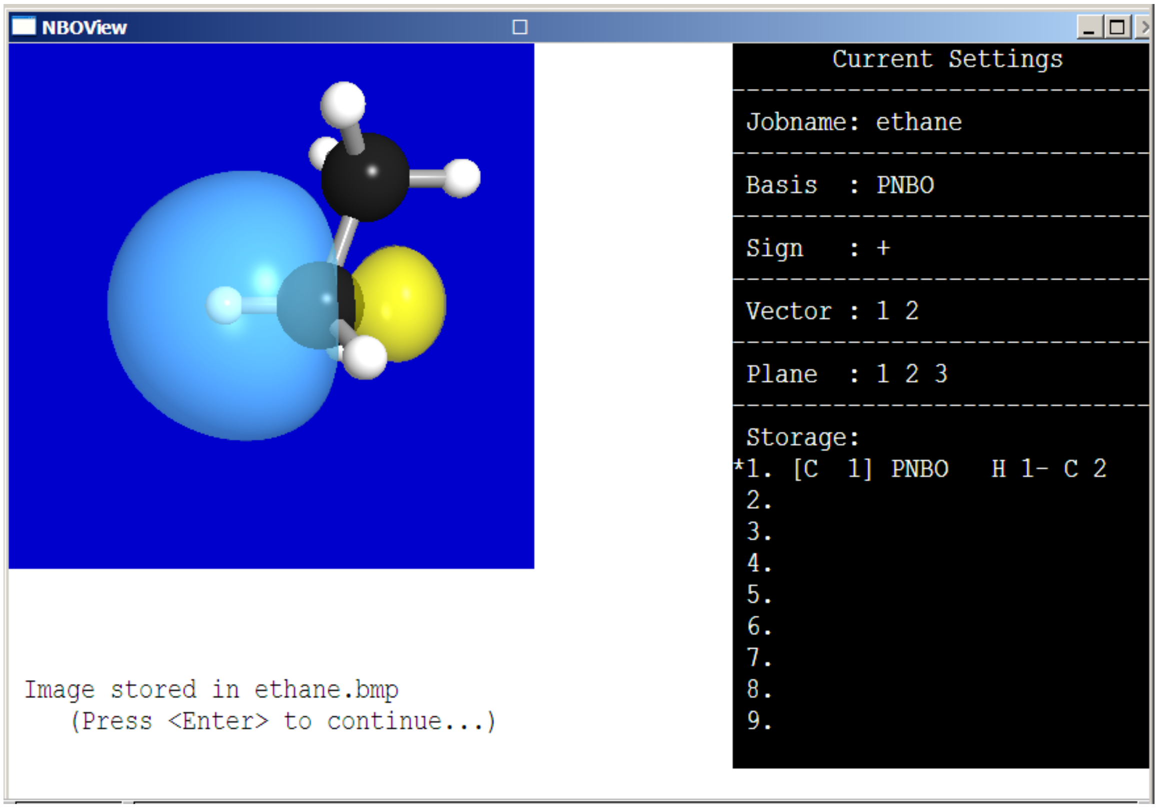


```
CONTOUR PARAMETERS

contour value     [ 0.0316]:
contour tolerance [ 0.0001]:
stepsize          [ 0.4000]:

Are these values OK ([Y]/N)?
Inner lobes of orbitals included (Y/[N])?
Width in inches [2.0]:
Resolution in d.p.i. [200.0]:
Picture width (& length) is 400 pixels
Bitmap filename [ethane.bmp]:
```

```
  Current Settings
-----------------------------
 Jobname: ethane
-----------------------------
 Basis  : PNBO
-----------------------------
 Sign   : +
-----------------------------
 Vector : 1 2
-----------------------------
 Plane  : 1 2 3
-----------------------------
 Storage:
*1. [C  1] PNBO   H 1- C 2
 2.
 3.
 4.
 5.
 6.
 7.
 8.
 9.
```

Alter the default values as desired. The default image size is 2 x 2 inches with 200 dot-per-inch resolution, adequate for ordinary screen display or printing. Note that *NBOView* employs an analytical algorithm (rather than surface triangulation) to give highest possible visual quality. Because the rendering time increases *quadratically* with image dimension or pixel resolution, long computer runs may be incurred if you select larger images or higher resolution.

After a pause for raytracing, the rendered view appears in the upper left corner as shown below:



```
Image stored in ethane.bmp
   (Press <Enter> to continue...)
```

```
        Current Settings
-----------------------------
Jobname: ethane
-----------------------------
Basis  : PNBO
-----------------------------
Sign   : +
-----------------------------
Vector : 1 2
-----------------------------
Plane  : 1 2 3
-----------------------------
Storage:
*1. [C  1] PNBO   H 1- C 2
 2.
 3.
 4.
 5.
 6.
 7.
 8.
 9.
```

The final ethane.bmp file can be viewed with a graphical browser or screen utility (such as PAINT) after you exit the *NBOView* program. The .bmp file can also be converted to .gif or other file formats for web display or other specialized graphical needs.

Specifying the 3-Dimensional Camera and Lighting Model

The CAMERA command initiates dialog to control the virtual "camera" and "lighting model" of the 3-dimensional photograph-like image produced by the VIEW command. The camera/lighting model is controlled by about 50 numerical parameters, arranged into five groups:

(1) Camera and light-source parameters
(2) Surface optical parameters
(3) Color parameters
(4) Atomic and bond radii
(5) Contour parameters

Default values can be accepted for each group by pressing the ENTER key, or the values within a group can be altered individually.

The dialog and default parameter values for each group are listed below, with brief discussion of the parameters in each case:

- ***Camera and light-source parameters***

```
camera distance from screen center  [           6.43]:
two rotation angles (about X, Y)    [    0.0,    0.0]:
camera view anle                    [           50.0]:
lighting (RL, UD, BF w.r.t.camera)  [ 2.0, 2.0,  0.0]:

Are these values OK ([Y]/N)?
```

The camera distance (in angstroms) is automatically adjusted to include the entire molecular skeleton within the viewing frame, for the fixed camera view angle. Adjust these values as needed to zoom in or out. The default rotation angles (degrees) correspond to the standard orientation in the original ESS calculation. Altering these angles gives the effect of rotating the molecule about a horizontal or vertical axis. The input rotation angles will be treated as the *change* with respect to a previous camera orientation, making it easy to pan around the viewed object (by the fixed values of the chosen rotation angles) in a movie-like sequence of VIEW images. The three "lighting" distances (angstroms) control the position of the light source right/left (RL), up/down (UD), and backward/forward (BF) with respect to camera position. The default light source is positioned to the upper right of the virtual camera.

- ***Surface optical parameters***

```
                 amb  diff  spec  pow  transp

     atoms    [ 0.60,  1.0,  1.0, 40.0,  0.0]:
     bonds    [ 0.60,  1.0,  1.0, 40.0,  0.0]:
     H-bonds  [ 0.60,  1.0,  1.0, 40.0,  0.0]:
     orbitals [ 0.60,  1.0,  1.0, 40.0,  0.0]:
```

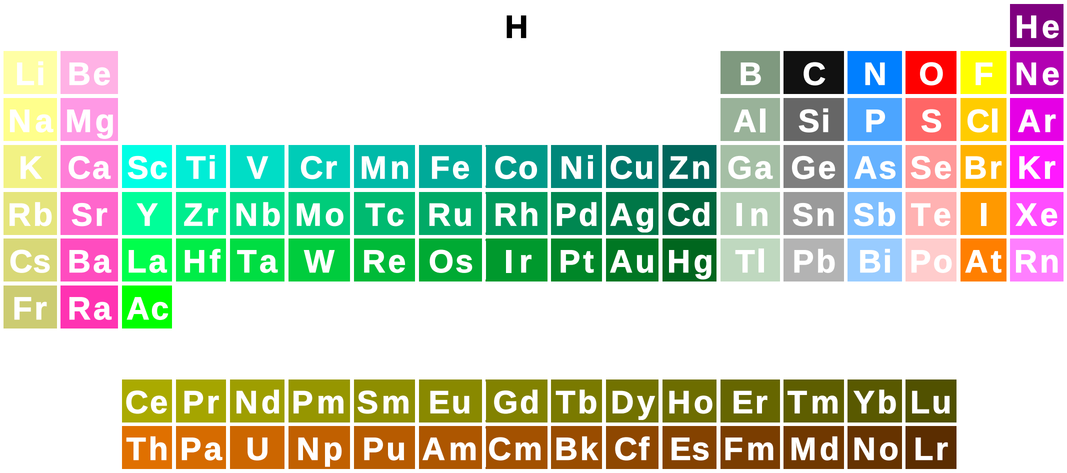
The parameters of this group control the *amb*ience, *diff*useness, *spec*ular reflection and *pow*er fall-off, and *transp*arency of the virtual surfaces of atoms, bonds, and orbitals, affecting apparent color in the rendered image. Values of these parameters (except *pow*) are in the range 0-1. For example, by changing *transp* to 1.0, the corresponding object can be rendered invisible.

- ***Color (blue/green/red) parameters***

```
                              blue  green  red

     light source color      [  1.0,  1.0,  1.0]:
     background color        [ 0.80,  0.0,  0.0]:
       [For clear background, use (1,1,1)]
     orbital (+ phase) color [  1.0, 0.80, 0.40]:
     orbital (- phase) color [  0.0,  1.0,  1.0]:
     bond color              [ 0.50, 0.50, 0.50]:
     H-bond color            [  0.0, 0.70,  1.0]:
```

Parameters of this group are the colors of the light source, background, and illuminated orbital and bond objects, each specified by its blue/green/red (BGR) components in the range 0-1. For example, the default light source is pure white (B=G=R=1) and the background is dark blue (B=0.8). The atom colors, distinguishable for every element of the periodic table, are fixed at the source code level. The complete *NBOView* atomic color table is shown below in schematic periodic table form:

NBOView **Color Periodic Table**



								H									He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

As seen, the colors for common elements correspond to familiar conventions of molecular model kits (viz., C = black, H = white, O = red, and so forth) while those for other elements are chosen to suggest chemical group and period relationships within the table (purple for noble gases, acid yellow-citrus colors for halogens, and so forth), with brightness and contrast diminishing for later members of a family.

- ***Atomic and bond radii***

```
     atomic radius for H      [ 0.22]:
     atomic radius for C      [ 0.50]:
     bond radius              [ 0.10]:
     H-bond radius            [ 0.05]:
```

Parameters in this group control the radii (angstroms) of atoms and bonds. C, H radii are independently variable, and atomic radii for other heavy atoms are automatically scaled with respect to the value chosen for C (dependent on a table of van der Waals radii embedded in source code). For example, setting the radii of H-bonds to 0.0 will remove them from view.

- ***Contour parameters***

```
     contour value     [ 0.0316]:
     contour tolerance [ 0.0001]:
     stepsize          [ 0.4000]:
```

Parameters of this group control the outermost contour (apparent orbital size) and numerical tolerances for tracing orbital surfaces. The default contour value should be kept consistent with that for 1D/2D (PROFILE/CONTOUR) plotting. Other values should not be adjusted except for unusual numerical convergence failures.

Saving Your Favorite Settings as Default Options

Each time you select new parameters under a BASIS, VECTOR, PLANE, or CAMERA command, your choices can be recorded in a special NBOVIEW.DEF options file to replace standard *NBOView* default values when you next enter the program. This allows you to recall or customize *NBOView* program settings for a particular application or general personal preference.

To record your current options for possible use in a future session, answer the EXIT question

```
     Save current settings to NBOVIEW.DEF file (Y/[N])?
```

in the affirmative by typing "Y" (or "y"). If this file exists on the *NBOView* directory, you will be asked whether you wish to use it the next time you enter the program:

```
     Use program settings in NBOVIEW.DEF file (Y/[N])?
```

Declining the invitation (or removing the NBOVIEW.DEF file from the directory) re-establishes the default *NBOView* program settings.

Running *NBOView* in Automated Batch Mode

For users with source code versions (only), it is possible to use *NBOView* in an automated batch mode, rather than interactively. In this case, the program is controlled by a special nboview.inp "script" file, prepared in advance, that serves in place of user keystrokes as the input to the program. This may be useful in automating long, repetitive tasks (such as preparing successive frames of a movie) that would be tedious for a human interactive user.

To use this option, you must set the IWBATCH ("I want batch") parameter to 1 by inserting a "C" as the first column of the “DATA IWBATCH/0/” command (near line 57 of the *nboview.f* source program file) and deleting the "C" in the first column of the following line, as shown below:

```
C      DATA IWBATCH/0/   !terminal mode
      DATA IWBATCH/1/   !batch mode (driven by NBOVIEW.INP)
```

Then rebuild the *NBOView* executable, just as you did at first installation. Next, prepare the nboview.inp file whose lines contain the input commands you would have typed at the keyboard. (For this file to work correctly, you must accurately visualize the sequence of prompts that the program gives to an actual interactive user typing the same commands.) Finally, submit the job to your system as a batch application, using standard OS commands.

NBOSearch: NBO Interactive Data Miner

What Does The *NBOSearch* Program Do?

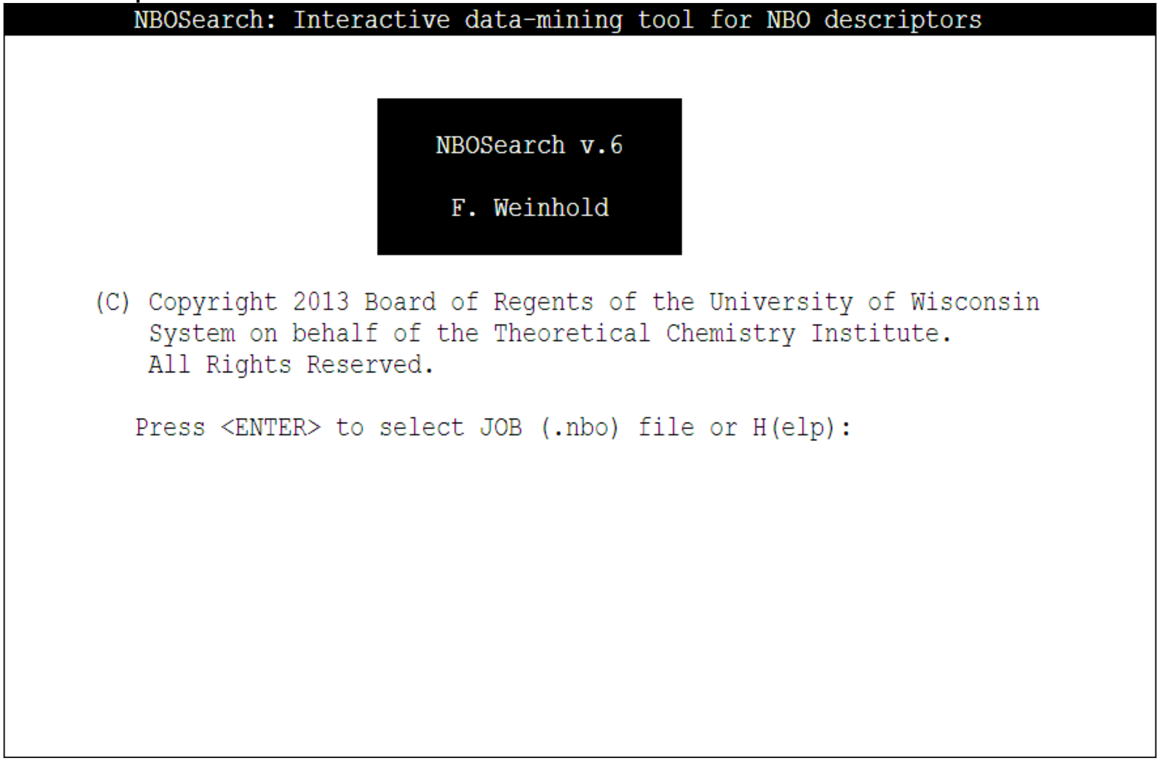
The *NBOSearch* program provides interactive access to many details of NBO analysis, whether or not you have access to (or experience in reading) conventional NBO output files. Instead of searching for a needle in an increasingly mountainous haystack of numerical output, you can get the direct answer to a direct question as promptly and conveniently as possible. If the answer can't be found in available .nbo files, *NBOSearch* will return the job to *NBORun* for re-analysis, calculating the desired result for the user in real time.

NBOSearch makes it easy to obtain comparison values from widely separated sections of NBO output, or from distinct output files of different jobs. Whether the focus is on NBO properties to be found at a specific atom or bonding site, or the most extremal such properties to be found anywhere in a molecule, or comparisons of properties across a variety of molecules or geometries (each represented by a different .nbo output file), *NBOSearch* can significantly simplify the task of data retrieval, presenting desired results in the form of numerical or graphical displays.

The range of *NBOSearch* extends far beyond default NBO output, spanning a broad variety of special keyword options. If the desired answer can in principle be found from *GenNBO* analysis, *NBOSearch* can probably deliver it to the user efficiently and accurately, without need to understand the underlying computational details.

