Chapter 1

Getting Started

1.1 TALKING TO YOUR ELECTRONIC STRUCTURE SYSTEM

In order to begin natural bond orbital (NBO) analysis of a wavefunction, you first need to establish communication between a chosen electronic structure system (ESS) that calculates the wavefunction and the NBO program that performs the analysis. Many ESS programs in common usage have integrated NBO capability or a convenient interface with the most recent version of the NBO program [currently *NBO 5.9* (NBO5)]. We assume you have access to such a program.

In favorable cases, the ESS and NBO programs may already be integrated into a linked ESS/NBO module (such as G09/NBO of current *Gaussian 09*™ distributions). In this case, communication between the ESS and NBO programs only requires appending the $NBO keylist (see below) to the end of the usual ESS input file that performs the desired wavefunction calculation. [Instructions for creating the ESS input file and appending the $NBO keylist are generally included in the ESS program documentation; see, for example, J. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Calculations: A Guide to Using Gaussian* (Gaussian Inc., Pittsburgh, PA, 1996) for the Gaussian program.] Such an integrated ESS/NBO program module allows the ESS and NBO programs to interactively cooperate on certain complex tasks that are unavailable in the unlinked stand-alone configurations described in the following paragraph. Optimally, the combined module will incorporate the latest NBO5 capabilities (ESS/NBO5), allowing the greatest possible range of analysis options; however, even older NBO versions (such as the older "NBO 3.1" incorporated in binary G09W Gaussian for Windows) can correctly perform most of the core NBO analysis options of Chapters 1–4. Ask your System Manager to upgrade the ESS to the latest NBO5-compatible form if a source-code version of the ESS is available. (Those fortunate readers with access to a full-featured ESS/NBO5 installation may skip to Section 1.2.)

Users of unlinked ESS hosts (including G09W users who wish to gain access to NBO5-level options) may use a stand-alone version of NBO5 (e.g., *GENNBO 5.0W* for PC-Windows users), but the process is a little trickier. In this case, the ESS program must first be instructed to produce the NBO "archive" file for the calculated

Discovering Chemistry With Natural Bond Orbitals, First Edition. Frank Weinhold and Clark R. Landis.

I/O-1.1

```
$GENNBO  NATOMS=1  NBAS=8  UPPER  BODM  $END
$NBO  $END
$COORD
H atom test job
     1     1       0.000000       0.000000       0.000000
$END
 :
 :
```

wavefunction (see Sidebar 1.1 for Gaussian users). This file normally has the extension .47 following the chosen job filename (e.g., JOBNAME.47) and will be found to contain an empty $NBO keylist ("$NBO $END") as the second line of the file, as illustrated in the sample I/O-1.1 listing.

You can use any text editor to add desired keyword entries to the $NBO keylist, specifying the analysis options to be performed by the ensuing GENNBO5 processing. You can also insert a new keylist after the $NBO keylist, just as though you were appending the keylist to the end of the input file for an integrated ESS/NBO5 program.

The JOBNAME.47 archive file becomes the input file for your GENNBO5 job, which performs the actual NBO analysis. With the PC-Windows *GENNBO5.0W* version, you merely launch the program by mouseclick and select the JOBNAME.47 job from the displayed menu selections. Alternatively, if the GENNBO5 program has been set up as a binary executable (gennbo5.exe) on your system, you can launch the job by a command of the form

```
gennbo5 < JOBNAME.47 > JOBNAME.OUT
```

that pipes the analysis output to a chosen "JOBNAME.OUT" file. Details of interfacing the ESS with GENNBO5 may have been set up differently on your particular installation or website, but logically this is what is going on.

No matter whether you are working with a linked or stand-alone NBO configurations, the manner of controlling NBO analysis through the keyword entries of the $NBO keylist (the subject of this book) is the same for all setups. Although different ESS hosts boast somewhat different capabilities, the implementation of $NBO keylist commands is consistent across all ESS platforms. We shall ignore further ESS-specific details as far as possible.

