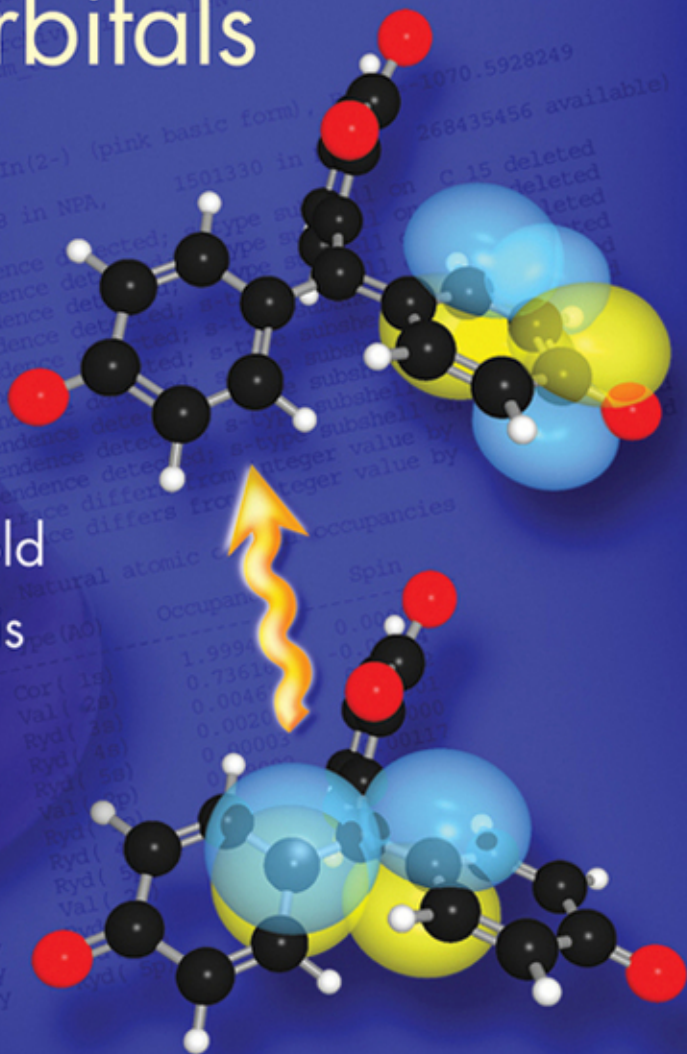


Discovering Chemistry with Natural Bond Orbitals

Frank Weinhold
Clark R. Landis



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With Natural Bond
Orbitals**

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The nature of the chemical bond is the problem at the heart of all chemistry.

Bryce Crawford

If anybody says he can think about quantum problems without getting giddy, that only shows he has not understood the first thing about them.

Neils Bohr

It is nice to know that the computer understands the problem, but I would like to understand it too.

Eugene Wigner

Contents

Preface	xi
1 Getting Started	1
1.1 Talking to your electronic structure system	1
1.2 Helpful tools	3
1.3 General \$NBO keylist usage	4
1.4 Producing orbital imagery	6
Problems and exercises	8
2 Electrons in Atoms	10
2.1 Finding the electrons in atomic wavefunctions	10
2.2 Atomic orbitals and their graphical representation	13
2.3 Atomic electron configurations	18
2.4 How to find electronic orbitals and configurations in NBO output	23
2.5 Natural atomic orbitals and the natural minimal basis Problems and exercises	29 31
3 Atoms in Molecules	34
3.1 Atomic orbitals in molecules	35
3.2 Atomic configurations and atomic charges in molecules	39
3.3 Atoms in open-shell molecules Problems and exercises	44 49
4 Hybrids and Bonds in Molecules	51
4.1 Bonds and lone pairs in molecules	52
4.2 Atomic hybrids and bonding geometry	60
4.3 Bond polarity, electronegativity, and Bent's rule	71
4.4 Hypovalent three-center bonds	78
4.5 Open-shell Lewis structures and spin hybrids	82
4.6 Lewis-like structures in transition metal bonding Problems and exercises	86 89

5 Resonance Delocalization Corrections	92
5.1 The natural Lewis structure perturbative model	93
5.2 Second-order perturbative analysis of donor–acceptor interactions	96
5.3 Δ Del energetic analysis [integrated ESS/NBO only]	105
5.4 Delocalization tails of natural localized molecular orbitals	113
5.5 How to Δ CHOOSE alternative Lewis structures	117
5.6 Natural resonance theory	123
Problems and exercises	133
6 Steric and Electrostatic Effects	135
6.1 Nature and evaluation of steric interactions	136
6.2 Electrostatic and dipolar analysis	145
Problems and exercises	153
7 Nuclear and Electronic Spin Effects	155
7.1 NMR chemical shielding analysis	156
7.2 NMR J-coupling analysis	162
7.3 ESR spin density distribution	168
Problems and exercises	173
8 Coordination and Hyperbonding	176
8.1 Lewis acid–base complexes	178
8.2 Transition metal coordinate bonding	193
8.3 Three-center, four-electron hyperbonding	204
Problems and exercises	206
9 Intermolecular Interactions	209
9.1 Hydrogen-bonded complexes	210
9.2 Other donor–acceptor complexes	217
9.3 Natural energy decomposition analysis	223
Problems and exercises	227
10 Transition State Species and Chemical Reactions	231
10.1 Ambivalent Lewis structures: the transition-state limit	232
10.2 Example: bimolecular formation of formaldehyde	236
10.3 Example: unimolecular isomerization of formaldehyde	243
10.4 Example: S_N2 halide exchange reaction	246
Problems and exercises	249