Getting Started

Select *NBOSearch* from the *NBOPro* main menu to enter the module title screen as shown below. Spending some time with the HELP screens can help you get acquainted with the basic "*M V n*" command syntax [(*M)enu s*election/(*V)*ariable type/item (*n*)umber] that is used to navigate the bewildering number of choices available to the user in the complex *NBOSearch* decision tree.



```
NBOSearch: Interactive data-mining tool for NBO descriptors

NBOSearch v.6

F. Weinhold

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    System on behalf of the Theoretical Chemistry Institute.
    All Rights Reserved.

   Press <ENTER> to select JOB (.nbo) file or H(elp):
```
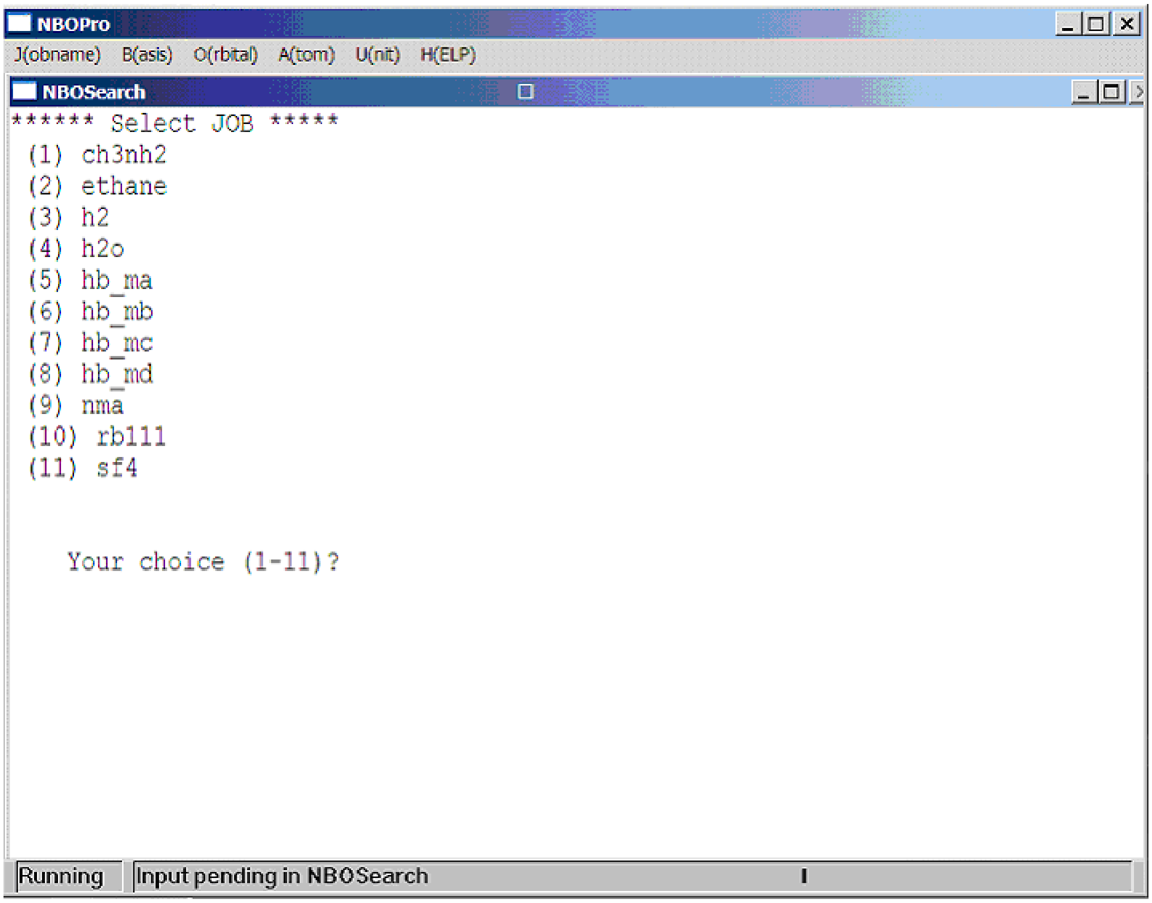
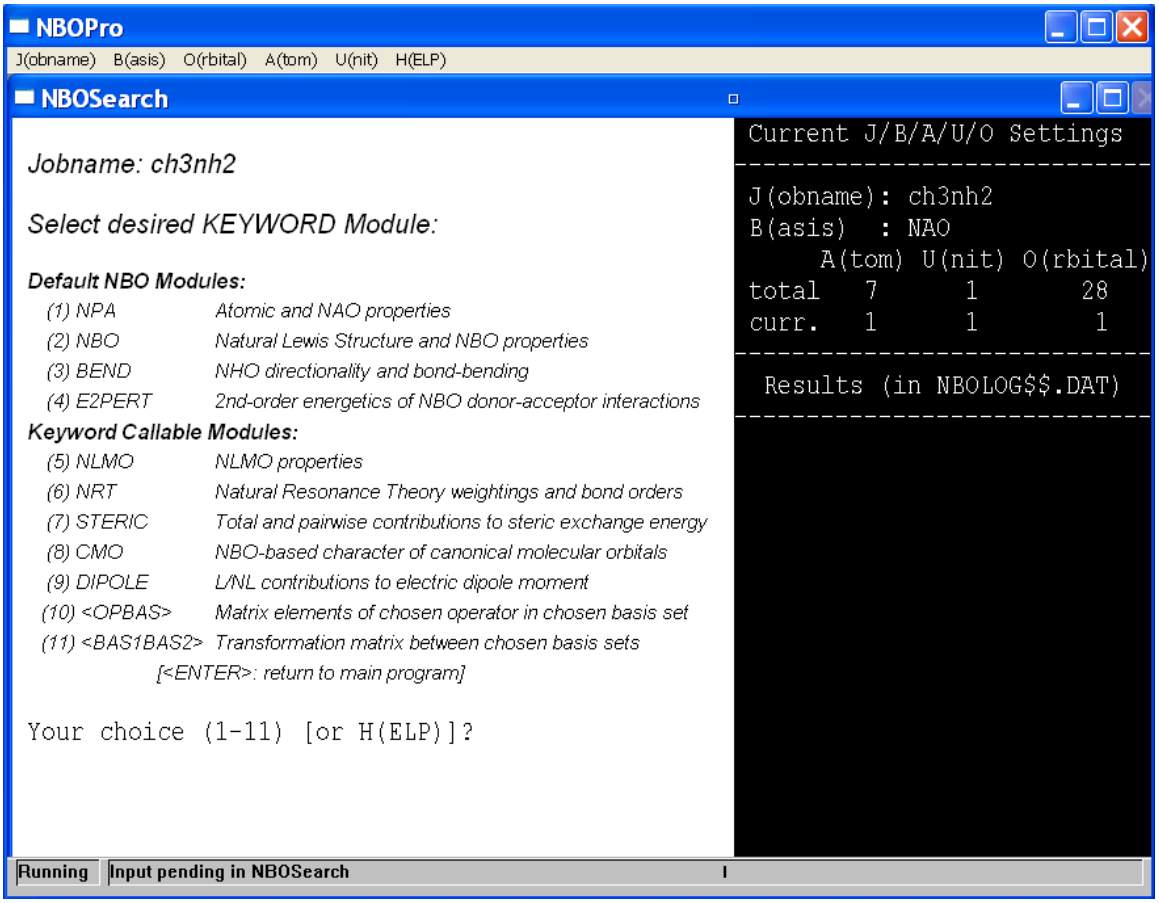

Pressing <ENTER> brings you to the JOB selection menu shown below. In this case, eleven NBO output (.nbo) files were found in the default directory. If necessary, return to the *NBORun* module to analyze additional wavefunction (archive .47) files for additional *NBOSearch* selections. We'll illustrate here with selection (1), methylamine (CH_3NH_2).



```
****** Select JOB *****
 (1) ch3nh2
 (2) ethane
 (3) h2
 (4) h2o
 (5) hb_ma
 (6) hb_mb
 (7) hb_mc
 (8) hb_md
 (9) nma
 (10) rb111
 (11) sf4


    Your choice (1-11)?
```

Selecting a JOB brings you to the main *NBOSearch* menu, as shown below. The main menu is the entryway to the eleven listed sub-menus, each corresponding to a major NBO keyword option. The first four keywords (NPA, NBO, BEND, E2PERT) are included in default .nbo output, whereas the remaining seven keywords (NLMO, NRT,...) are optional, each involving more advanced concepts. (Selecting one of the latter may involve a pause while *NBORun* re-analyzes the selected JOB with the new keyword.)



Jobname: ch3nh2

Select desired KEYWORD Module:

Default NBO Modules:

(1) NPA	*Atomic and NAO properties*
(2) NBO	*Natural Lewis Structure and NBO properties*
(3) BEND	*NHO directionality and bond-bending*
(4) E2PERT	*2nd-order energetics of NBO donor-acceptor interactions*

Keyword Callable Modules:

(5) NLMO	*NLMO properties*
(6) NRT	*Natural Resonance Theory weightings and bond orders*
(7) STERIC	*Total and pairwise contributions to steric exchange energy*
(8) CMO	*NBO-based character of canonical molecular orbitals*
(9) DIPOLE	*L/NL contributions to electric dipole moment*
(10) <OPBAS>	*Matrix elements of chosen operator in chosen basis set*
(11) <BAS1BAS2>	*Transformation matrix between chosen basis sets*

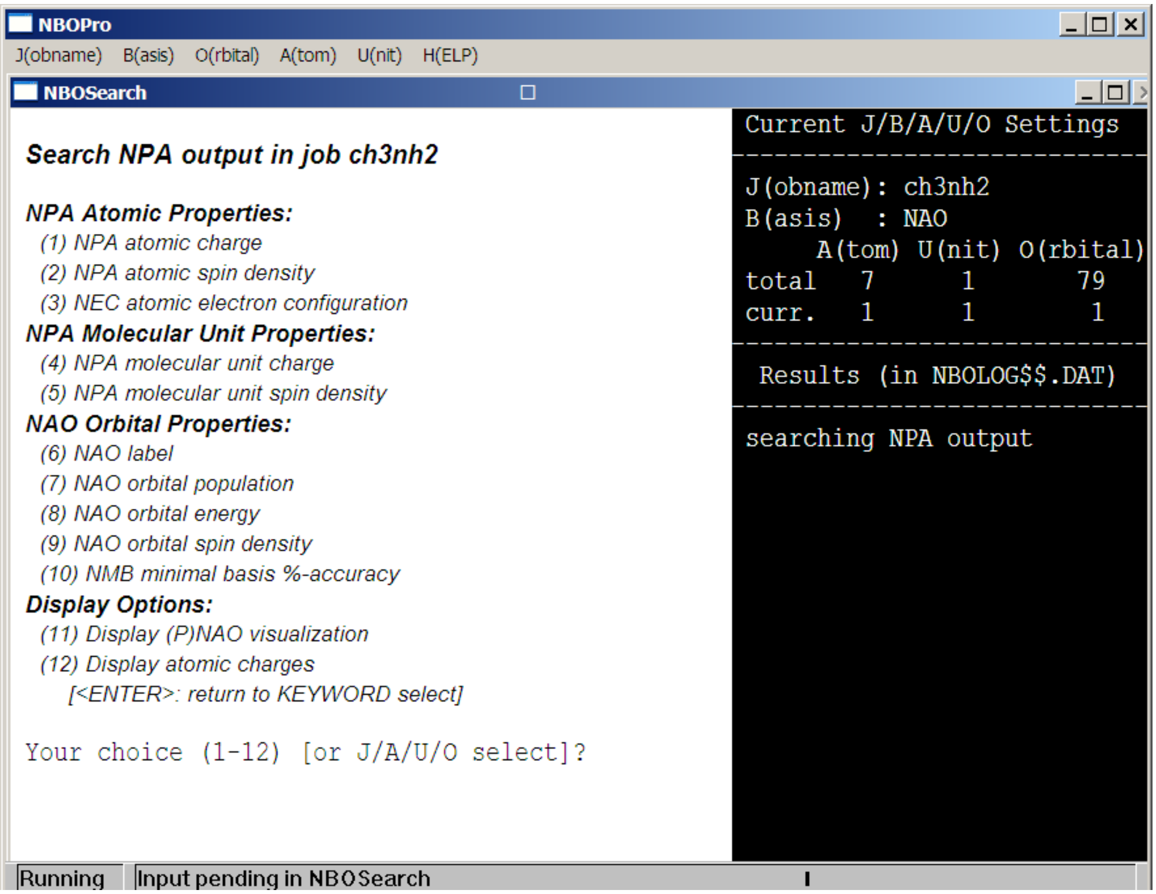
[<ENTER>: return to main program]

```
Your choice (1-11) [or H(ELP)]?
```

```
 Current J/B/A/U/O Settings
-----------------------------
 J(obname): ch3nh2
 B(asis)  : NAO
      A(tom) U(nit) O(rbital)
 total   7      1       28
 curr.   1      1        1
-----------------------------
  Results (in NBOLOG$$.DAT)
-----------------------------
```

The command bar at the right displays the current "J/B/A/U/O settings," referring to the "*V*" of a general "*M V n*" selection for your choice of J(obname), B(asis set), A(tom), U(nit), or (O)rbital. The command bar will generally be rewritten for each menu selection ("*M*") to exhibit the relevant variables ("*V*") and the number ("*n*", both current selection and total number), either set by default (as in the displayed screen) or by your most recent "*M V n*" or "*V n*" command. The "Results (in NBOLOG$$.DAT)" heading reminds you that subsequent dialog in the scrolling section of the command bar will also be echoed to the NBOLOG$$.DAT file for later reference.

Let's begin with the NPA keyword [selection (1)], which encompasses all results of Natural Population Analysis, including natural atomic charges and orbital populations for all NAOs. Hence, (A)tom numbers and (O)rbital numbers [for the default (B)asis = NAO and selected (J)obname = ch3nh2] will be the "*V n*" specifications of principal interest in this case. The screen below shows the NPA sub-menu as it first appears, with default J/B/A/U/O settings unchanged in the command bar, and with "J/A/U/O" identified as the selectable "*V*" variables in the command prompt at the lower left:

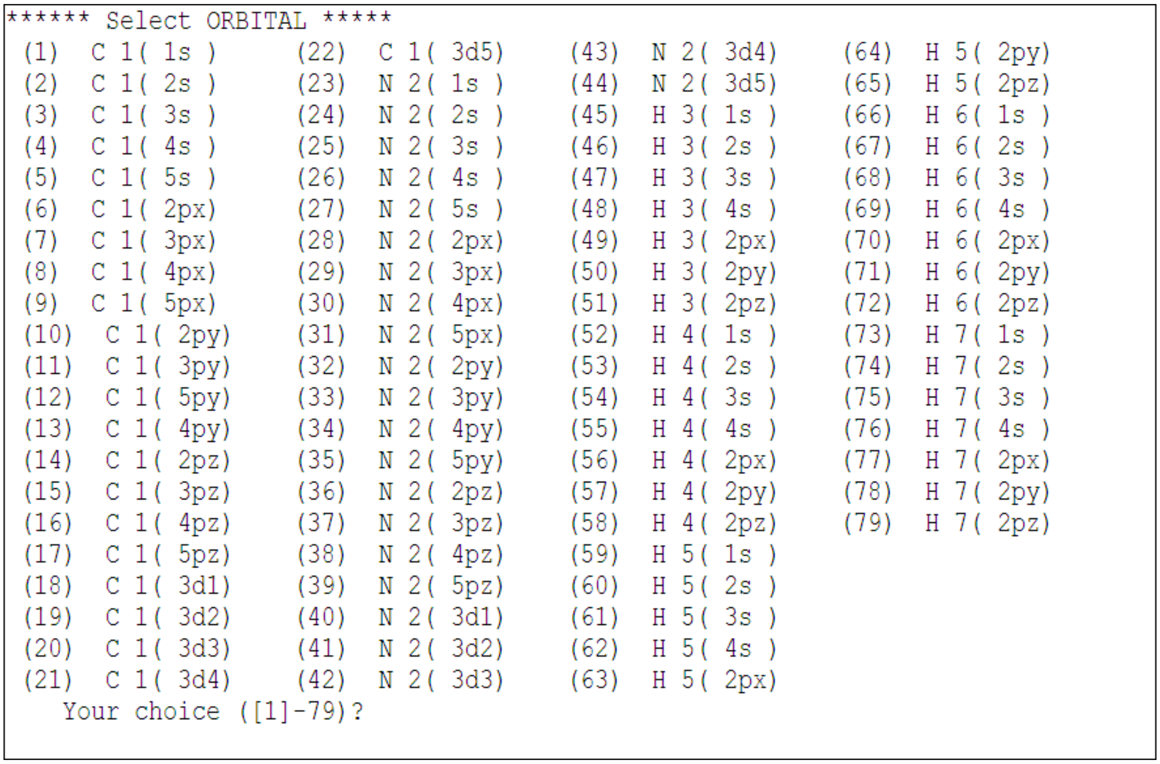


```
Search NPA output in job ch3nh2

NPA Atomic Properties:
  (1) NPA atomic charge
  (2) NPA atomic spin density
  (3) NEC atomic electron configuration
NPA Molecular Unit Properties:
  (4) NPA molecular unit charge
  (5) NPA molecular unit spin density
NAO Orbital Properties:
  (6) NAO label
  (7) NAO orbital population
  (8) NAO orbital energy
  (9) NAO orbital spin density
  (10) NMB minimal basis %-accuracy
Display Options:
  (11) Display (P)NAO visualization
  (12) Display atomic charges
     [<ENTER>: return to KEYWORD select]

Your choice (1-12) [or J/A/U/O select]?
```

```
Current J/B/A/U/O Settings
---------------------------
J(obname): ch3nh2
B(asis)   : NAO
      A(tom) U(nit) O(rbital)
total    7       1        79
curr.    1       1         1
---------------------------
 Results (in NBOLOG$$.DAT)
---------------------------
searching NPA output
```

The twelve menu selections (10 numerical and 2 display options) describe the accessible NPA-based data types in this sub-menu. However, options (4) and (5) are superfluous in this case, because there is only one molecular unit. The “Current J/B/A/U/O Settings” sidebar lists the J(obname) and B(asis) choices already selected, as well as current default values of the A(tom), U(nit), and O(rbital).

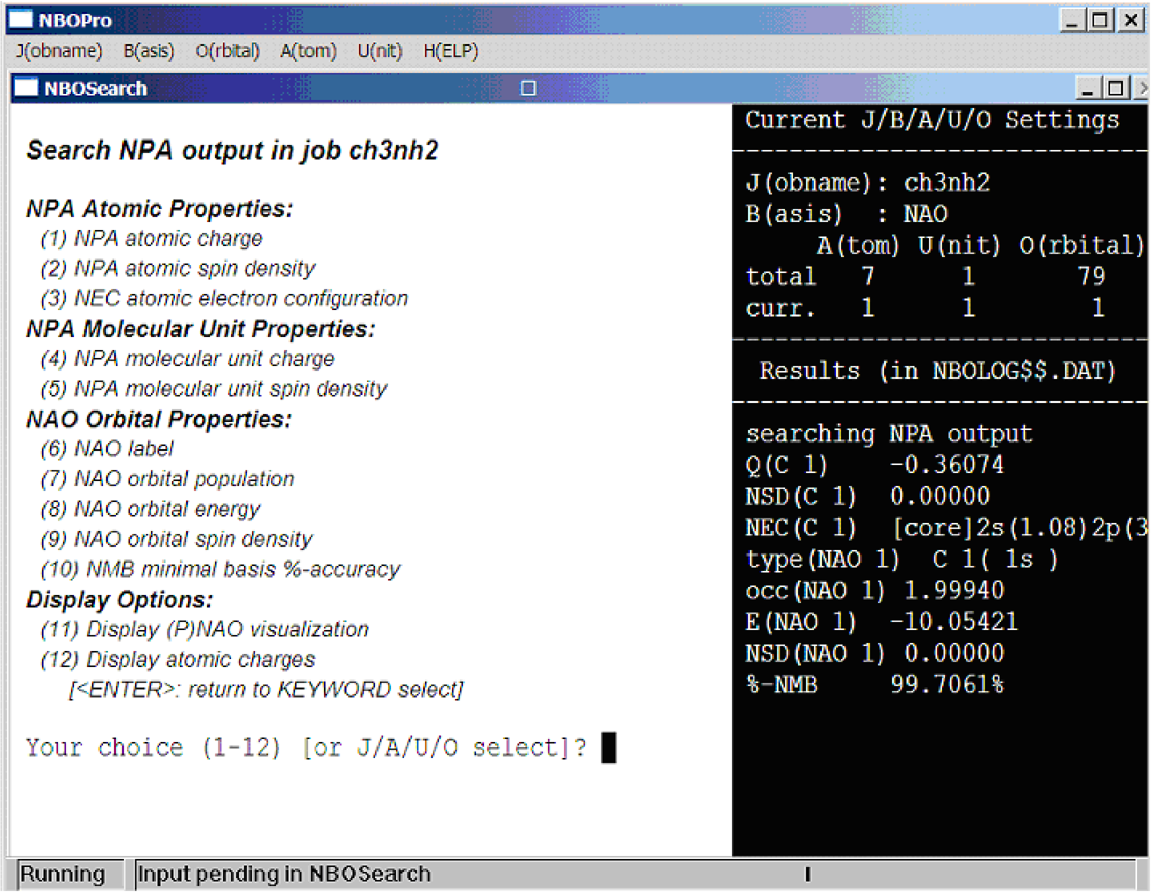
Typing “A”, “U”, or “O” without a new selected value will display a list of the available options. For example, typing “O” (or “o”) would display the available list of 79 NAOs, as shown below:



```
****** Select ORBITAL *****
 (1)  C 1( 1s )     (22)  C 1( 3d5)    (43)  N 2( 3d4)    (64)  H 5( 2py)
 (2)  C 1( 2s )     (23)  N 2( 1s )    (44)  N 2( 3d5)    (65)  H 5( 2pz)
 (3)  C 1( 3s )     (24)  N 2( 2s )    (45)  H 3( 1s )    (66)  H 6( 1s )
 (4)  C 1( 4s )     (25)  N 2( 3s )    (46)  H 3( 2s )    (67)  H 6( 2s )
 (5)  C 1( 5s )     (26)  N 2( 4s )    (47)  H 3( 3s )    (68)  H 6( 3s )
 (6)  C 1( 2px)     (27)  N 2( 5s )    (48)  H 3( 4s )    (69)  H 6( 4s )
 (7)  C 1( 3px)     (28)  N 2( 2px)    (49)  H 3( 2px)    (70)  H 6( 2px)
 (8)  C 1( 4px)     (29)  N 2( 3px)    (50)  H 3( 2py)    (71)  H 6( 2py)
 (9)  C 1( 5px)     (30)  N 2( 4px)    (51)  H 3( 2pz)    (72)  H 6( 2pz)
 (10)  C 1( 2py)    (31)  N 2( 5px)    (52)  H 4( 1s )    (73)  H 7( 1s )
 (11)  C 1( 3py)    (32)  N 2( 2py)    (53)  H 4( 2s )    (74)  H 7( 2s )
 (12)  C 1( 5py)    (33)  N 2( 3py)    (54)  H 4( 3s )    (75)  H 7( 3s )
 (13)  C 1( 4py)    (34)  N 2( 4py)    (55)  H 4( 4s )    (76)  H 7( 4s )
 (14)  C 1( 2pz)    (35)  N 2( 5py)    (56)  H 4( 2px)    (77)  H 7( 2px)
 (15)  C 1( 3pz)    (36)  N 2( 2pz)    (57)  H 4( 2py)    (78)  H 7( 2py)
 (16)  C 1( 4pz)    (37)  N 2( 3pz)    (58)  H 4( 2pz)    (79)  H 7( 2pz)
 (17)  C 1( 5pz)    (38)  N 2( 4pz)    (59)  H 5( 1s )
 (18)  C 1( 3d1)    (39)  N 2( 5pz)    (60)  H 5( 2s )
 (19)  C 1( 3d2)    (40)  N 2( 3d1)    (61)  H 5( 3s )
 (20)  C 1( 3d3)    (41)  N 2( 3d2)    (62)  H 5( 4s )
 (21)  C 1( 3d4)    (42)  N 2( 3d3)    (63)  H 5( 2px)
    Your choice ([1]-79)?
```

This allows you to select a new default value (if desired) or simply hit <ENTER> to return to the main NPA menu with the original default value. Similar listings of your J/A/O... options (or related options, as appropritate) can be obtained throughout the *NBOSearch* menu tree.