SIDEBAR 1.1 *HOW GAUSSIAN USERS OBTAIN THE NBO ARCHIVE FILE FOR NBO5-LEVEL PROCESSING*

For Gaussian G09W (Windows binary) users wishing to bypass the limitations of the integrated NBO 3.1, the "trick" is to include the ARCHIVE keyword (and suitable FILE name) in the $NBO keylist that follows ordinary Gaussian input. As an example, for a simple H-atom calculation, the input file takes the form

```
#B3LYP/6-311++G** POP=NBOREAD

H atom test job

0 2
H

$NBO ARCHIVE FILE=H_atom $END
```

This produces the "H_atom.47" archive file that serves as input to GENNBO5, as described above.

Several points should be particularly noted:

(1) The Gaussian route card should include the "POP=NBOREAD" keyword to read and process the $NBO keylist (or the "POP=NBODEL" keyword to process a $DEL keylist). Follow the instructions of the Gaussian manual or Foresman–Frisch supplementary manual for further details of NBO-specific keyword options.

(2) Keyword input in both Gaussian and NBO is generally case-insensitive, except for literals such as the FILE specification.

(3) Certain keyword options that superficially appear to "work" in NBO 3.1 are obsolete or erroneous with respect to more recent NBO versions. This applies particularly to the PLOT keyword, where the files produced by NBO 3.1 are incompatible with the *NBOView* orbital viewer (Appendix B). Significant algorithmic differences between NBO3 and NBO5 are particularly apparent in details of natural population analysis for transition metals and rare-earth species. In addition, NBO5-level methodological improvements often result in significant numerical discrepancies between NBO3-level and NBO5-level output, particularly in cases of near-linear dependence (e.g., large basis sets including diffuse functions). NBO5 also includes numerous keyword options (e.g., NRT, STERIC, NEDA, NCS, NJC, and numerous checkpointing and matrix output options) with no counterpart in NBO3. Gaussian users are therefore advised to use the NBO3-level program only to generate the necessary ARCHIVE file for accessing higher NBO5-level analysis whenever possible.

1.2 HELPFUL TOOLS

The reader should be aware of three important resources that complement the present book and provide additional useful details on many topics:

(1) The *NBO 5.0 Program Manual* (which accompanies every authorized copy of the *NBO 5*-level program) is an essential resource for every serious NBO user. In addition to documentation of all program keywords, sample output, and background references, the manual contains (Section C, pp. C1–C72) extensive documentation of the Fortran source program itself, including brief descriptions of each SUBROUTINE and FUNCTION. For those so determined (presumably a small fraction of readers of this book!), it thereby becomes possible to locate the source code and program comments that connect back to the original description of the program algorithm in the

research literature. Together with the documentation within the NBO source code itself, the NBO Manual should be relied upon as the ultimate authority on many points of details beyond the scope of the present book.

(2) The *NBO website* [www.chem.wisc.edu/∼nbo5] contains a variety of important resources for both novice and accomplished NBO users, including tutorials, interactive "self-explaining" output samples for all major program options, FAQ (frequently asked questions), comprehensive literature references to recent NBO applications, and much else. The NBO website also contains program documentation for the *NBOView* orbital viewer program that is used extensively throughout this book (see Appendix B).

(3) The authors' companion research monograph *Valency and Bonding: A Natural Bond Orbital Donor–Acceptor Perspective* (Cambridge University Press, Cambridge, 2005) describes applications of NBO analysis to a broad variety of chemical problems spanning the periodic table. This monograph also provides extensive theoretical background (*V&B*, Chapter 1) on the physical and mathematical concepts that underlie NBO program options, allowing the interested student to trace calculated NBO descriptors back to fundamental quantum mechanical principles.

While the goal of this book is to facilitate the student's entry into the ranks of accomplished NBO users with minimal prerequisites or assumed background, we shall freely include cross-references to *NBO Manual* pages, *NBO website* URLs, or *V&B* content where appropriate.