11 Excited State Chemistry	252
11.1 Getting to the “root” of the problem	252
11.2 Illustrative applications to NO excitations	256
11.3 Finding common ground: NBO versus MO state-to-state transferability	269
11.4 NBO/NRT description of excited-state structure and reactivity	277
11.5 Conical intersections and intersystem crossings Problems and exercises	282 289
Appendix A: What’s Under the Hood?	297
Appendix B: Orbital Graphics: The NBOView Orbital Plotter	300
Appendix C: Digging at the Details	302
Appendix D: What If Something Goes Wrong?	304
Appendix E: Atomic Units (a.u.) and Conversion Factors	307
Index	309

Preface

Recent advances in computers, networking, and electronic structure software now make it feasible for practically every student of chemistry to gain access to powerful computational tools for solving Schrödinger's equation, the ultimate oracle of chemical knowledge. With proper guidance, students having but little quantum mechanical background can undertake creative explorations of modern bonding and valency concepts that often surpass common textbook expositions in accuracy and sophistication. The goal of this book is to provide a practical "how to" guide for such chemical explorers, giving nuts and bolts examples of how chemical questions can be addressed with the help of modern wavefunction or density functional technology, as translated into familiar chemical language through the "Rosetta stone" of Natural Bond Orbital analysis.

The "natural" orbital concept, as originally formulated by Per-Olov Löwdin, refers to a mathematical algorithm by which *best possible* orbitals (optimal in a certain maximum-density sense) are determined from the system wavefunction itself, with no auxiliary assumptions or input. Such orbitals inherently provide the most compact and efficient numerical description of the many-electron molecular wavefunction, but they harbor a type of residual multicenter indeterminacy (akin to that of Hartree-Fock molecular orbitals) that somewhat detracts from their chemical usefulness.

However, a localized adaptation of the natural orbital algorithm allows one to similarly describe *few*-center molecular subregions in optimal fashion, corresponding to the localized lone pairs (one-center) and bonds (two-center) of the chemist's Lewis structure picture. The "Natural Bond Orbitals" (NBOs) that emerge from this algorithm are intrinsic to, uniquely determined by, and optimally adapted to localized description of, the system wavefunction. The compositional descriptors of NBOs map directly onto bond hybridization, polarization, and other freshman-level bonding concepts that underlie the modern electronic theory of valency and bonding.

The NBO mathematical algorithms are embedded in a well-tested and widely used computer program (currently, *NBO 5.9*) that yields these descriptors conveniently, and is attached (or attachable) to many leading electronic structure packages in current usage. Although the student is encouraged to "look under the hood" (Appendix A), the primary goal of this book is to enable students to gain proficiency in *using* the NBO program to re-express complex many-electron wavefunctions in terms of intuitive chemical concepts and orbital imagery, with minimal distractions from underlying mathematical or programming details. "NBO analysis" should be considered a *strategy* as well as a collection of keyword *tools*. Successful usage of the NBO toolkit involves intelligent visualization of the blueprint as well as mastery of individual tools to construct a sound explanatory framework.

This book owes an obvious debt to Foresman and Frisch's useful supplementary manual, *Exploring Chemistry with Electronic Structure Methods* (2nd ed., Gaussian Inc., Pittsburgh, PA, 1996), which provides an analogous how to guide for the popular *Gaussian*TM electronic structure program. Combined with popular utilities such as those made available on the WebMO website, the Gaussian program often makes calculating a wavefunction as simple as a few mouse-clicks, and many such choices of electronic structure system (ESS) are now widely available. The current Gaussian version, *Gaussian 09* (G09), is still the most widely used ESS in the chemical literature, and it includes an elementary NBO module (the older "NBO 3.1" version) that lets the student immediately perform many of the exercises described in this book. However, the NBO program is indifferent to which ESS provided the wavefunction, or even what *type* of wavefunction or density was provided, and the current book is largely independent of such choices. For options that involve intricate interactions with the host ESS and are implemented in only a select set of ESS packages, the Gaussian/NBO form of input file will be used for illustrative purposes. However, the present book has no specific association with the Gaussian program or the Foresman–Frisch guidebook, and the only requirement is that the chosen host ESS can pass wavefunction information to an NBO program (linked or stand-alone) that allows the ESS wavefunction to be analyzed in chemically meaningful terms with the help of the procedures and keywords described herein.