Back at the NPA menu, we can now sequentially enter numerical “*M*” selections (such as 1-3, 5-10) to obtain the successive replies shown in the dialog section of the command bar in the screen below:

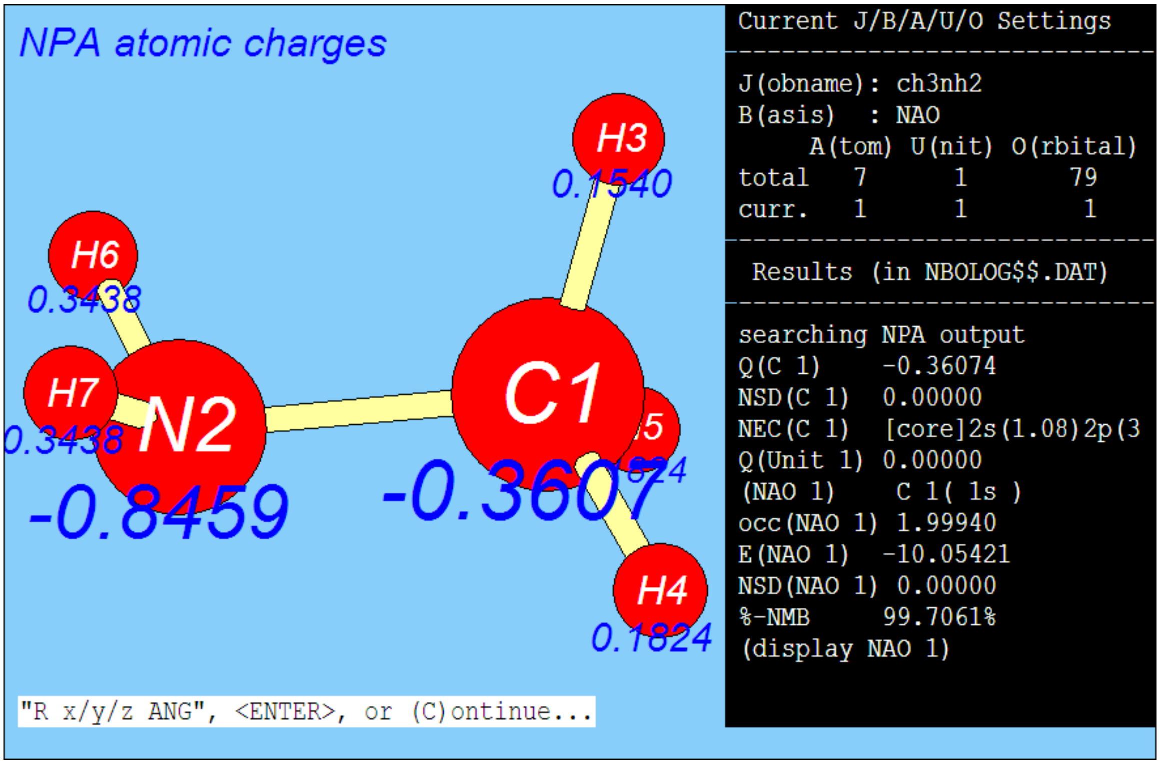


```
Search NPA output in job ch3nh2

NPA Atomic Properties:
  (1) NPA atomic charge
  (2) NPA atomic spin density
  (3) NEC atomic electron configuration
NPA Molecular Unit Properties:
  (4) NPA molecular unit charge
  (5) NPA molecular unit spin density
NAO Orbital Properties:
  (6) NAO label
  (7) NAO orbital population
  (8) NAO orbital energy
  (9) NAO orbital spin density
  (10) NMB minimal basis %-accuracy
Display Options:
  (11) Display (P)NAO visualization
  (12) Display atomic charges
      [<ENTER>: return to KEYWORD select]

Your choice (1-12) [or J/A/U/O select]?
```

```
Current J/B/A/U/O Settings
--------------------------
J(obname): ch3nh2
B(asis)  : NAO
     A(tom) U(nit) O(rbital)
total   7      1        79
curr.   1      1         1
--------------------------
 Results (in NBOLOG$$.DAT)
--------------------------
searching NPA output
Q(C 1)     -0.36074
NSD(C 1)    0.00000
NEC(C 1)    [core]2s(1.08)2p(3
type(NAO 1)   C 1( 1s )
occ(NAO 1) 1.99940
E(NAO 1)   -10.05421
NSD(NAO 1) 0.00000
%-NMB      99.7061%
```

The first three replies show the charge (“Q”), natural spin density (“NSD”), and natural electron configuration (“NEC”) for atom C(1) (the default “A 1” atom). The next four replies show the orbital label (“type”), population (“occ”), energy (“E”), and NSD for the C 1s orbital (NAO 1, the default “O 1” orbital). The final reply shows the high %-accuracy (>99.7%) of natural minimal basis (NMB) description.

Selection (11) will display the *NBOView*-type image of NAO 1 (rather uninformative in this case). Selection (12) displays the full set of NPA atomic charges in a graphical ball-and-stick diagram, as shown in the screen below (recall that double-clicking the screen allows you to “capture” this screen view to the NBOSCR$$.BMP file at any time):



```
Current J/B/A/U/O Settings
-----------------------------
J(obname): ch3nh2
B(asis)   : NAO
     A(tom) U(nit) O(rbital)
total   7      1       79
curr.   1      1        1
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching NPA output
Q(C 1)     -0.36074
NSD(C 1)   0.00000
NEC(C 1)   [core]2s(1.08)2p(3
Q(Unit 1)  0.00000
(NAO 1)     C 1( 1s )
occ(NAO 1) 1.99940
E(NAO 1)   -10.05421
NSD(NAO 1) 0.00000
%-NMB      99.7061%
(display NAO 1)
```

```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```

[As indicated ("R x/y/z ANG") in the image caption, you can rotate the image about x (horizontal), y (vertical), or z (out-of-screen) axes by any ANGle to improve the viewing perspective.]

Now, try some other simple "*V*", "*Vn*", or "*M Vn*" commands. For example, type "A" to see the selection of atoms, or type "A 2" to directly select N(2) as default atom. Similarly, type "O" to see the orbital selections, or "O 28" to directly select NAO 28, the $2p_x$ NAO on N(2). Then you can step through the menu selections as before for your new atom and orbital selections. However, if you know you're specifically interested in, e.g., the orbital energy (selection "*M*" = 8) of the $2p_x$ NAO on N(2) (variable "*V*" = O, number "*n*" = 28), you can simply type in "8 O 28" (or "8 O28") to get the value (–0.21146) more directly. Practicing with the (relatively) simple options of the NPA menu can help you prepare for the "*M V n*" commands of remaining keyword options to be summarized in the following section.

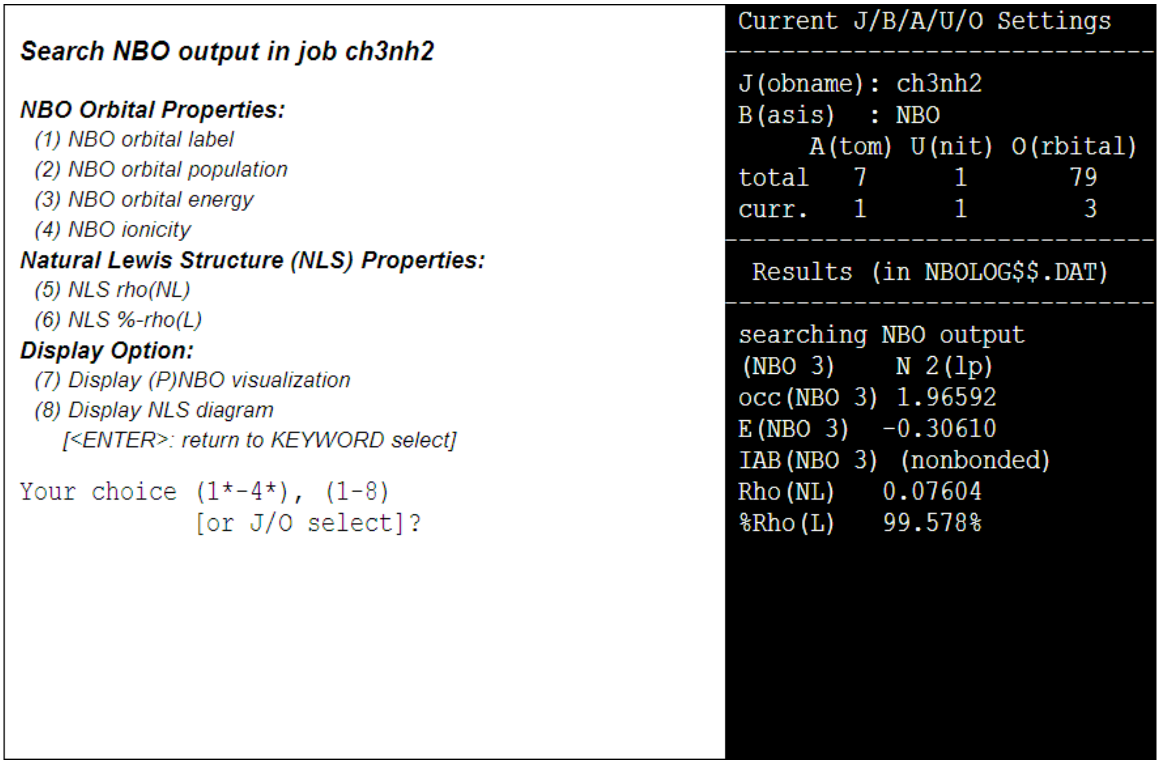
Other *NBOSearch* Keyword Options

The present section provides sketches and selected illustrations of remaining *NBOSearch* keyword options, emphasizing differences in variables, search targets, and display features that distinguish each option from the simpler NPA example discussed above. Introductory experience with *NBOSearch* search syntax and general familiarity with the bonding descriptors accessible under each keyword (e.g., hybrid properties under the “BEND” keyword, bond orders and resonance weights under the “NRT” keyword, and so forth) should adequately prepare the user for self-guided exploration of particular keyword searches of interest.

NBO: Natural Lewis Structure and NBO Properties

The screen below shows the menu (*M* = 1-8) and variable (*V* = J/O) selections that control *NBOSearch* data retrieval under the “NBO” keyword. The current assignments for J(obname), B(asis), A(tom), U(nit), and O(rbital) variables are again listed in the header of the command bar, as in the “NPA” keyword. However, as shown in the command prompt, only “J” and “O” are selectable variables in this menu, because B(asis) = NBO is fixed, and A(tom) and U(nit) are both determined by the current choice of O(rbital). Type “J” or “O” to see the available selections of each type or choose a new default setting.

The menu selections — six for alphanumeric data, two for graphical display — are also similar to analogous “NPA” selections and should be largely self-explanatory. The six final dialog lines in the command bar show the sequence of *NBOSearch* replies to each of the first six menu selections:



Search NBO output in job ch3nh2

NBO Orbital Properties:
- *(1) NBO orbital label*
- *(2) NBO orbital population*
- *(3) NBO orbital energy*
- *(4) NBO ionicity*

Natural Lewis Structure (NLS) Properties:
- *(5) NLS rho(NL)*
- *(6) NLS %-rho(L)*

Display Option:
- *(7) Display (P)NBO visualization*
- *(8) Display NLS diagram*
  - *[<ENTER>: return to KEYWORD select]*

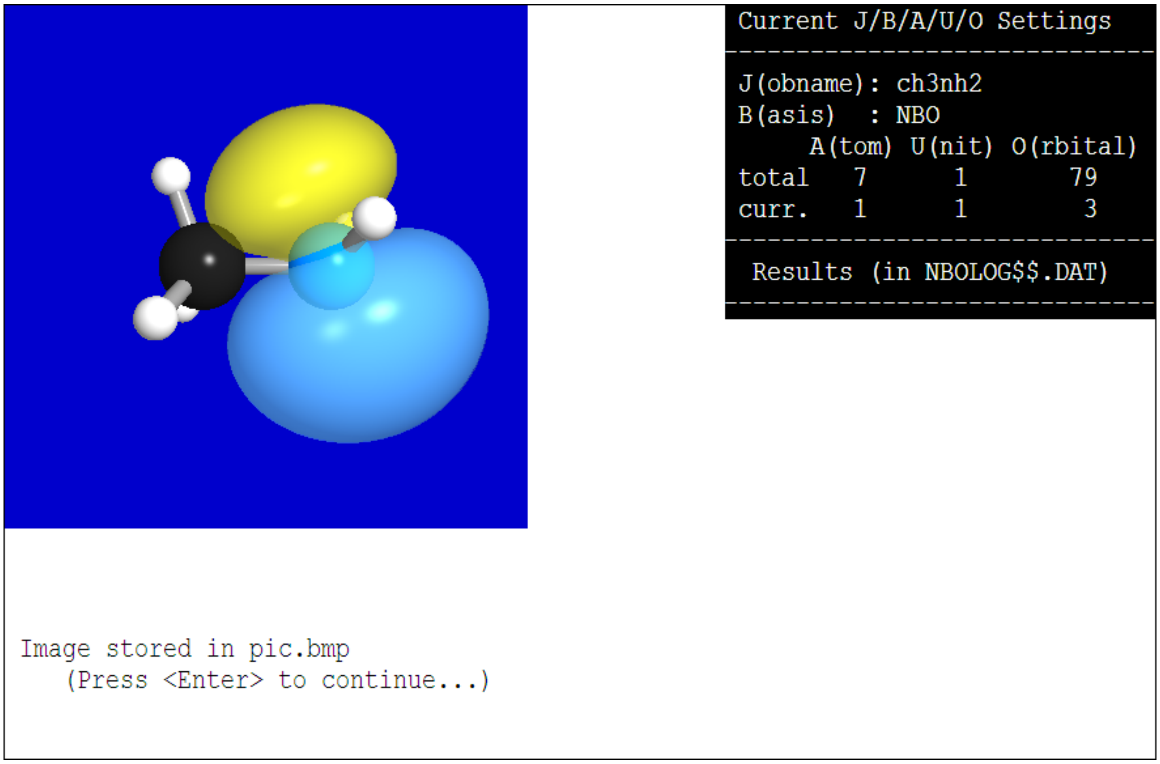
```
Your choice (1*-4*), (1-8)
            [or J/O select]?
```

```
Current J/B/A/U/O Settings
-----------------------------
J(obname): ch3nh2
B(asis)  : NBO
     A(tom) U(nit) O(rbital)
total   7      1       79
curr.   1      1        3
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching NBO output
(NBO 3)    N 2(lp)
occ(NBO 3) 1.96592
E(NBO 3)  -0.30610
IAB(NBO 3) (nonbonded)
Rho(NL)   0.07604
%Rho(L)   99.578%
```

Menu entries *M* = 1-4 pertain to properties of a particular NBO (as specified by current J = “ch3nh2” and O = 3 selections). In this case, the NBO orbital label (*M* = 1) is found to be “`N 2(lp)`” [the lone pair on nitrogen N(2)], its occupation (*M* = 2) is 1.96592e, its orbital energy (*M* = 3) is –0.30610 a.u., and its ionicity (*M* = 4) is “nonbonded”.

Menu items *M* = 5, 6 pertain to accuracy of the Natural Lewis Structure (NLS) representation of the total electron density ρ, showing the low absolute “non-Lewis” error ρ_{NL} = 0.07604e (*M* = 5) and high percentage NLS accuracy %-ρ_L = 99.578% (*M* = 6) in this case.

The final two menu entries request graphical displays of NBO (*M* = 7) or NLS (*M* = 8) properties. The *M* = 7 selection leads to the screen shown below, which provides a surface-plot visualization of the nitrogen lone pair (current O = 9) in pre-orthogonal (PNBO) representation (necessitating a short delay as the *NBOView* module is called to prepare the ray-traced image):

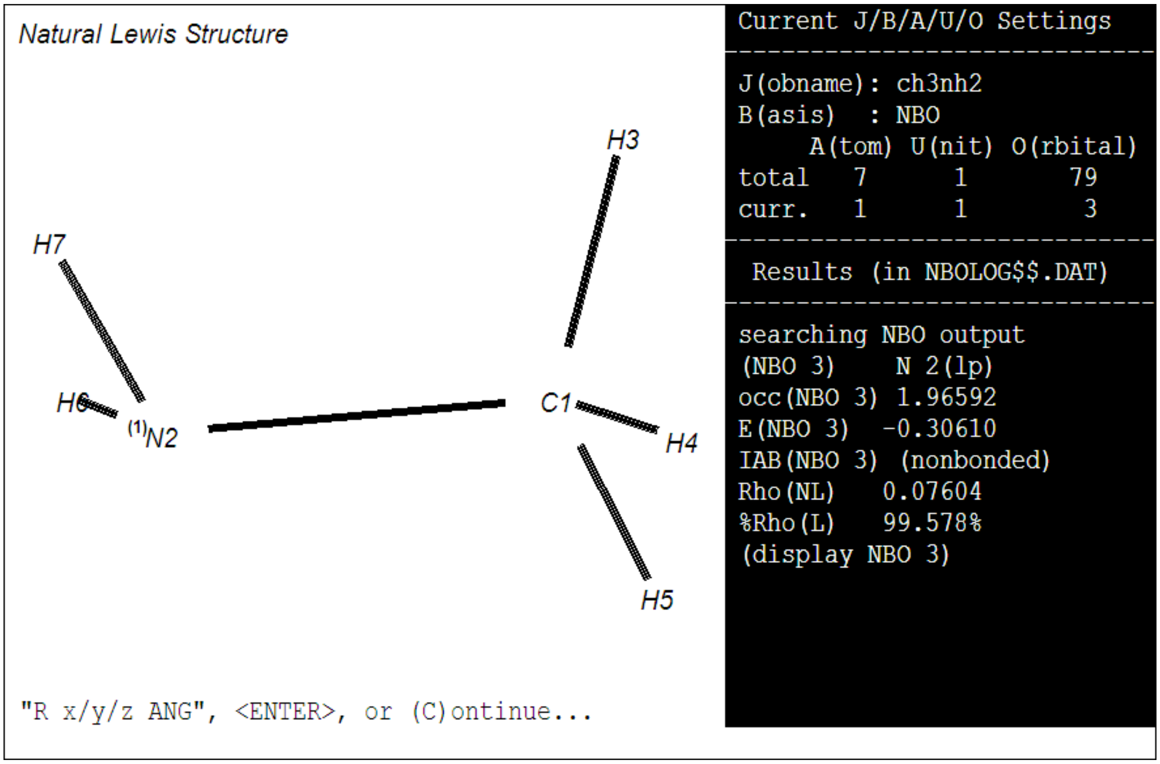