1.3 GENERAL $NBO KEYLIST USAGE

The entryway to communication with your NBO program is the $NBO keylist, which allows you to include desired keywords between initial $NBO and final $END delimiters, namely,

```
$NBO (chosen keywords) $END
```

Other NBO keylists to be described below (such as the $GENNBO . . . $END and $COORD . . . $END keylists shown in I/O-1.1) are similarly opened by an identifying $KEY identifier and closed by a matching $END delimiter, so it is important that these delimiters be correctly located and spelled. A given keylist may extend over multiple lines, for example,

```
$NBO
(chosen keywords)
$END
```

but no two keylists (or portions thereof) may occur on the same line. (In some non-U.S. installations, the "$" identifier of keylist delimiters may be replaced by a more convenient keyboard character.)

The keywords appearing between $NBO . . . $END delimiters may generally occur in any order, and both keywords and keylist delimiters are case-insensitive (though we generally write them in upper case in this book). Keywords can be separated by a comma or any number of spaces. A keyword may also include a single parameter PARM in the form

```
KEYWORD=PARM
```

or a set of parameters PARM1, PARM2, . . . , PARM*n* in "bracket-list" format

```
KEYWORD < PARM1/PARM2/.../PARMn>
```

Bracket-list syntax rules are summarized in Sidebar 1.2.

The $NBO keylist may contain any assortment of plain, parameterized, and bracket-listed keywords, such as

```
$NBO FILE=tryout
FNBO < 13,27/8,34>
STERIC=0.4 < 16,22/8,24/17,6 > PLOT NRT $END
```

Each input keyword will be echoed near the top of the NBO output file (as shown in I/O-1.2 for the above keylist), allowing you to check that the program "understands" your input commands.

The listing includes some extra keywords that were automatically activated as prerequisites for requested options. If a requested keyword fails to appear in this list, you may find it (perhaps misspelled?) in a list of "Unrecognized keywords" that appears before any other NBO output. The *NBO website* gives many other illustrations of $NBO keylist entry for main program keyword options (www.chem.wisc.edu/∼nbo5/mainprogopts.htm).

In preparing an NBO input file, it is important to use an ordinary text editor (rather than *Word* or other word processor) in order to scrupulously avoid tabs or other control characters embedded in the plain-ASCII text file. Unseen control characters, corresponding to ASCII characters outside the printable range 32–126, cause unpredictable errors in processing the input file. Check also that *text-file format* is consistent between the platform on which the input file was prepared and that under which the

I/O-1.2

```
/NLMO   / : Form Natural Localized Molecular Orbitals
/NRT    / : Natural Resonance Theory Analysis
/FNBO   / : Print the NBO Fock matrix
            for user-requested matrix elements
/STERIC / : Print NBO/NLMO steric analysis
            with user-requested <NBO indices>
            Print threshold set to  0.40
/LFNPR  / : set to 21
/PLOT   / : Write information for the orbital plotter
/FILE   / : Set to tryout
```

NBO program will run; a particularly exasperating inconsistency is the different choice of CR/LF versus CR "end-line" markers in PC-Windows versus Macintosh or linux text files. When in doubt, use a file-transfer protocol (ftp) or file-conversion utility (dos2unix, etc.) to transfer text files from one platform to another.

SIDEBAR 1.2 *BRACKET-LIST SYNTAX*

Several NBO keywords can be modified by inclusion of parameters (PARM1, PARM2, . . ., PARM*n*) of numerical or text content. In such cases, the parameters are enclosed in a "bracket-list" that is associated with the keyword through an input entry of the form

```
KEYWORD <PARM1/PARM2/.../PARMn>
```

The bracket-list "<", ">" terminators must be separated by at least one space from the preceding keyword, as well as from any following keyword. Bracket-lists may be broken up onto separate lines following any "/" separator,

```
KEYWORD <PARM1/
PARM2/
.../
PARMn>
```

The entries of the bracket-list vary considerably according to the keyword they modify. A common usage is to specify selected index pairs (*i*, *j*) of an array to be printed; for example, the command

```
FNBO <13 27/8 24>
```

specifies that only the $F_{13,27}$ and $F_{8,24}$ elements of the NBO Fock matrix ("FNBO" array) should be printed, rather than the entire array. A bracket-list may also follow a parameterized keyword (separated, as always, by at least one space at either end); for example, the command

```
STERIC=0.4 <16 22/ 8 24/ 17 6>
```

resets the STERIC output threshold to 0.4 kcal/mol and restricts printout of pairwise steric interactions to the NBO pairs (16, 22), (8, 24), and (17, 6). In case of text entries, each "/" separator should be set off by at least one blank (on each side) from text characters of the entry. Consult the *NBO Manual* for further details of allowed bracket-list options for each keyword.