```
Current J/B/A/U/O Settings
-----------------------------
J(obname): ch3nh2
B(asis)  : NBO
     A(tom) U(nit) O(rbital)
total   7      1       79
curr.   1      1        3
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
```

```
Image stored in pic.bmp
   (Press <Enter> to continue...)
```

As indicated near the bottom of the screen, this image is saved in the "pic.bmp" file (for renaming or copying to an alternative filename) until overwritten by the next such graphical display option.

The final menu selection (*M* = 8) leads to a Lewis-structural depiction of the NLS bonding pattern, as shown in the screen below (after slight rotation to bring the 3D Lewis diagram to better perspective). The pre-superscript on the "$^{(1)}$N" symbol indicates that the nitrogen atom has one lone pair, but other aspects of the bond-stick diagram are unexceptional in this elementary saturated molecule.

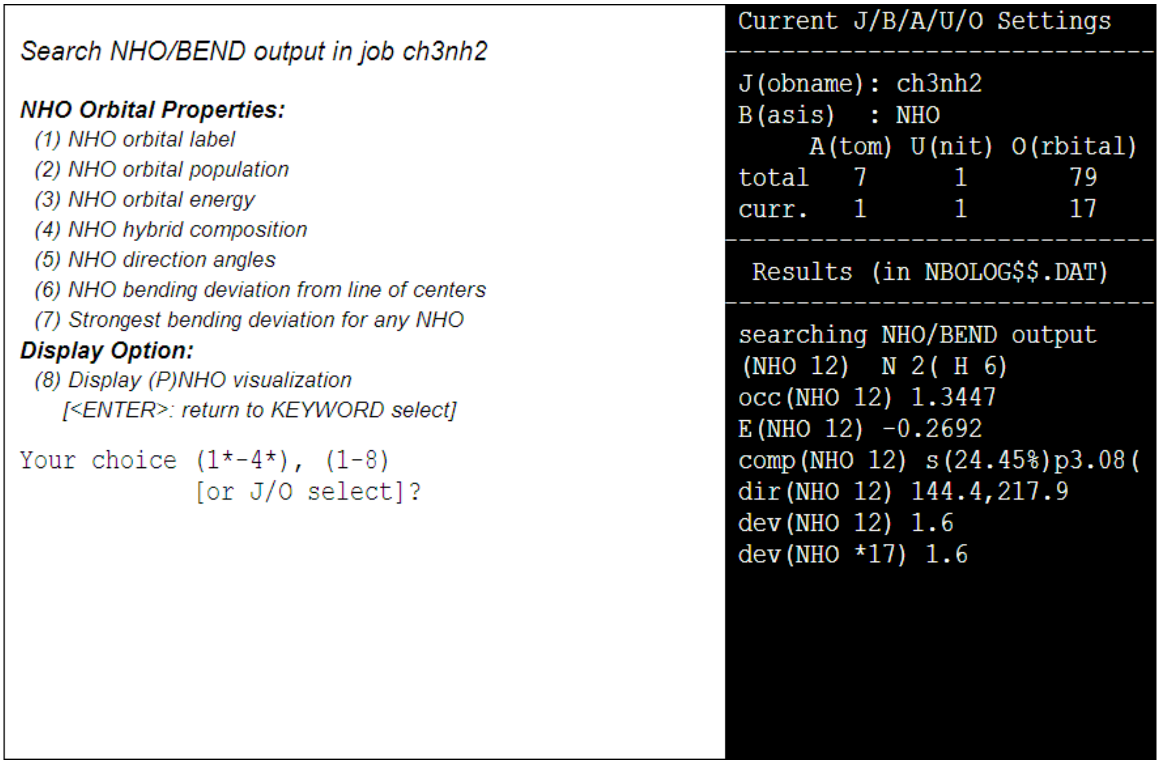


```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```

```
Current J/B/A/U/O Settings
------------------------------
J(obname): ch3nh2
B(asis)  : NBO
     A(tom) U(nit) O(rbital)
total   7      1       79
curr.   1      1        3
------------------------------
 Results (in NBOLOG$$.DAT)
------------------------------
searching NBO output
(NBO 3)    N 2(lp)
occ(NBO 3) 1.96592
E(NBO 3)  -0.30610
IAB(NBO 3) (nonbonded)
Rho(NL)    0.07604
%Rho(L)    99.578%
(display NBO 3)
```

BEND: Natural Hybrid Orbital Directionality and Bond-Bending

Selecting the “BEND” option leads to a menu as shown in the screen below. The current J/B/A/U/O assignments appear at the top of the command bar, as in the “NPA” or “NBO” menus, and the selectable J/O variables (for fixed B = NHO) are identified in the command prompt at the lower left of the screen. The menu selections — seven for alphanumeric data, one for graphical display — are also similar to analogous “NPA” or “NBO” selections and should be largely self-explanatory. The seven final lines in the dialog section of the command bar show the sequence of *NBOSearch* replies to each of the first seven menu selections. As usual, type “J” or “O” to see the available selections of each type or choose new default settings in the sidebar.



Search NHO/BEND output in job ch3nh2

NHO Orbital Properties:
- *(1) NHO orbital label*
- *(2) NHO orbital population*
- *(3) NHO orbital energy*
- *(4) NHO hybrid composition*
- *(5) NHO direction angles*
- *(6) NHO bending deviation from line of centers*
- *(7) Strongest bending deviation for any NHO*

Display Option:
- *(8) Display (P)NHO visualization*
  - *[<ENTER>: return to KEYWORD select]*

```
Your choice (1*-4*), (1-8)
            [or J/O select]?
```

```
Current J/B/A/U/O Settings
-----------------------------
J(obname): ch3nh2
B(asis)  : NHO
     A(tom) U(nit) O(rbital)
total   7      1       79
curr.   1      1       17
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching NHO/BEND output
(NHO 12)  N 2( H 6)
occ(NHO 12) 1.3447
E(NHO 12) -0.2692
comp(NHO 12) s(24.45%)p3.08(
dir(NHO 12) 144.4,217.9
dev(NHO 12) 1.6
dev(NHO *17) 1.6
```

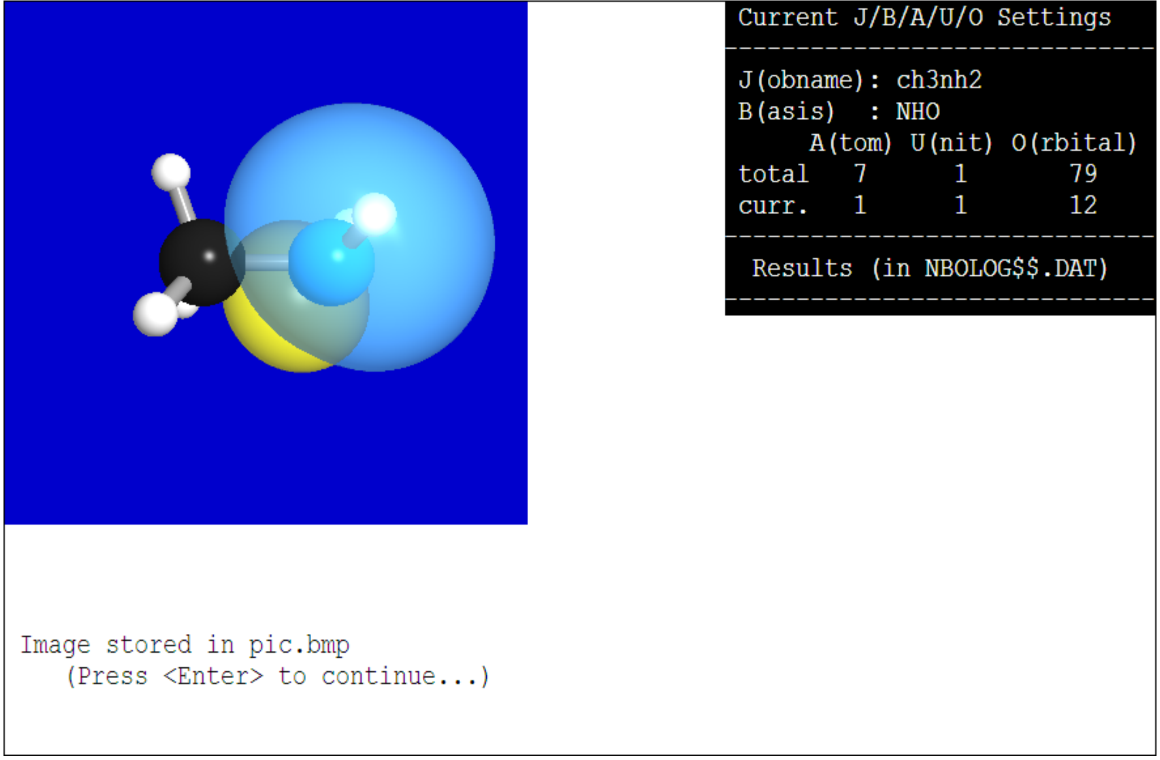
The replies for NHO properties requested by menu selections *M* = 1-4 are straightforward: For the selected NHO (O = 9) that was current when the menu was entered, the NHO label "`N 2(H 6)`" denotes the hybrid on N(2) that points toward H(6), with electronic occupancy 1.3447e, orbital energy –0.2692 a.u., and sp$^{3.08}$ hybrid composition (24.45% s-character, 75.55% p-character).

[After menu selection *M* = 3, you may notice an interruption as the *NBORun* module is summoned to evaluate the NHO orbital energies, which are not included in default NBO output. In this case, *NBORun* automatically inserts the "FNHO" keyword and re-runs the analysis to include NHO orbital energies, allowing *NBOSearch* to complete the request. All such interruptions occur as necessary "in background," without requiring special attention by the user.]

Menu selections 5, 6 request directional spherical polar angles of the hybrid (θ = 144.4°, φ = 217.9° in the usual polar and azimuthal angles of the ESS-chosen coordinate system) and its "bond-bending" deviation from the direct line of N(2)-H(6) centers (1.6°, nearly imperceptible in this unstrained acyclic species).

Menu selection 7 is a request to look for the *largest* such bond-bending deviation in the molecule. The extremal value (also 1.6°) is found at the carbon rydberg NHO 17, thereby causing the “curr.” orbital to be reset to O = 17 in the header section of the command bar. Such a reset for a variable of extremal character is indicated by the asterisk identifying the extremal “*17” NHO in the “dev(`NHO *17) 1.6`” reply, a convention that applies to extremal searches in other keyword options to follow. (Type “012” to reset back to the starting orbital, NHO 12.)

The final menu selection, *M* = 8, displays the ray-traced surface plot of the current (P)NHO, as shown in the screen below:



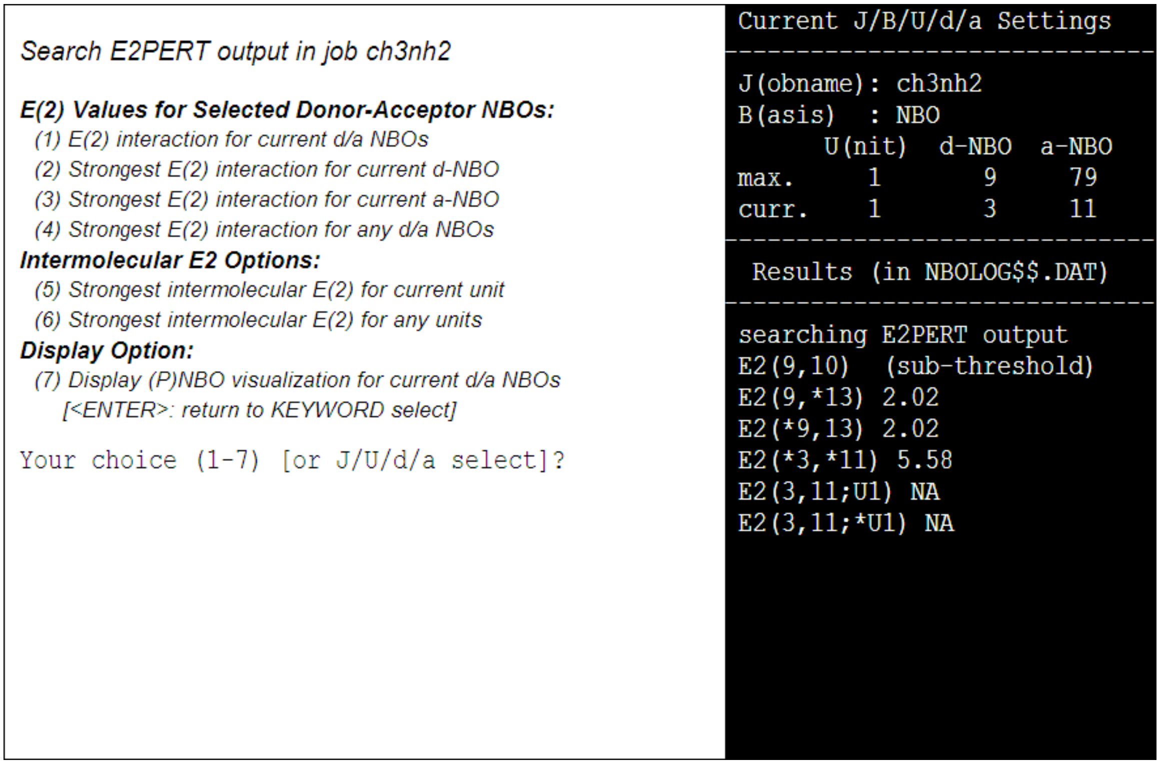
```
Current J/B/A/U/O Settings
------------------------------
J(obname): ch3nh2
B(asis)  : NHO
         A(tom) U(nit) O(rbital)
total    7      1        79
curr.    1      1        12
------------------------------
 Results (in NBOLOG$$.DAT)
------------------------------
```

```
Image stored in pic.bmp
   (Press <Enter> to continue...)
```

[As usual, the orbital image is fetched from *NBOView* using default settings of the camera and lighting model. If you’d prefer a better view of the hybrid, return to the *NBOView* menu by hitting the <ENTER> key until the main *NBOPro* menu appears, allowing entry to a new module.]

E2PERT: 2^{nd}-Order Energetics of NBO Donor-Acceptor Interactions

Selecting “E2PERT” leads to a menu as shown in the screen below, with dialog lines that result from successive selection of menu options *M* = 1-6:



Search E2PERT output in job ch3nh2

E(2) Values for Selected Donor-Acceptor NBOs:
- (1) E(2) interaction for current d/a NBOs
- (2) Strongest E(2) interaction for current d-NBO
- (3) Strongest E(2) interaction for current a-NBO
- (4) Strongest E(2) interaction for any d/a NBOs

Intermolecular E2 Options:
- (5) Strongest intermolecular E(2) for current unit
- (6) Strongest intermolecular E(2) for any units

Display Option:
- (7) Display (P)NBO visualization for current d/a NBOs
  - [<ENTER>: return to KEYWORD select]

```
Your choice (1-7) [or J/U/d/a select]?
```

```
Current J/B/U/d/a Settings
-----------------------------
J(obname): ch3nh2
B(asis)  : NBO
      U(nit)  d-NBO  a-NBO
max.     1       9     79
curr.    1       3     11
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching E2PERT output
E2(9,10)  (sub-threshold)
E2(9,*13) 2.02
E2(*9,13) 2.02
E2(*3,*11) 5.58
E2(3,11;U1) NA
E2(3,11;*U1) NA
```

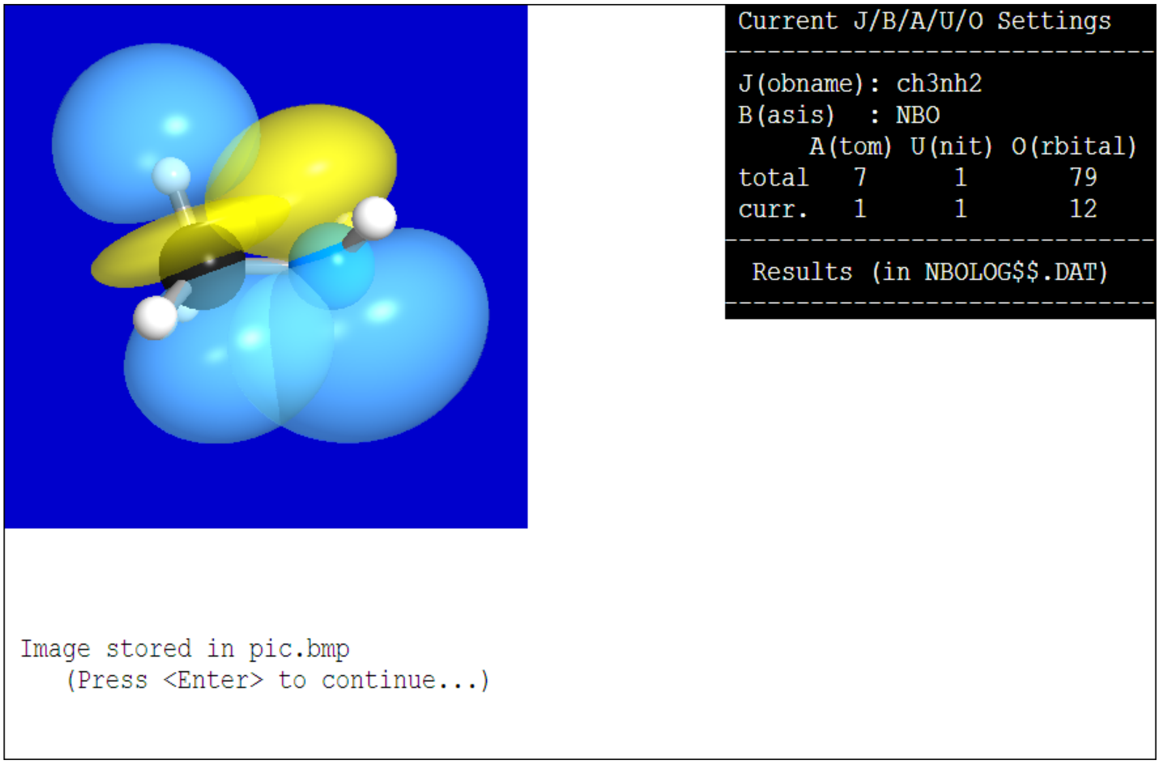
The variable "*V*" options "J/B/U/d/a" listed in the header section of the command bar now include the "d" [(d)onor NBO] and "a" [(a)cceptor NBO] numbers of a selected donor-acceptor interaction, whose perturbative energy "E2" estimate is the quantity of principal interest. Because B = NBO is the fixed basis set, only variables J/U/d/a are selectable at the command prompt.

As usual, you can type the variable abbreviation "d" or "a" to see the listing of available donor (Lewis) and acceptor (non-Lewis) NBOs. By default, "d" is chosen as the highest Lewis-type NBO (here, d = 9) and "a" as the lowest non-Lewis NBO (here, d = 10). However, menu selection *M* = 1 leads to the dialog line "`E2(9,10) (sub-threshold)`", indicating that this default interaction is too weak (<0.5 kcal/mol) for inclusion in *E2PERT* output.

Menu items *M* = 2-4 provide searches for *extremal* interactions involving the default donor NBO (*M* = 2), the default acceptor NBO (*M* = 3), or any donor/acceptor NBOs of the species (*M* = 4). As shown in the corresponding dialog lines, NBO 13 [the C(1)-H(5) antibond] is identified by asterisk ("`*13`") as having the strongest interaction (2.02 kcal/mol) with donor NBO 9 ("`E2(9,*13)`"). The same interaction is found to be strongest for acceptor NBO 13 ("`E2(*9,13)`"). The largest overall *E(2)* interaction (5.58 kcal/mol) is that between donor NBO 3 (the N lone pair) and acceptor NBO 11 (the antiperiplanar C1-H3 antibond), as shown in the "E2(*3,*11) 5.58" response to *M* = 4. This menu item often provides the information that an accomplished NBO user is most interested in seeing.

[Because there is only one molecular unit in this species, menu options *M* = 5, 6 are "not applicable" for intermolecular E2 values.]

Finally, display option *M* = 7 leads to the PNBO visualization of the "E2(3,11)" [vicinal antiperiplanar $n_N \rightarrow \sigma^*_{CH}$) interaction, as shown in the screen below:



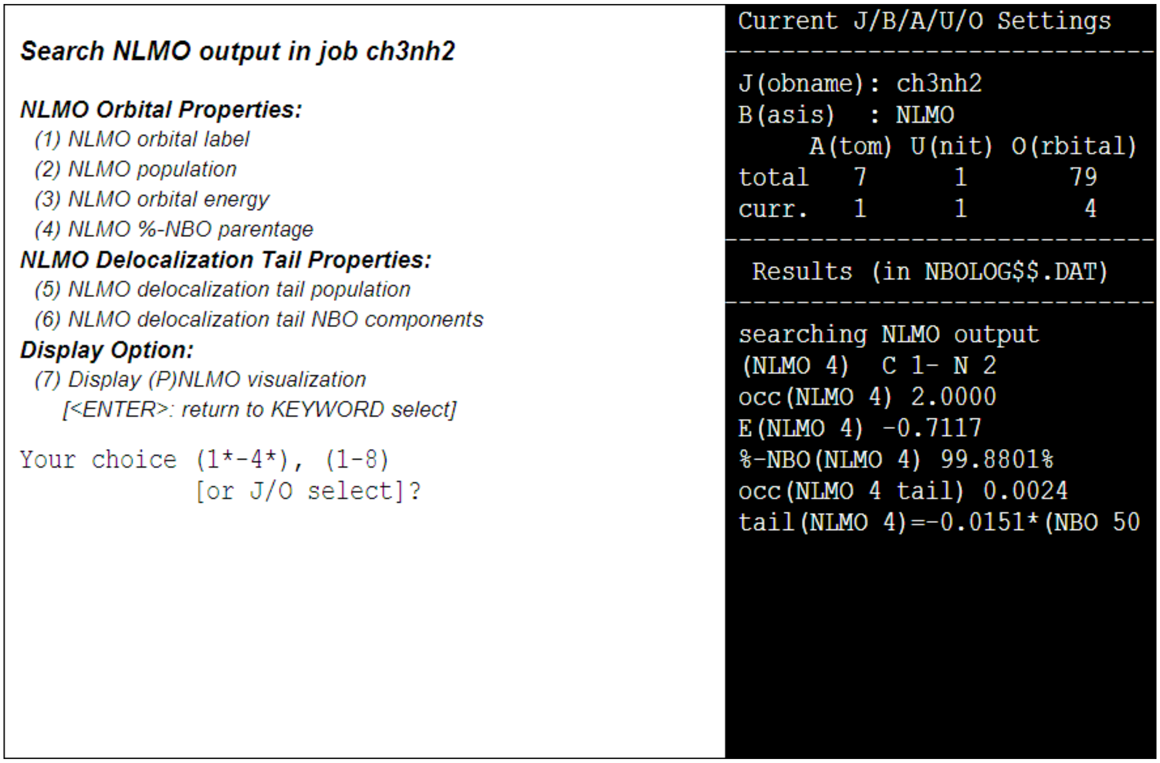
```
Current J/B/A/U/O Settings
-----------------------------
J(obname): ch3nh2
B(asis)  : NBO
     A(tom) U(nit) O(rbital)
total   7      1       79
curr.   1      1       12
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
```

```
Image stored in pic.bmp
   (Press <Enter> to continue...)
```

NLMO: Natural Localized Molecular Orbital Properties

The NLMO menu is similar to previous NAO ("NPA), NHO ("BEND"), and NBO orbital-oriented menus. Only the jobname ("J") and orbital number ("O") variables are selectable for fixed basis B = NLMO. As usual, type "J" or "O" to list the available selections.

For the currently selected NLMO 4, menu options 1-3 lead to the familiar orbital descriptors shown in the first three dialog lines of the screen below, giving the NLMO label [`"C 1-N 2",` the $\sigma_{C(1)\text{-}N(2)}$ bond), identified by the same label as its parent NBO], occupancy (exactly 2, as must be true for all L-type NLMOs), and orbital energy (–0.7117 a.u.). Options 4-6 successively report on the high %-contribution from parent Lewis-type NBO 11 (>99.88%) and the low occupancy (0.0024e) and leading NBO component of the non-Lewis “delocalization tail” (NBO 50, with coefficient –0.0151).



Search NLMO output in job ch3nh2

NLMO Orbital Properties:
- *(1) NLMO orbital label*
- *(2) NLMO population*
- *(3) NLMO orbital energy*
- *(4) NLMO %-NBO parentage*

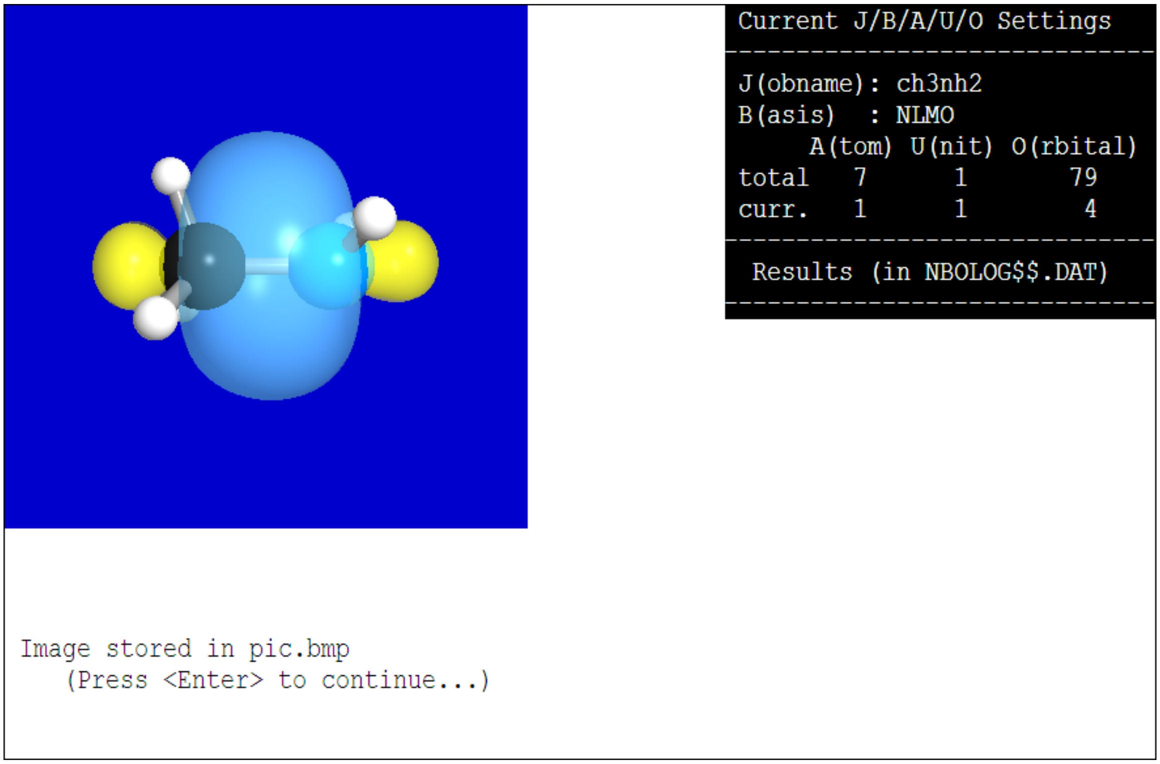
NLMO Delocalization Tail Properties:
- *(5) NLMO delocalization tail population*
- *(6) NLMO delocalization tail NBO components*

Display Option:
- *(7) Display (P)NLMO visualization*
  - *[<ENTER>: return to KEYWORD select]*

```
Your choice (1*-4*), (1-8)
            [or J/O select]?
```

```
Current J/B/A/U/O Settings
------------------------------
J(obname): ch3nh2
B(asis)  : NLMO
     A(tom) U(nit) O(rbital)
total   7      1       79
curr.   1      1        4
------------------------------
 Results (in NBOLOG$$.DAT)
------------------------------
searching NLMO output
(NLMO 4)  C 1- N 2
occ(NLMO 4) 2.0000
E(NLMO 4) -0.7117
%-NBO(NLMO 4) 99.8801%
occ(NLMO 4 tail) 0.0024
tail(NLMO 4)=-0.0151*(NBO 50
```

Display option (7) gives the PNLMO visualization of this orbital, as shown in the screen below.



```
Current J/B/A/U/O Settings
-----------------------------
J(obname): ch3nh2
B(asis)   : NLMO
     A(tom) U(nit) O(rbital)
total    7      1       79
curr.    1      1        4
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
```

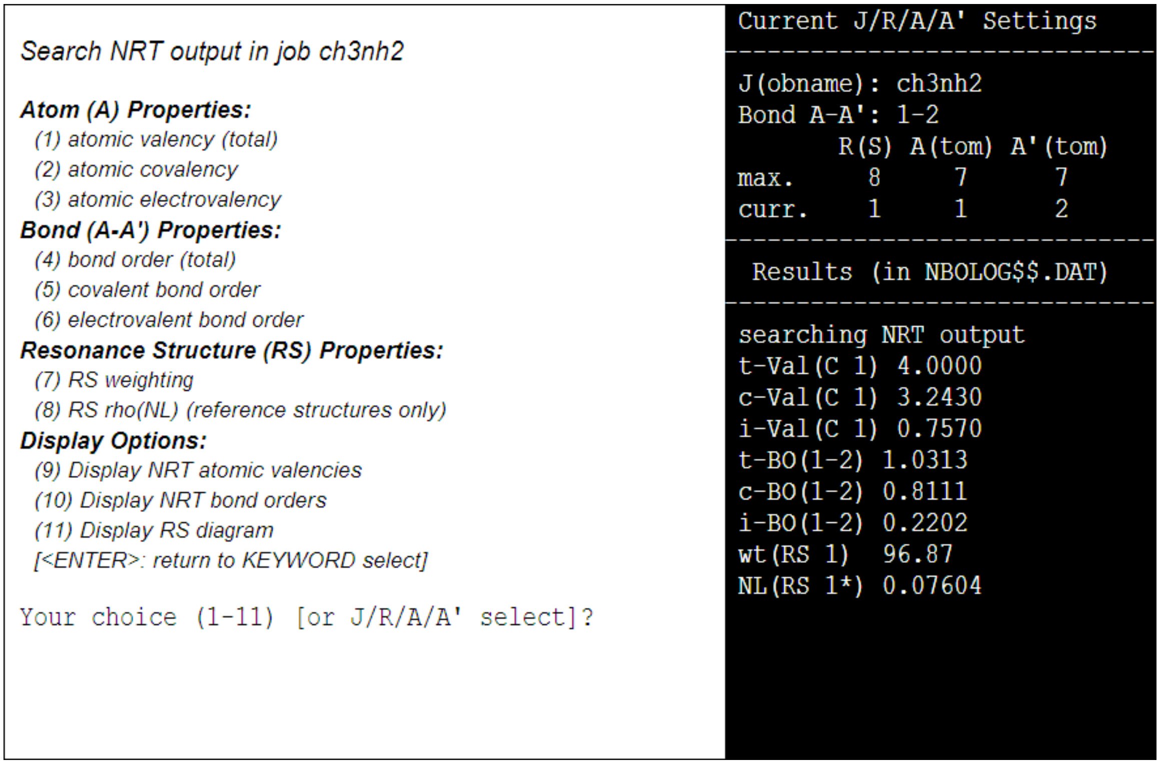
```
Image stored in pic.bmp
   (Press <Enter> to continue...)
```

The graphical image of NLMO 4 differs imperceptibly from that of the parent NBO 4, as the numerical results from menu options *M* = 5, 6 strongly suggest.

NRT: Natural Resonance Theory Weightings and Bond Orders

The NRT (natural resonance theory) keyword menu presents a new set of menu selections (*M* = 1-11) and control variables (*V* = J, R, A, A’). The J(obname) and A(tom) variables are familiar from previous menus, but an additional atom variable A’ is needed to identity a general A-A’ bond order, and a resonance-structure number “R” (in order of resonance weighting) is also selectable. As usual, typing “J”, “R”, “A”, or “A’” by itself displays the available selections.

The screen below shows the NRT selection screen with the dialog that results from the first eight (non-display) selections for default variables A = 1, A’ = 2, R = 1:



Search NRT output in job ch3nh2

Atom (A) Properties:
- *(1) atomic valency (total)*
- *(2) atomic covalency*
- *(3) atomic electrovalency*

Bond (A-A') Properties:
- *(4) bond order (total)*
- *(5) covalent bond order*
- *(6) electrovalent bond order*

Resonance Structure (RS) Properties:
- *(7) RS weighting*
- *(8) RS rho(NL) (reference structures only)*

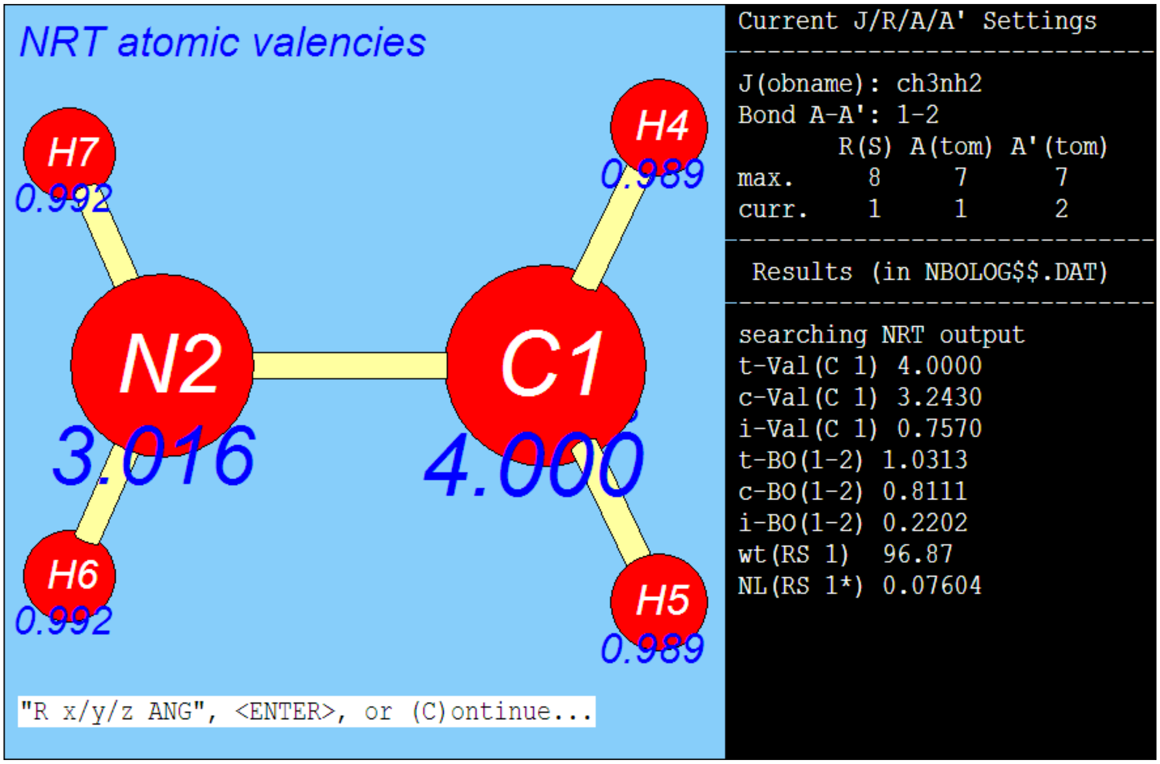
Display Options:
- *(9) Display NRT atomic valencies*
- *(10) Display NRT bond orders*
- *(11) Display RS diagram*
- *[<ENTER>: return to KEYWORD select]*

```
Your choice (1-11) [or J/R/A/A' select]?
```

```
Current J/R/A/A' Settings
-----------------------------
J(obname): ch3nh2
Bond A-A': 1-2
       R(S) A(tom) A'(tom)
max.     8     7      7
curr.    1     1      2
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching NRT output
t-Val(C 1) 4.0000
c-Val(C 1) 3.2430
i-Val(C 1) 0.7570
t-BO(1-2) 1.0313
c-BO(1-2) 0.8111
i-BO(1-2) 0.2202
wt(RS 1)  96.87
NL(RS 1*) 0.07604
```

Menu selections M = 1-3 request numerical details of NRT atomic valency for the default atom C(1), either total valency ("t", 4.000), covalency ("c", 3.2430), or electrovalency ("i", 0.7570). Selections M = 4-6 request analogous details of NRT bond order for the default C(1)-N(2) atom pair (A = 1, A' = 2): total (1.0313), covalent (0.8111), or electrovalent (0.2202). Finally, selection M = 7 requests the numerical weighting for default resonance structure R = 1 (w_1 = 96.87%) and selection M = 8 requests the value of the associated non-Lewis density "error" ρ_{NL} for this resonance structure (0.07604e). In the latter case, a ρ_{NL} value is returned only for asterisk-marked "reference" structures, as shown in the "RS 1*" label for resonance structure 1 (the only reference structure in this well-localized case).