1.4 PRODUCING ORBITAL IMAGERY

In many cases, the key to developing effective chemical intuition about NBOs is accurate *visualization* of their shapes and sizes. For this purpose, it is important to gain

access to a suitable graphical utility for displaying images of NBOs and other orbitals. NBO graphical output can be exported to many popular orbital-viewing programs, such as *Gaussview*, *Jmol*, *Molden*, *Spartan*, *Molekel*, and *ChemCraft*, each offering distinctive features or limitations with respect to other programs. Sidebar 1.3 summarizes some details of how NBO "talks" to such programs and provides links to their further description.

The orbital images of this book are produced by the *NBOView 1.0* program, whose usage is briefly described in Appendix B. *NBOView* is specifically adapted to flexible display of the entire gamut of localized NBO-type (NAO, NHO, NBO, NLMO, and preorthogonal PNAO, PNHO, PNBO, and PNLMO "visualization orbitals") as well as conventional AO/MO-type orbitals in a variety of 1D (profile), 2D (contour), and 3D (view) display forms. The *NBOView Manual* link on the NBO website (http://www.chem.wisc.edu/∼nbo5/v_manual.htm) provides full documentation and illustrative applications of *NBOView* usage.

SIDEBAR 1.3 *EXPORTING NBO OUTPUT TO ORBITAL VIEWERS*

Most orbital viewers are designed to import orbital data from the checkpoint file of the host ESS program or to directly read NBO "PLOT" (.31–.46) or "ARCHIVE" (.47) files. Communication with a chosen orbital viewer will therefore depend on details of its interface to the host ESS or NBO program.

For programs that read from a Gaussian or GAMESS checkpoint file, such as

Gaussview (http://www.gaussian.com/g_prod/gv5.htm)

Molden (http://www.cmbi.ru.nl/molden/)

Molekel (http://molekel.cscs.ch/wiki/pmwiki.php/Main/DownloadBinary)

Chemcraft (http://www.chemcraftprog.com/)

NBO5 users need only to specify the LCAO transformation matrix (AOBAS matrix) for the desired orbital basis set. This set is designated for checkpointing (storage in the checkpoint file) by a command of the form "AOBAS=C" in the $NBO keylist. For example, the NBO basis (AONBO transformation matrix) can be checkpointed by the $NBO keylist of the form

```
$NBO AONBO=C $END
```

and other orbital choices can be specified analogously. By default, checkpointed NBOs or other sets are numbered as in NBO output. However, numerous options are available to reorder checkpointed orbitals according to occupancy or other specified permutation (see *NBO Manual*, Section B-12). For users of linked G09/NBO5 or GMS/NBO5 programs, the NBO checkpointing options are flexible and convenient for graphical purposes.

[Note however that these options are unavailable in NBO3 and older versions. Users of linked G09/NBO3 binaries must therefore follow an alternative path by including the "POP=SAVENBO" command on the Gaussian route card (*not* in the $NBO keylist). The

POP=SAVENBO command has been included in recent Gaussian versions to provide a simple emulation of NBO checkpointing, principally for CAS/NBO and other nongraphical applications. Although SAVENBO enables basic displays of occupied NBOs, it cannot do so for PNBOs or other visualization orbitals that provide more informative graphical displays. The SAVENBO command is, therefore, a rather inflexible and error-prone form of checkpointing that serves as a last resort for G09/NBO3 users, but is "unrecognizable" and should *not* be considered in G09/NBO5 applications.]

For programs that read native NBO plot files, such as

Jmol (http://jmol.sourceforge.net)

NBOView (http://www.chem.wisc.edu/∼nbo5)

NBO5 users need only to include the PLOT keyword (together with a FILE=NAME identifier) in the $NBO keylist, namely,

```
$NBO FILE=MYJOB PLOT $END
```

This writes out the necessary plotfiles (MYJOB.31, MYJOB.32, . . . , MYJOB.46) for the orbital viewer to display any chosen orbital from the broad NAO/NBO/NLMO repertoire.