The final three menu selections M = 9-11 provide graphical displays of NRT descriptors or resonance structures. Selection M = 9 displays the NRT atomic valencies (total) on a 3D molecular model, as shown in the screen below:

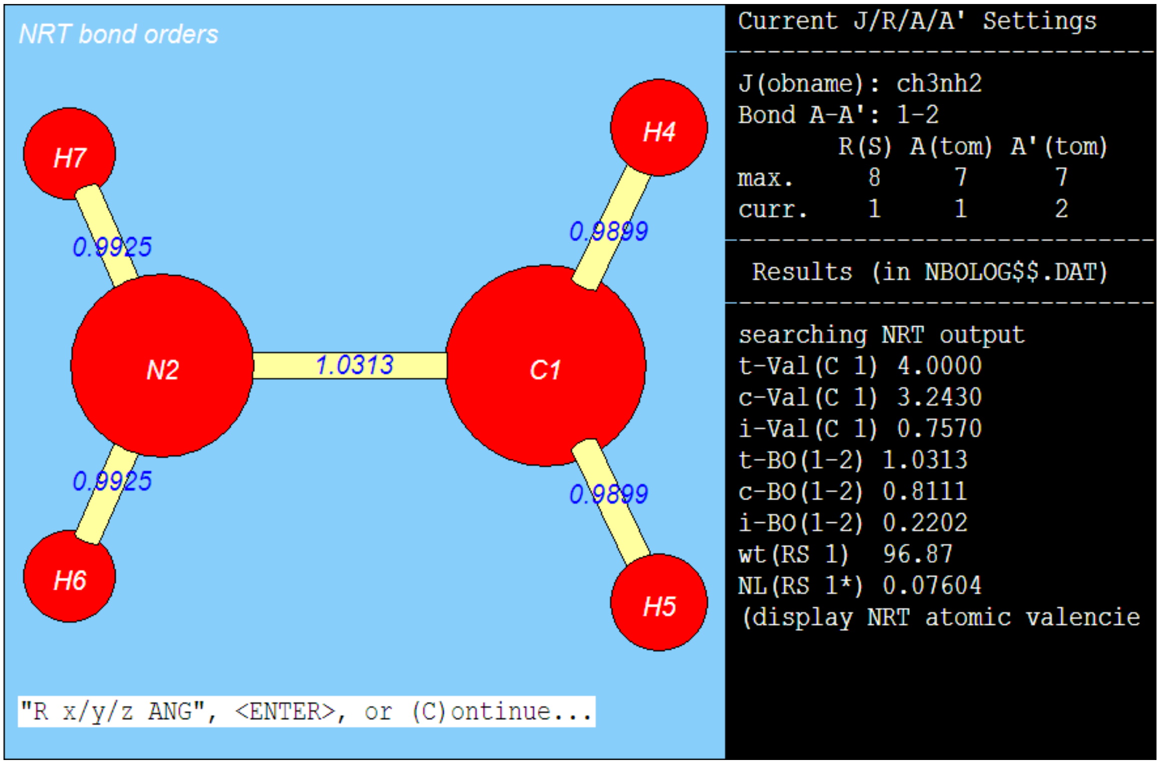


```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```

```
Current J/R/A/A' Settings
-----------------------------
J(obname): ch3nh2
Bond A-A': 1-2
       R(S)  A(tom)  A'(tom)
max.     8      7       7
curr.    1      1       2
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching NRT output
t-Val(C 1) 4.0000
c-Val(C 1) 3.2430
i-Val(C 1) 0.7570
t-BO(1-2) 1.0313
c-BO(1-2) 0.8111
i-BO(1-2) 0.2202
wt(RS 1)  96.87
NL(RS 1*) 0.07604
```

As usual, the model can be rotated (e.g., “`R x 20`”) to improve the view of atoms that are obscured in the default orientation.

Selection *M* = 10 similarly displays the NRT bond orders (total) centered on bond-sticks of the model, as shown in the screen below:

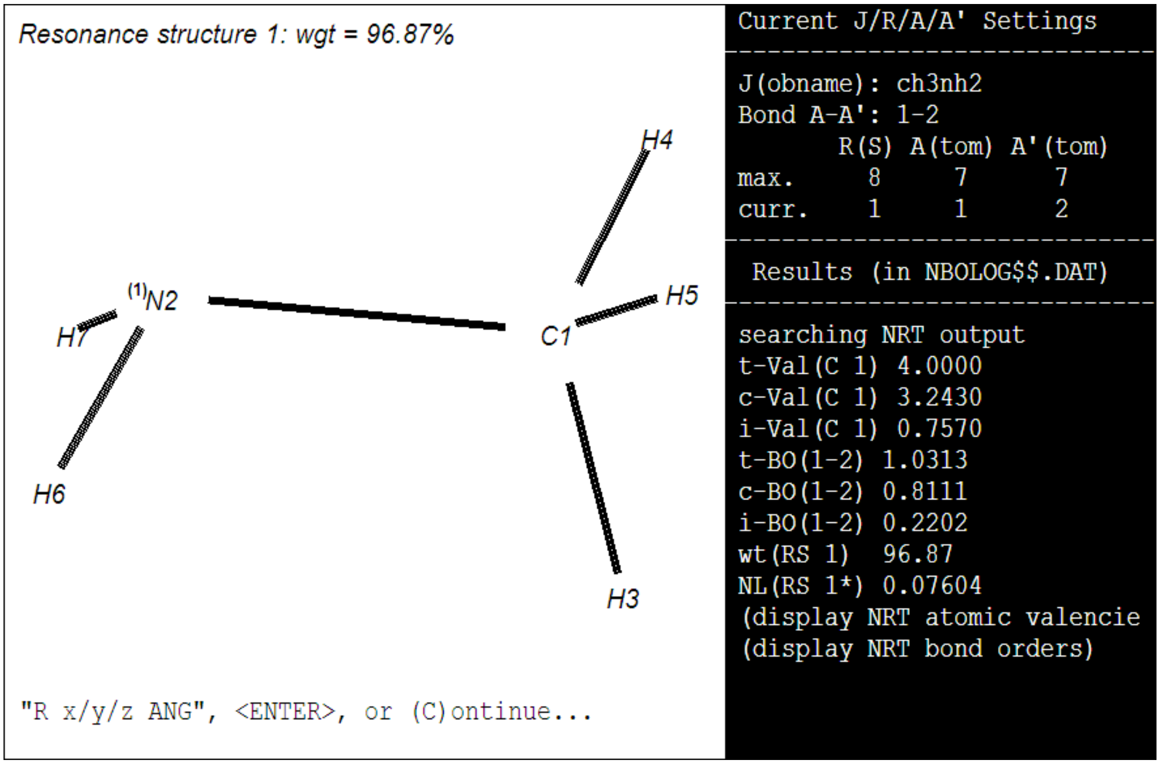


```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```

```
Current J/R/A/A' Settings
------------------------------
J(obname): ch3nh2
Bond A-A': 1-2
       R(S) A(tom) A'(tom)
max.     8     7      7
curr.    1     1      2
------------------------------
 Results (in NBOLOG$$.DAT)
------------------------------
searching NRT output
t-Val(C 1) 4.0000
c-Val(C 1) 3.2430
i-Val(C 1) 0.7570
t-BO(1-2) 1.0313
c-BO(1-2) 0.8111
i-BO(1-2) 0.2202
wt(RS 1)  96.87
NL(RS 1*) 0.07604
(display NRT atomic valencie
```

Note that graphical display *M* = 9 shows the bond order value only for atom pairs that are connected by the usual bond-sticks, whereas the *M* = 4 option gives the numerical value for any selected A, A’ atom pair, whether “expected” to have significant bond order or not.

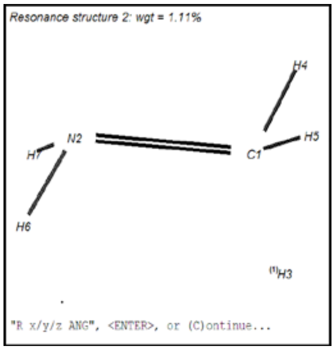
Finally, selection *M* = 11 requests a simple 3D Lewis-structural diagram for the current resonance structure, with lone pairs (if any) indicated by a parenthesized superscript on the atom. The 3D diagram is similar to that used to depict the NLS in the NBO keyword menu, and will normally coincide with the NLS diagram for R = 1, but the weighting of each structure now appears in the caption, as shown in the screen below (after “`r x -70`” to improve 3D perspective):


Resonance structure 1: wgt = 96.87%

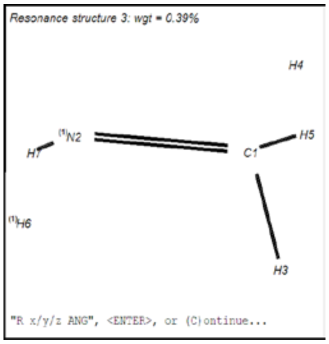
```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```

```
Current J/R/A/A' Settings
------------------------------
J(obname): ch3nh2
Bond A-A': 1-2
       R(S) A(tom) A'(tom)
max.     8     7      7
curr.    1     1      2
------------------------------
 Results (in NBOLOG$$.DAT)
------------------------------
searching NRT output
t-Val(C 1) 4.0000
c-Val(C 1) 3.2430
i-Val(C 1) 0.7570
t-BO(1-2) 1.0313
c-BO(1-2) 0.8111
i-BO(1-2) 0.2202
wt(RS 1)  96.87
NL(RS 1*) 0.07604
(display NRT atomic valencie
(display NRT bond orders)
```

By similarly requesting this option for higher resonance structures R = 2-8 (with “`r2`”, “`r3`”,`...`) we obtain the three unique structure types that contribute partial CN double-bond character, as shown below (all with “`r x -70`” rotation):

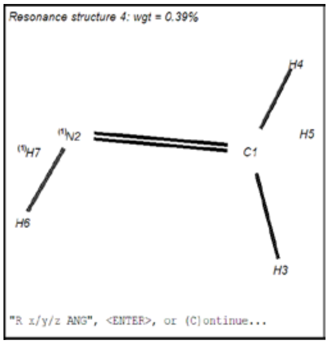

Resonance structure 2: wgt = 1.11%

```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```


Resonance structure 3: wgt = 0.39%

```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```

(four equivalent)


Resonance structure 4: wgt = 0.39%

```
"R x/y/z ANG", <ENTER>, or (C)ontinue...
```

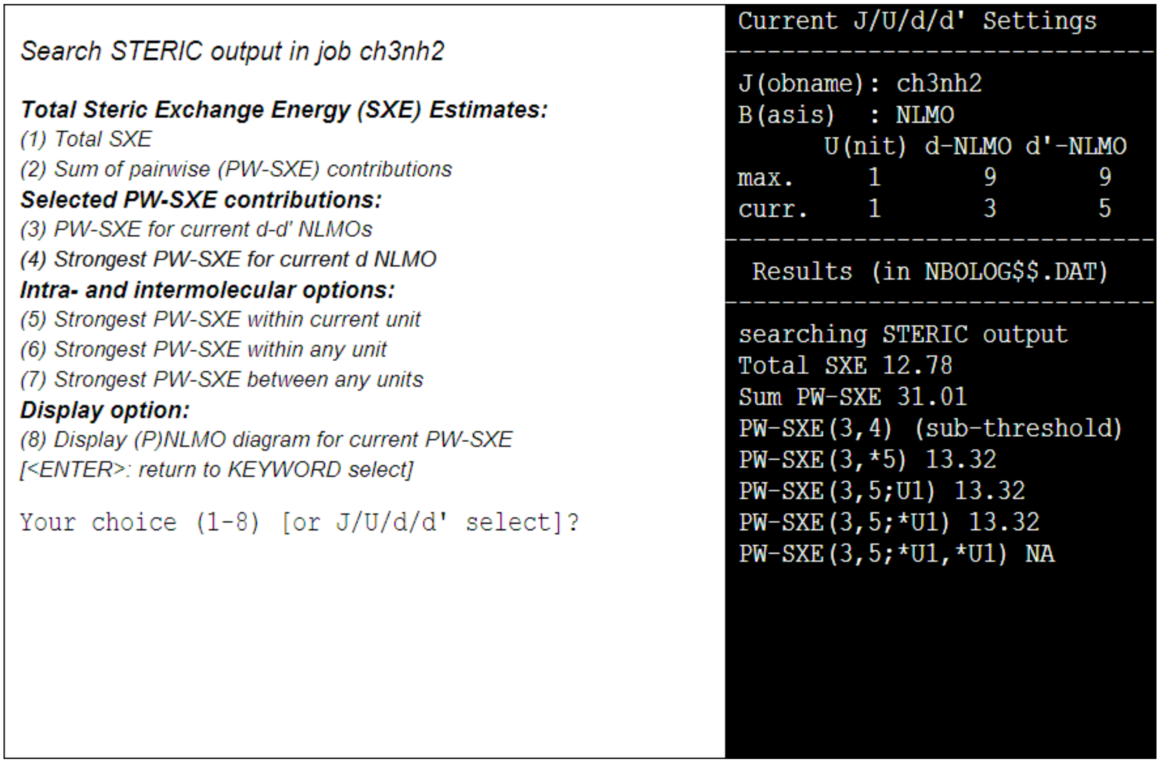
(two equivalent)

(Recall that double-clicking on any screen will capture the image to the NBOSCR$$.BMP file for later usage.)

STERIC: Total and Pairwise Contributions to Steric Exchange Energy

In contrast to the attractive donor/acceptor (d/a) interactions of the *E2Pert* keyword option, the *STERIC* keyword option describes the repulsive donor/donor (d/d’) interactions of steric exchange type. Two distinct assessments of steric exchange energy are provided, identified as “total” (SXE) and “pairwise” (PW-SXE). Total SXE and the sum of pairwise PW-SXE contributions are obtained from menu selections *M* = 1, 2, whereas selections *M* = 3-7 provide the values of individual PW-SXE descriptors, which tend to be more directly interpretable. Menu option *M* = 8 displays graphical features of the selected d/d’ orbitals that underlie the current PW-SXE value.

In each case, the algorithms make fixed use of the B = NLMO basis set. Accordingly, current assignments of J(obname), U(nit), d(onor orbital), and d’(onor orbital) variables are shown in the command bar header. As usual, typing “J”, “U”, “d” or “d’” shows the available selections for each variable. The dialog lines in the screen below show the sequential replies to menu selections *M* = 1-7 for default J/U/d/d’ variables:



Search STERIC output in job ch3nh2

Total Steric Exchange Energy (SXE) Estimates:
(1) Total SXE
(2) Sum of pairwise (PW-SXE) contributions
Selected PW-SXE contributions:
(3) PW-SXE for current d-d' NLMOs
(4) Strongest PW-SXE for current d NLMO
Intra- and intermolecular options:
(5) Strongest PW-SXE within current unit
(6) Strongest PW-SXE within any unit
(7) Strongest PW-SXE between any units
Display option:
(8) Display (P)NLMO diagram for current PW-SXE
[<ENTER>: return to KEYWORD select]

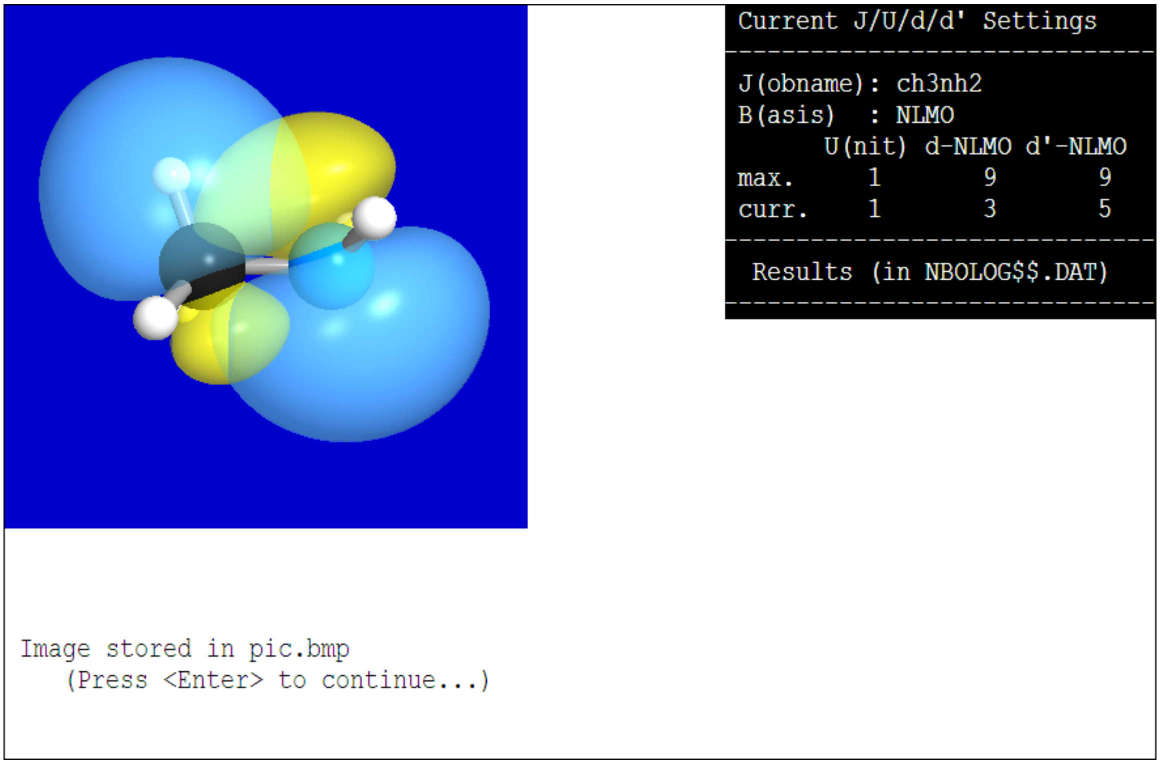
```
Your choice (1-8) [or J/U/d/d' select]?
```

```
Current J/U/d/d' Settings
----------------------------
J(obname): ch3nh2
B(asis)  : NLMO
      U(nit) d-NLMO d'-NLMO
max.     1      9      9
curr.    1      3      5
----------------------------
 Results (in NBOLOG$$.DAT)
----------------------------
searching STERIC output
Total SXE 12.78
Sum PW-SXE 31.01
PW-SXE(3,4) (sub-threshold)
PW-SXE(3,*5) 13.32
PW-SXE(3,5;U1) 13.32
PW-SXE(3,5;*U1) 13.32
PW-SXE(3,5;*U1,*U1) NA
```

As shown in the first line of dialog for *M* = 1, the total SXE (representing the totality of antisymmetric exchange interactions for all electrons of the species) is 91.47 kcal/mol. However, only *changes* in this value (e.g., with respect to a chosen reference geometry) can be easily interpreted. For *M* = 2, the total sum of PW-SXE values is 37.86 kcal/mol, which must be similarly compared to a physical reference state for interpretive purposes. Further use of these menu option therefore involves additional “J” selections for the chosen reference state.

Menu selections *M* = 3-7 provide estimates of the steric clashes of individual electron pairs in the selected d/d' NLMOs that are more directly interpretable (although *M* = 6 is redundant and *M* = 7 is "not applicable" in this single-unit species). From selection *M* = 3, the steric repulsion between initial NLMOs d = 3 ($n_{N(2)}$) and d' = 4 ($\sigma_{C(1)N(2)}$) is found to be below the printing threshold (<0.5 kcal/mol). From *M* = 4, we learn that the strongest steric repulsions (13.32 kcal/mol) involving the $n_{N(2)}$ lone pair NLMO are found at NLMO 5 (the antiperiplanar $\sigma_{C(1)H(3)}$). From *M* = 5, we learn that the *strongest* steric repulsion in molecular unit 1 (the entire molecule, in this case) is the $n_{N(2)}$-$\sigma_{C(1)H(3)}$ interaction found above, as confirmed also in *M* = 6. This is quite surprising from the superficial viewpoint of a ball-and-stick model, which seems to position the antiperiplanar CH bond *as far as possible* from steric conflicts with the nitrogen lone pair!

Option *M* = 8 displays the orbital imagery of $n_{N(2)}$-$\sigma_{C(1)H(3)}$ orbital overlap for the (now default) NLMOs 3, 5, as shown below. The diagram shows that the unexpectedly high steric repulsion arises primarily from the *backside* lobe of the $n_{N(2)}$ lone pair colliding with the "shoulder" of the $\sigma_{C(1)H(3)}$ bond. (In contrast, the corresponding n_N-σ_{CH} orbital overlap diagram in *eclipsed* geometry shows *no* comparable steric clash between occupied lobes.) Such comparisons emphasize the superficiality of common rationalizations of torsional phenomena still to be found in many elementary textbooks, based on cartoon-like orbital images that foster an unphysical picture of the actual sterics.



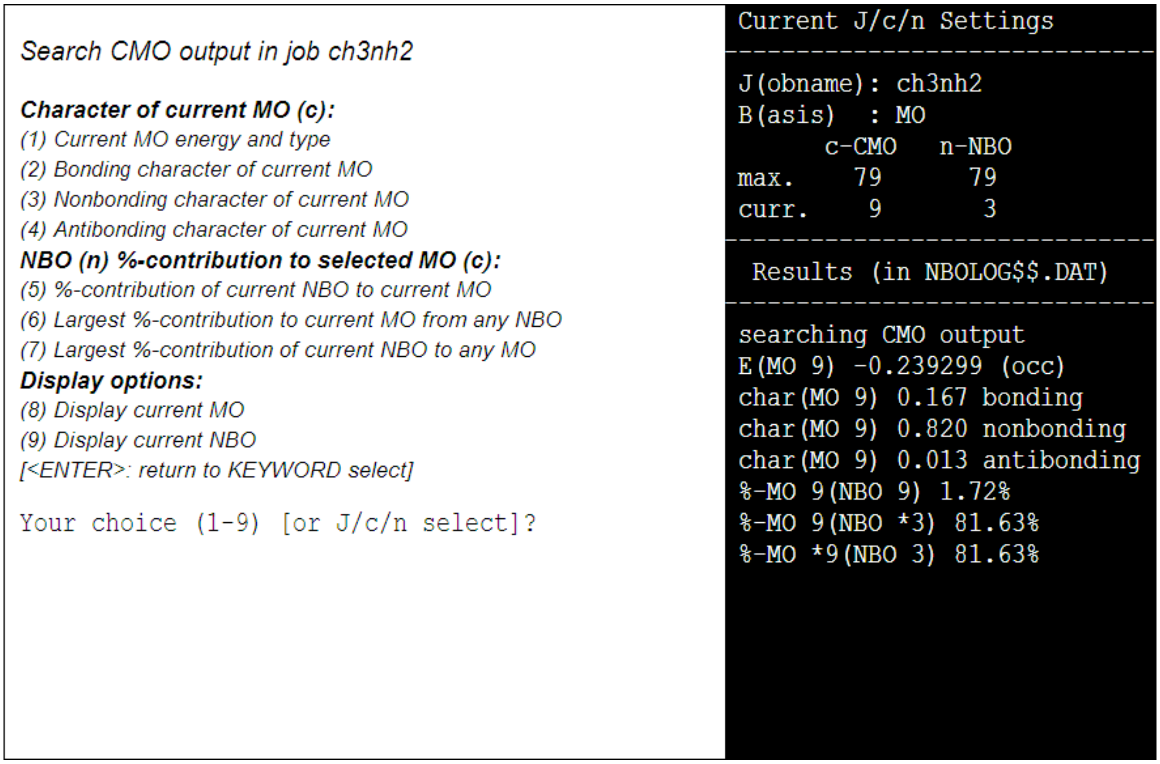
```
Current J/U/d/d' Settings
------------------------------
J(obname): ch3nh2
B(asis)   : NLMO
       U(nit) d-NLMO d'-NLMO
max.      1       9       9
curr.     1       3       5
------------------------------
 Results (in NBOLOG$$.DAT)
------------------------------
```

```
Image stored in pic.bmp
   (Press <Enter> to continue...)
```

[Note that the orbital lobes in the default *NBOView* diagram above seem to have "antibonding" (out-of-phase; yellow on blue) overlap. However, the physical interactions depend only on the *square* of such orbital overlaps, so one could fairly *reverse* the overall sign of either orbital (e.g., using the ***sign*** command in the *NBOView* module) to give the expected in-phase (blue-on-blue, yellow-on-yellow) patterns of direct steric overlap.]

CMO: NBO-Based Character of Canonical Molecular Orbitals

The CMO menu resets the default basis to B = MO (canonical molecular orbitals). The nine selection options are displayed below, with the replies from options *M* = 1-*7* included as dialog:



Search CMO output in job ch3nh2

Character of current MO (c):
(1) Current MO energy and type
(2) Bonding character of current MO
(3) Nonbonding character of current MO
(4) Antibonding character of current MO
NBO (n) %-contribution to selected MO (c):
(5) %-contribution of current NBO to current MO
(6) Largest %-contribution to current MO from any NBO
(7) Largest %-contribution of current NBO to any MO
Display options:
(8) Display current MO
(9) Display current NBO
[<ENTER>: return to KEYWORD select]

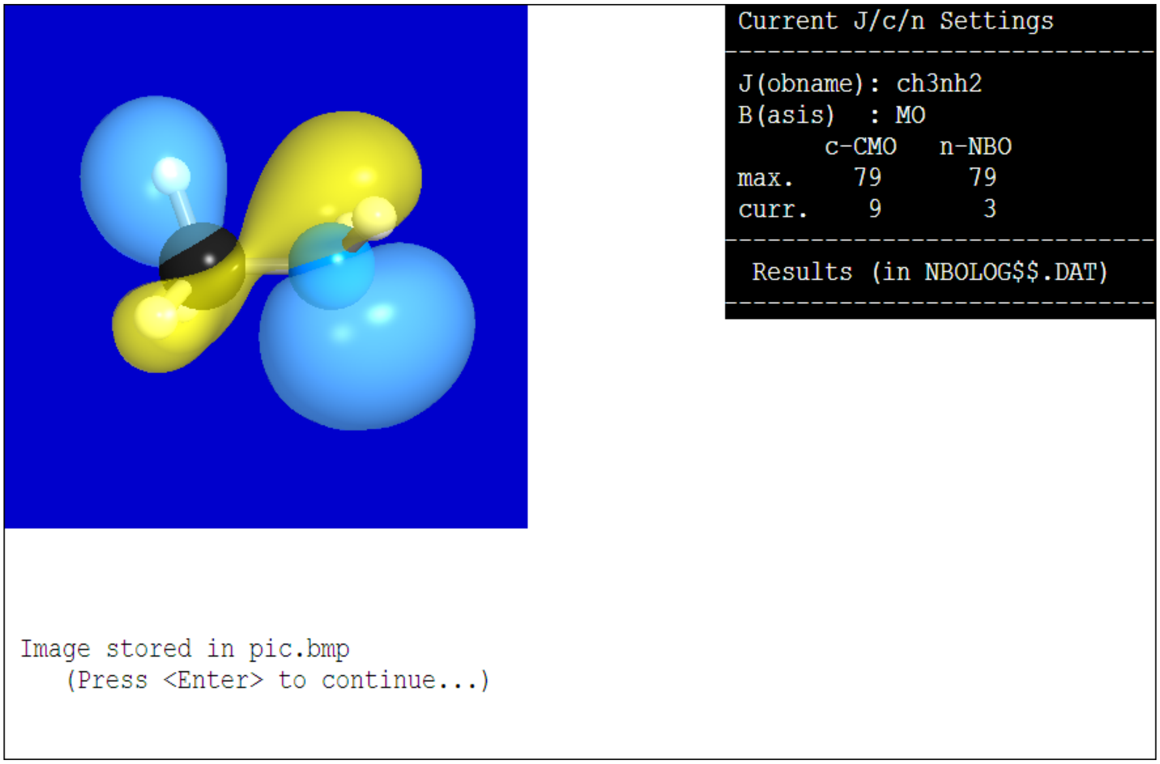
```
Your choice (1-9) [or J/c/n select]?
```

```
Current J/c/n Settings
-----------------------------
J(obname): ch3nh2
B(asis)  : MO
       c-CMO   n-NBO
max.    79      79
curr.    9       3
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching CMO output
E(MO 9) -0.239299 (occ)
char(MO 9) 0.167 bonding
char(MO 9) 0.820 nonbonding
char(MO 9) 0.013 antibonding
%-MO 9(NBO 9) 1.72%
%-MO 9(NBO *3) 81.63%
%-MO *9(NBO 3) 81.63%
```

As shown in the prompt line, the three selectable "*V*" variables for this menu are "J"(obname) and the serial numbers "c", "n" of selected CMO and NBO, respectively. As usual, you can enter the single character for each variable to see available selections or change the default settings. The initial default values, c = 9, n = 9, correspond to the highest occupied member of each set (HOMO and $n_{N(2)}$ lone pair NBO, respectively).

From the dialog lines for menu selections *M* = 1-7, we first see (*M* = 1) that the orbital energy of MO 9 is –0.239299 a.u. and the MO is of "occ"(upied) type. Selections *M* = 2-4 then show sequentially the fractional bonding (0.167), nonbonding (0.820), and antibonding (0.013) character of this MO in terms of its NBO composition. Selections *M* = 5, 6 then provide further details of CMO composition, including (*M* = 5) the %-contribution from the current c = 9 NBO (1.72%), and (*M* = 6) the largest %-contribution from *any* NBO (the 81.63% from maximal contributor NBO 3, the nitrogen lone pair). Selection *M* = 7 shows conversely which MO has the largest %-contribution from current NBO 3 (the same MO 9 and percentage value, in the present case).

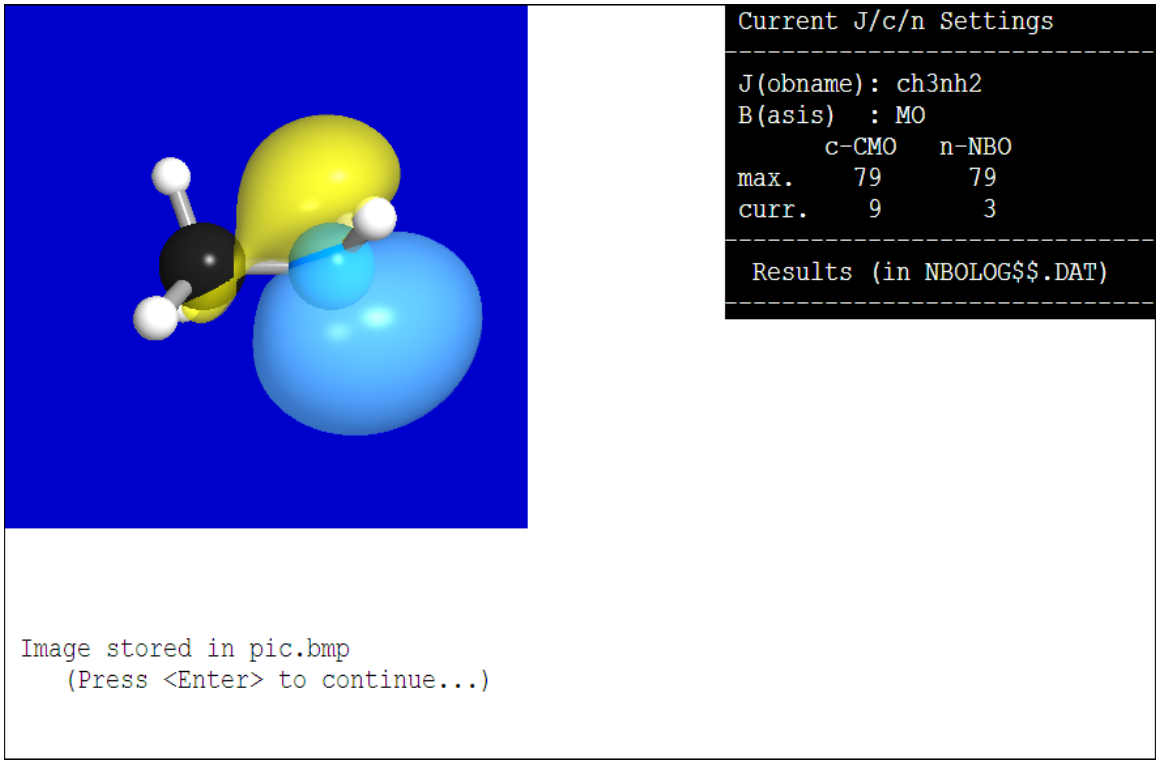
Display menu options *M* = 8, 9 then show the informative comparisons of orbital shape for currently selected delocalized MO (*M* = 8) vs. localized NBO (*M* = 9), as shown in the screens below:



```
Current J/c/n Settings
----------------------------
J(obname): ch3nh2
B(asis)  : MO
       c-CMO   n-NBO
max.    79      79
curr.    9       3
----------------------------
 Results (in NBOLOG$$.DAT)
----------------------------
```

```
Image stored in pic.bmp
   (Press <Enter> to continue...)
```

(MO 9: HOMO)



```
Current J/c/n Settings
----------------------------
J(obname): ch3nh2
B(asis)  : MO
       c-CMO   n-NBO
max.    79      79
curr.    9       3
----------------------------
 Results (in NBOLOG$$.DAT)
----------------------------
```

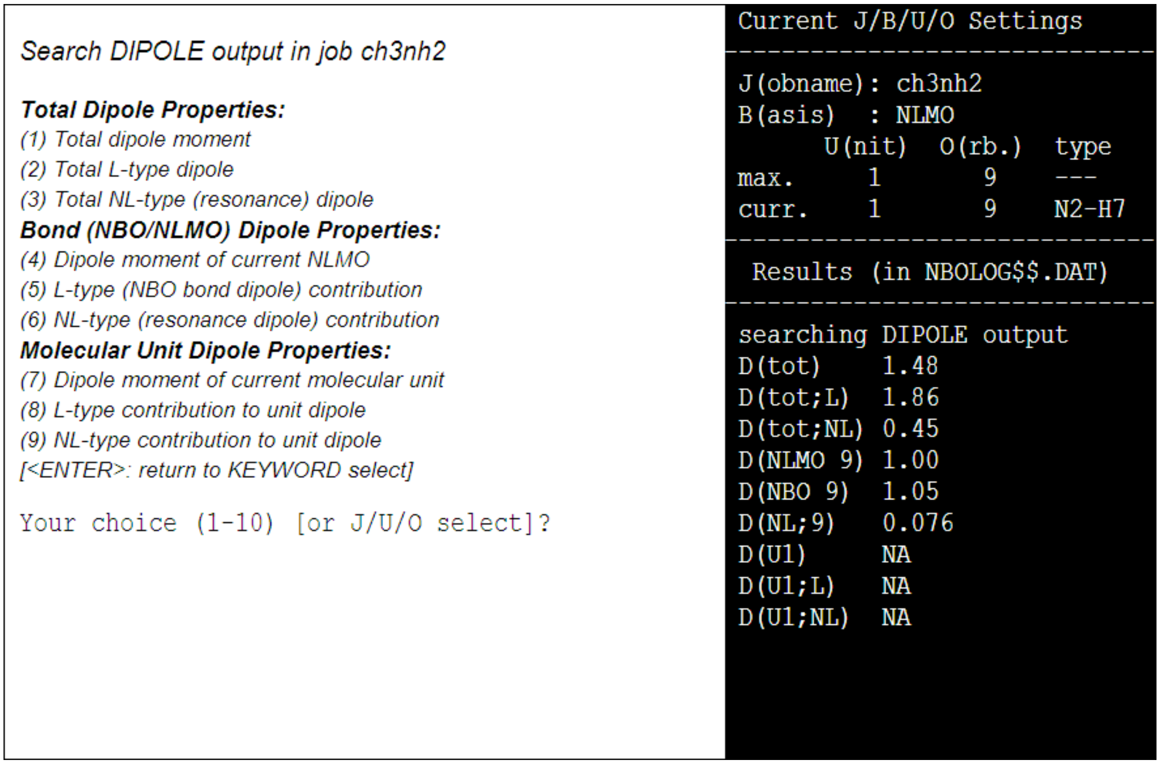
```
Image stored in pic.bmp
   (Press <Enter> to continue...)
```

(NBO 3: $n_{N(2)}$ lone pair)

As the numerical values of *M* = 2-4 indicate, the MO 9 "HOMO" is a weird mixture of the expected $n_{N(2)}$ lone pair (81.6%) and miscellaneous bonding (18%) and antibonding (1%) contributions from throughout the molecule, with no clear relationship to structural bonding features. NBO 3 has the expected form of a nitrogen lone pair, similar to the PNBO diagram of p. 64 except for the weak steric "ripples" at the adjacent carbon atom that assure orthogonality to the antiperiplanar $\sigma_{C(1)H(3)}$ NBO.

DIPOLE: L/NL Contributions to Electric Dipole Moment

Selections *M* = 1-9 of the DIPOLE keyword menu are shown in the screen below, with illustrative dialog from each selection. In this case, the basis set B = NLMO is fixed, so the selectable "*V*" variables are J(obname), U(nit), and O(rbital) number, with O = 9 (highest Lewis-type orbital) as default. As usual, enter the single character for each variable to see available selections or re-set the default selection.



Search DIPOLE output in job ch3nh2

Total Dipole Properties:
(1) Total dipole moment
(2) Total L-type dipole
(3) Total NL-type (resonance) dipole
Bond (NBO/NLMO) Dipole Properties:
(4) Dipole moment of current NLMO
(5) L-type (NBO bond dipole) contribution
(6) NL-type (resonance dipole) contribution
Molecular Unit Dipole Properties:
(7) Dipole moment of current molecular unit
(8) L-type contribution to unit dipole
(9) NL-type contribution to unit dipole
[<ENTER>: return to KEYWORD select]

```
Your choice (1-10) [or J/U/O select]?
```

```
Current J/B/U/O Settings
-----------------------------
J(obname): ch3nh2
B(asis)  : NLMO
      U(nit)  O(rb.)  type
max.     1       9    ---
curr.    1       9    N2-H7
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching DIPOLE output
D(tot)     1.48
D(tot;L)   1.86
D(tot;NL)  0.45
D(NLMO 9)  1.00
D(NBO 9)   1.05
D(NL;9)    0.076
D(U1)      NA
D(U1;L)    NA
D(U1;NL)   NA
```

As shown on the menu, selections *M* = 1-3 refer to total dipole properties, *M* = 4-6 to bond dipole properties, and *M* = 7-9 to dipole properties of individual molecular units ("not applicable" in the present case).

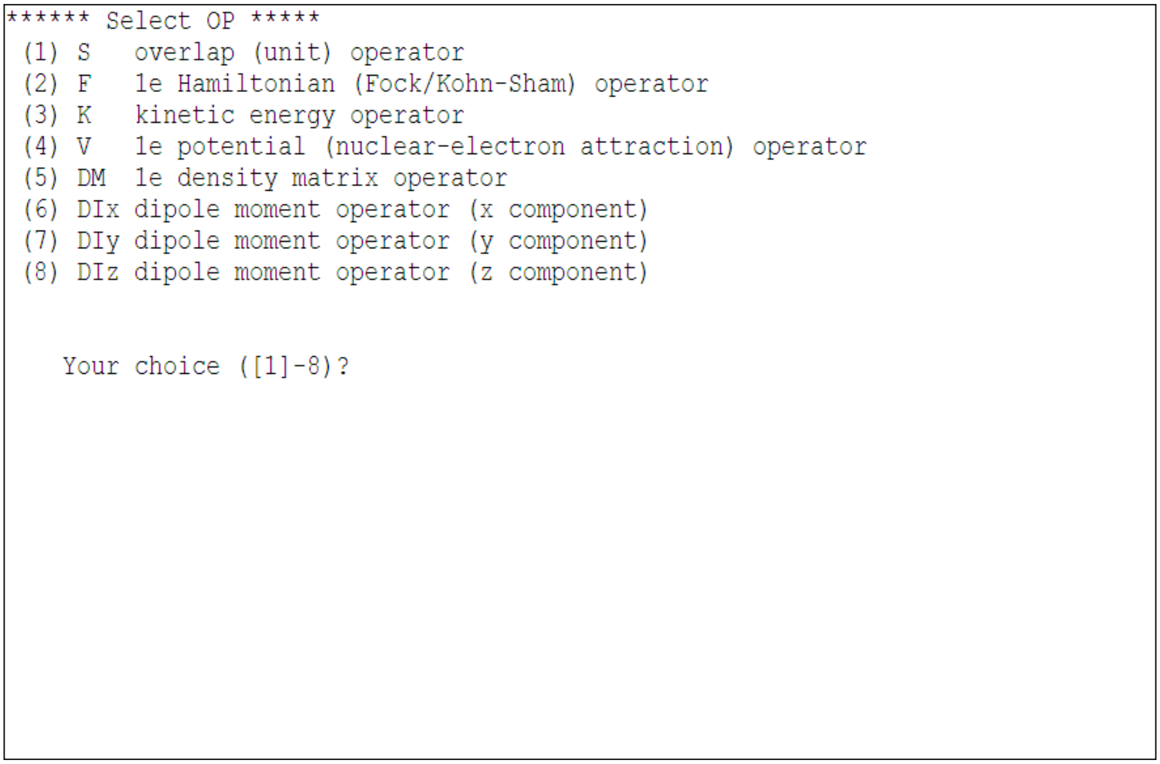
For the total dipole, M = 1 gives the overall length (1.48 D) of the dipole moment vector $\boldsymbol{\mu}_{\text{tot}}$, while M = 2 gives the corresponding length of the sum of localized Lewis-like "bond-dipole" contributions $\boldsymbol{\mu}_{\text{L}}$ (1.96 D), and M = 3 the corresponding length of resonance-type non-Lewis contributions $\boldsymbol{\mu}_{\text{NL}}$ (0.45 D). These three lengths can be used to build the triangle of orientational relationships between the three vectors, with the resonance-type $\boldsymbol{\mu}_{\text{NL}}$ vector oriented nearly opposite to $\boldsymbol{\mu}_{\text{L}}$ vector to reduce the final $\boldsymbol{\mu}_{\text{tot}}$ vector. (More complete details of cartesian *x, y, z* components of each vector are found in the full DIPOLE output.)

Selections M = 4-6 provide similar L/NL/tot detail for the individual "bond dipole" <NLMO|$\boldsymbol{\mu}^{(\text{op})}$|NLMO> contribution of the currently selected orbital O = 9 ($\sigma_{\text{N(2)H(7)}}$ bond NBO). Although often neglected in elementary textbook presentations, the total magnitude of the "lone pair dipole" contribution will also be found to be quite appreciable (2.88 D, greater than the entire molecular $\boldsymbol{\mu}_{\text{tot}}$!). Indeed, the Lewis (3.18 D) and non-Lewis (0.36 D) contributions to the lone pair dipole indicate that resonance-type lone pair delocalization is a principal contributor to overall $\boldsymbol{\mu}_{\text{NL}}$ charge shifts, as chemical intuition would suggest. These details warn that many assumptions underlying simple "bond dipole models" of dielectric properties are unjustified.

Selections M = 7-9 (although "not applicable" in the present case) will often show the powerful *intermolecular* resonance-type ("charge transfer") effects on dipolar properties of H-bonded species or other coordination complexes. However, interest in such dipolar properties will normally require attention to vectorial details of full DIPOLE output, rather than the simple scalar dipole properties that are accessible in the *NBOSearch* menu.

<OPBAS>: Matrix Elements of Chosen Operator and Basis Set

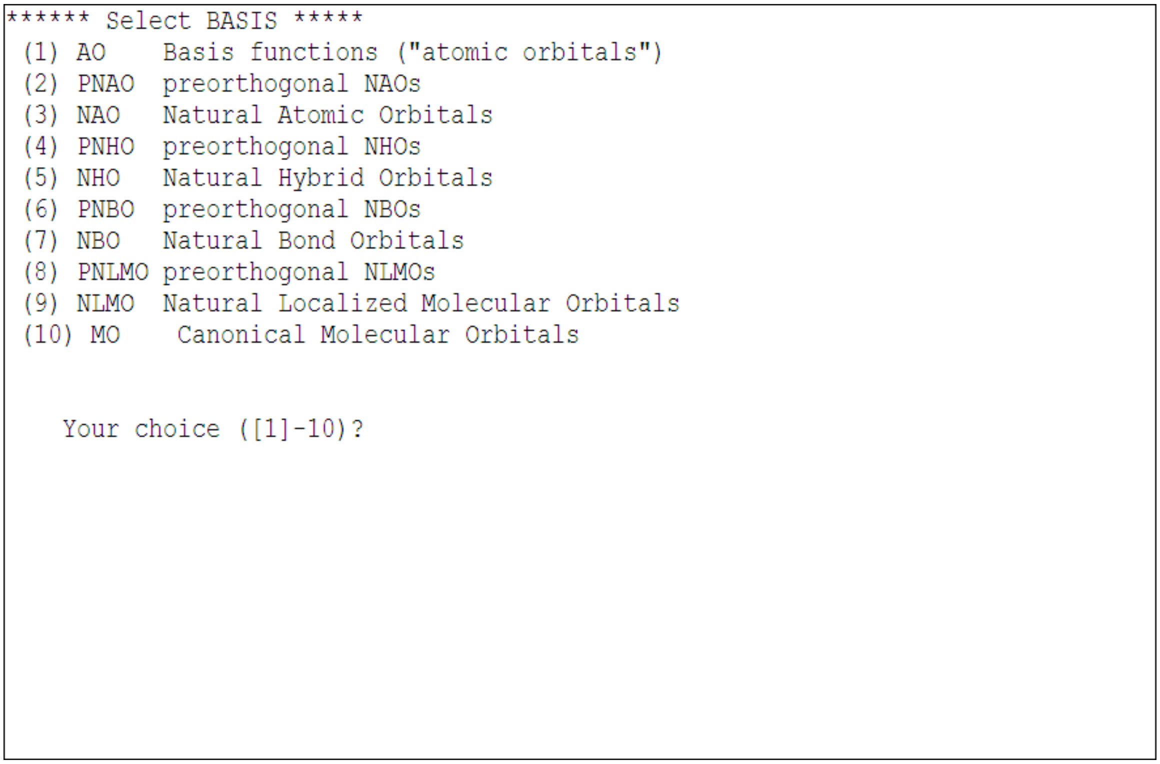
The "<OPBAS>" keyword selection provides entry into a very general procedure for accessing specified row ("r") and column ("c") matrix elements of a chosen "OP"(erator) and "BAS"(is set). Selecting this option leads first to a menu of available operators [1]-(8):