[G09/NBO3 binary users must again follow a more circuitous path. As described in Sidebar 1.1, one must first obtain the ARCHIVE (.47) file, then insert the "PLOT" keyword in the $NBO keylist of the .47 file, and finally process this file with *GENNBO 5.0W* to produce valid plot files. (Note that files produced by the PLOT command in antiquated *NBO 3.1* are no longer recognized by *NBOView*.)]

For the *Spartan* program (only), the NBO program provides a "SPARTAN" keyword option, namely,

```
$NBO SPARTAN $END
```

that writes out a Spartan-style archive file.

PROBLEMS AND EXERCISES

1.1. Use the resources of the *NBO website* (www.chem.wisc.edu/∼nbo5) to find the following:

(a) References to three recent applications of NBO analysis in *J. Am. Chem. Soc., J. Chem. Phys., J. Org. Chem.*, *Inorg. Chem.*, or any other chosen journal of specialized interest.

(b) References to the original papers on NBO analysis (or STERIC analysis, or NRT resonance theory analysis, or other chosen keyword options of NBO program).

(c) Names (and links) of ESS program systems that currently provide NBO interfaces or internal linkages.

(d) Reference to a general review article describing NBO methods or applications.

(e) One or more frequently asked questions or problems that sometimes bedevil new NBO users, for which you found a helpful answer.

(f) The date of the latest posted code correction for bugs in the NBO program.

1.2. Use the Tutorials section of the *NBO website* to discover the following:

(a) What is the "natural transition state" between reactant and product species of a chemical reaction? Why is this concept applicable even in barrierless reactions, for example, of ion–molecule type?

(b) Dihaloalkenes (e.g., dichloroethylene, a common cleaning fluid) exhibit a strange preference for the *cis*-isomer, despite the obvious steric and electrostatic advantages of the *trans*-isomer which keeps the "bulky" and "polar" halide ligands further separated. What is the primary electronic effect that stabilizes the *cis*-isomer compared to the *trans*-isomer of difluoroethylene (or related dihaloalkenes)?

(c) What is the best Lewis structure formulation for phosphine oxide (H_3PO), and how would it be compared with other representations commonly found in journals or textbooks?

1.3. Prepare sample input \$NBO keylists to discover (with help from Appendix C, if needed) the following:

(a) The orbital interaction integral

$$\int \varphi_i^{(\mathrm{NBO})} * F_{\mathrm{op}} \varphi_j^{(\mathrm{NBO})} \mathrm{d}\tau$$

[off-diagonal $(\mathbf{F}^{(\mathrm{NBO})})_{ij}$ matrix element of the NBO-based Fock matrix that represents the effective 1-electron Hamiltonian operator F_{op} of the system] between NBOs 14 and 27.

(b) The orbital energy integral

$$\int \varphi_i^{(\mathrm{AO})} * F_{\mathrm{op}} \varphi_i^{(\mathrm{AO})} \mathrm{d}\tau$$

[diagonal $(\mathbf{F}^{(\mathrm{AO})})_{ii}$ matrix element of the AO-based Fock matrix] for basis AO 16; and similarly the orbital energies of NAO 27, NBO 18, NLMO 23, and MOs 8, 9, and 10.

(c) The overlap integrals

$$\int \varphi_i^{(\mathrm{AO})} * \varphi_j^{(\mathrm{AO})} \mathrm{d}\tau$$

[off-diagonal matrix elements of the $\mathbf{S}^{(\mathrm{AO})}$ overlap matrix] between basis AOs (3, 4), (3, 5), and (4, 5).

1.4. Using your favorite orbital viewer package, prepare one or more orbital images of a chosen NBO for a chosen system (such as the H-atom example of Sidebar 1.1). Explain in words what each image portrays and how different images (e.g., from different packages or different viewing options in the same package) are related, including advantages and disadvantages of each form.