```
****** Select OP *****
 (1) S   overlap (unit) operator
 (2) F   1e Hamiltonian (Fock/Kohn-Sham) operator
 (3) K   kinetic energy operator
 (4) V   1e potential (nuclear-electron attraction) operator
 (5) DM  1e density matrix operator
 (6) DIx dipole moment operator (x component)
 (7) DIy dipole moment operator (y component)
 (8) DIz dipole moment operator (z component)


   Your choice ([1]-8)?
```

For simplicity of illustration, we select default option (1), the unit or “overlap” operator, whose matrix elements are simply the orbital overlap integrals S_{rc} = <*basis*(r)|*basis*(c)> in whatever *basis* set may be selected.

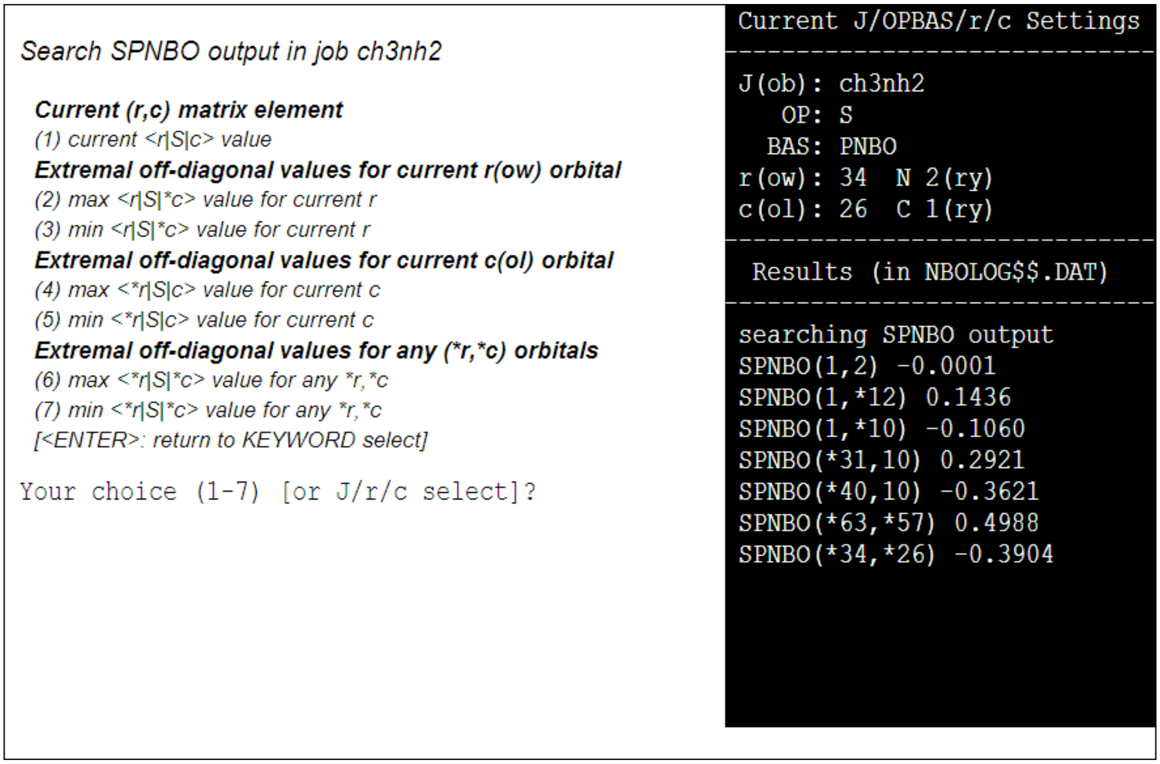
The menu of available basis sets [1]-(10) is next displayed, as shown below:



```
****** Select BASIS *****
 (1) AO    Basis functions ("atomic orbitals")
 (2) PNAO  preorthogonal NAOs
 (3) NAO   Natural Atomic Orbitals
 (4) PNHO  preorthogonal NHOs
 (5) NHO   Natural Hybrid Orbitals
 (6) PNBO  preorthogonal NBOs
 (7) NBO   Natural Bond Orbitals
 (8) PNLMO preorthogonal NLMOs
 (9) NLMO  Natural Localized Molecular Orbitals
 (10) MO    Canonical Molecular Orbitals


   Your choice ([1]-10)?
```

For present illustrative purposes we select the “PNBO” option (6), the usual “visualization orbitals” of NBO analysis. In the spirit of the Mulliken approximation ($S_{rc} \approx -kF_{rc}$, where k is a proportionality constant of order unity), the PNBO overlap diagrams give a powerful visual impression of interaction strength, allowing beginning students to visualize how orbital interactions are maximized by using Pauling’s “principle of maximum overlap.”

The combination of “OP” = S and “BAS” = PNBO corresponds to the “SPNBO” keyword, which normally leads to printout of the entire set of <PNBO(r)|PNBO(c)> (“<r|S|c>”) matrix elements in the full *ch3nh2.nbo* output file. For these choices, *NBOSearch* leads to the “SPNBO output” menu, as shown below:



```
Current J/OPBAS/r/c Settings
-----------------------------
J(ob): ch3nh2
   OP: S
  BAS: PNBO
r(ow): 34  N 2(ry)
c(ol): 26  C 1(ry)
-----------------------------
 Results (in NBOLOG$$.DAT)
-----------------------------
searching SPNBO output
SPNBO(1,2) -0.0001
SPNBO(1,*12) 0.1436
SPNBO(1,*10) -0.1060
SPNBO(*31,10) 0.2921
SPNBO(*40,10) -0.3621
SPNBO(*63,*57) 0.4988
SPNBO(*34,*26) -0.3904
```

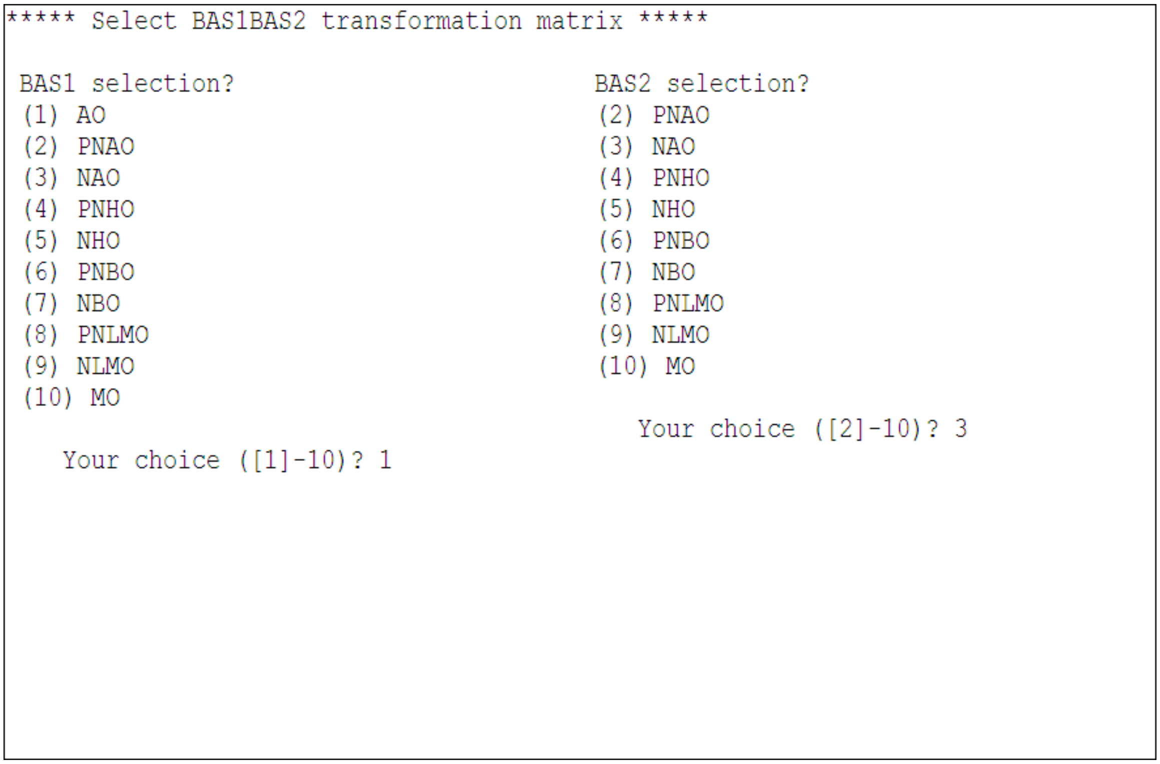
As usual, the menu includes the list of selectable “V” variables: J(obname), r(ow), and c(olumn) indices. The initial default values (r = 1, c = 2) then lead to the replies shown in the dialog section of the command bar, which correspond to selecting menu options M = 1-7 in order.

As the reply for M = 1 shows, the <1|S|2> = $S_{1,2}$ overlap value is very weak (-0.0001) between “C 1(cr)” (r = 1) and “N 2(cr)” (c = 2) PNBOs. Selections M = 2 or 3 [for extremal overlap with the C(1) core of row 1] lead to the maximal overlap value 0.1436 with antibond C(1)-H(4)*, c = 12, or minimal (most negative) value –0.1060 with the C(1)-N(2)* antibond, c = 10. (As usual, entering “r” or “c” will display a list of orbitals and labels to identify a particular orbital number.) Similarly, selections M = 4 or 5 for extremal overlaps with the currently selected column (c = 10) lead to the maximal overlap $S_{31,10}$ = 0.2921 or minimal overlap $S_{40,10}$ = –0.3621. Finally, selections M = 6 or 7 lead to the maximum ($S_{63,57}$ = 0.4988) or minimum ($S_{34,26}$ = –0.3904) values found anywhere in the overlap matrix. The <*OPBAS*> menu selections therefore simplify basic data retrieval and JOB comparisons for many orbital properties of interest.

<BAS1BAS2>: Transformation Matrix Between Chosen Basis Sets

The “*<BAS1/BAS2>”* keyword selection is similar to the previous “<OPBAS>” selection in giving access to desired r/c elements of a selected matrix. In this case, the specified matrix tabulates the transformation coefficients from one basis set (“*BAS1”,* with orbitals identified by row index “r”) to another (“*BAS2”,* with orbitals identified by column index “c”).

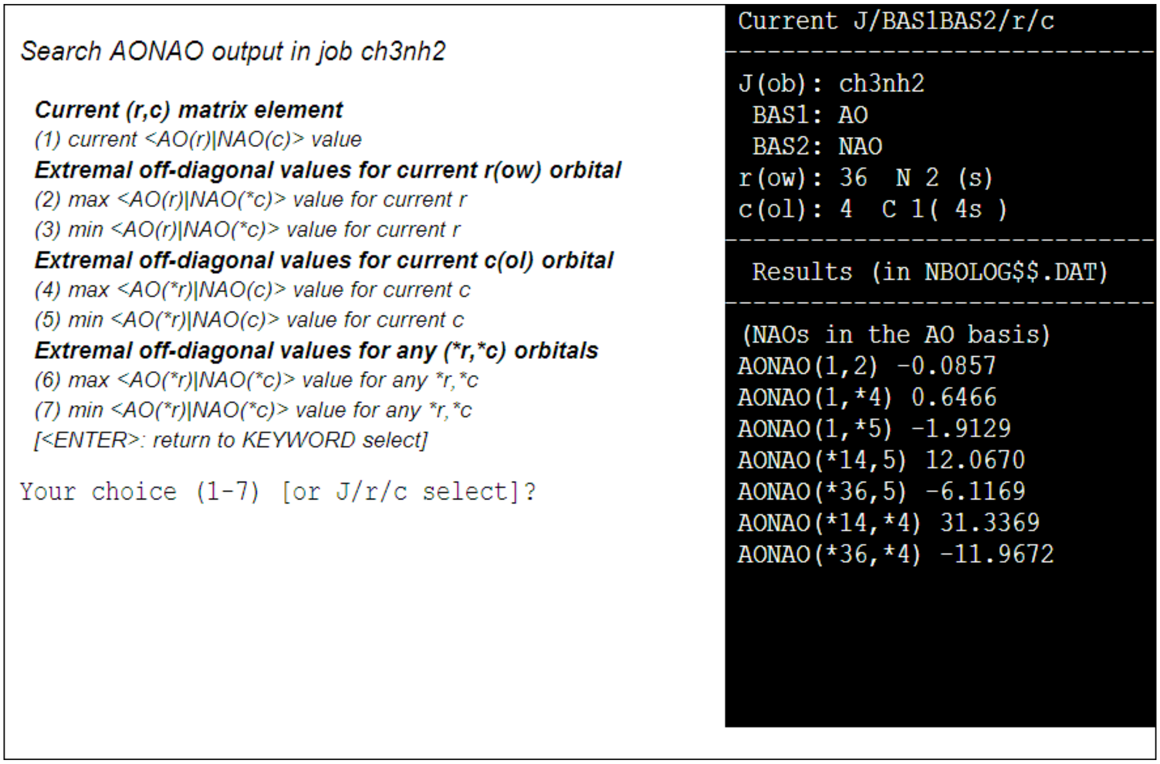
The first step is to select the two basis sets, as shown in the menu below:



```
***** Select BAS1BAS2 transformation matrix *****

 BAS1 selection?                       BAS2 selection?
 (1) AO                                (2) PNAO
 (2) PNAO                              (3) NAO
 (3) NAO                               (4) PNHO
 (4) PNHO                              (5) NHO
 (5) NHO                               (6) PNBO
 (6) PNBO                              (7) NBO
 (7) NBO                               (8) PNLMO
 (8) PNLMO                             (9) NLMO
 (9) NLMO                              (10) MO
 (10) MO
                                          Your choice ([2]-10)? 3
    Your choice ([1]-10)? 1
```

As shown in the menu, for present illustrative purposes we select “1” (AOs) as “*BAS1”* and “3” (NAOs) as “*BAS2*“. The chosen transformation matrix therefore corresponds to the LCAO-NAO expansion coefficients that express NAOs in terms of basis AOs, or to the “AONAO” keyword that prints out this matrix in full to the general .nbo output file.

With this selection, one enters the “AONAO output” menu as shown below, with the same “J/r/c” selectable “*V*” options and very similar *M* = 1-7 menu selections as in the “*<OPBAS>*” section above. The seven replies listed in the dialog should therefore be self-explanatory and are left as an exercise to the reader.



Search AONAO output in job ch3nh2

Current (r,c) matrix element

(1) current <AO(r)|NAO(c)> value

Extremal off-diagonal values for current r(ow) orbital

*(2) max <AO(r)|NAO(*c)> value for current r*

*(3) min <AO(r)|NAO(*c)> value for current r*

Extremal off-diagonal values for current c(ol) orbital

*(4) max <AO(*r)|NAO(c)> value for current c*

*(5) min <AO(*r)|NAO(c)> value for current c*

Extremal off-diagonal values for any (*r,*c) orbitals

*(6) max <AO(*r)|NAO(*c)> value for any *r,*c*

*(7) min <AO(*r)|NAO(*c)> value for any *r,*c*

[<ENTER>: return to KEYWORD select]

```
Your choice (1-7) [or J/r/c select]?
```

```
Current J/BAS1BAS2/r/c
------------------------------
J(ob): ch3nh2
 BAS1: AO
 BAS2: NAO
r(ow): 36  N 2 (s)
c(ol): 4  C 1( 4s )
------------------------------
 Results (in NBOLOG$$.DAT)
------------------------------
(NAOs in the AO basis)
AONAO(1,2) -0.0857
AONAO(1,*4) 0.6466
AONAO(1,*5) -1.9129
AONAO(*14,5) 12.0670
AONAO(*36,5) -6.1169
AONAO(*14,*4) 31.3369
AONAO(*36,*4) -11.9672
```

Please report errors, malfunctions, or suggestions for improvements to weinhold@chem.wisc.edu