This book also serves as a complementary companion volume to the authors' research monograph, *Valency and Bonding: A Natural Bond Orbital Donor–Acceptor Perspective* (Cambridge University Press, 2005). The latter is theory- and applications-dominated, offering little or no practical know-how for coaxing the NBO program to yield the displayed numerical tables or graphical images. However, the instructions and examples given in this book should allow the student to easily reproduce any of the results given in *Valency and Bonding*, or to extend such treatment to other chemical systems or higher levels of approximation. For complete consistency with the numerical values and graphical orbital displays of *Valency and Bonding*, we employ the same B3LYP/6-311++G** density functional theoretic (DFT) methodology in this work. However, the student is encouraged to pursue independent explorations of other computational methodologies (correlated or uncorrelated, perturbative or variational, DFT or wavefunction-based, etc.) and other chemical systems after mastering the illustrative examples of this book.

We thank Franklin Chen, Ken Fountain, John Harriman, J. R. Schmidt, Peter Tentscher, and Mark Wendt for comments and suggestions on earlier drafts, with special thanks to Mohamed Ayoub for reviewing Problems and Exercises throughout the book.

We wish all readers of this book success on the path to discovery of enriched chemical understanding from modern electronic structure calculations.

FRANK WEINHOLD AND CLARK R. LANDIS
Madison, May, 2011

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*TM 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

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/mainproopts.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:
- 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.
 - References to the original papers on NBO analysis (or STERIC analysis, or NRT resonance theory analysis, or other chosen keyword options of NBO program).
 - Names (and links) of ESS program systems that currently provide NBO interfaces or internal linkages.
 - 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 (H₃PO), 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

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

[off-diagonal ($\mathbf{F}^{(\text{NBO})}$)_{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

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

[diagonal ($\mathbf{F}^{(\text{AO})}$)_{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

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

[off-diagonal matrix elements of the $\mathbf{S}^{(\text{AO})}$ 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.

Chapter 2

Electrons in Atoms

2.1 FINDING THE ELECTRONS IN ATOMIC WAVEFUNCTIONS

From a quantum mechanical perspective, electrons are described by the orbitals they occupy. Each orbital “electron container” is a three-dimensional (3D) spatial function having a positive or negative numerical value (orbital amplitude) at every point in space. Around an atomic nucleus, such electron containers are called atomic orbitals (AOs), with characteristically large amplitudes (including large amplitude swings between positive and negative values) near the nucleus, but rapidly decaying values at large distances from the nucleus. The analytical forms of such atomic orbitals are exactly known only for the hydrogen atom, but good numerical approximations are now available for all atoms of the periodic table.

In the present chapter, we examine the basic building blocks of atomic and molecular wavefunctions, the atomic spin-orbitals of individual electrons (Section 2.2), and the “configurations” of occupied spin-orbitals that characterize the chosen electronic state (Section 2.3). This leads to introduction of intrinsic “natural” orbitals that optimally describe the final wavefunction, and are often found to differ surprisingly from the assumed “basis atomic orbitals” that were used to construct the numerical wavefunction (Sidebar 2.1). We then describe how these intrinsic building blocks are “found” in natural bond orbital (NBO) output, taking advantage of the simplicity of the atomic limit to introduce general NBO terminology, output conventions, and orbital display modes that are employed throughout this book. Readers familiar with basic NBO program usage and output may prefer to skip forward to chapters dealing with systems and properties of greater chemical interest.

SIDEBAR 2.1

WHAT ARE “NATURAL” ORBITALS?

An “orbital” refers to a one-electron wavefunction, and more specifically to the spatial part of a one-electron “spin-orbital.” Electronic orbitals are often associated with the simple Hartree–Fock (HF) approximation, a single-configuration approximation to the complex

many-electron wavefunction Ψ , but the usefulness of the orbital concept goes beyond HF level. In HF theory, each electron is assigned to occupy a unique spin-orbital and the total wavefunction Ψ_{HF} is specified by the associated “electron configuration,” a listing of its occupied spin-orbitals. For a closed-shell system with α and β spin-orbitals of identical spatial form, we usually focus on the spatial (\mathbf{r}) dependence of each doubly occupied orbital in the configuration.

Mathematically, the single-configuration Ψ_{HF} wavefunction is expressed as a “Slater determinant” (antisymmetrized product) of the occupied spin-orbitals. In this limit, only the chosen N occupied spin-orbitals contribute to description of the N -electron system, whereas an infinite number of remaining “virtual” spin-orbitals are ignored. This crude HF-type (or molecular orbital) description of the true many-electron $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ exerts a powerful hold on chemical pedagogy, but is often seriously defective in quantitative terms.

When the errors of the single-configuration HF-type description become nonnegligible, the orbital concept seems to become problematic. More accurate “correlated” many-electron wavefunctions can still be expressed in terms of orbitals and Slater determinants, but *unlimited* numbers of determinants, each with a distinct set of N occupied spin-orbitals, are now required for precise description of Ψ . Moreover, as the list of Slater determinants increases without limit, the starting choice of orbitals becomes increasingly *unimportant*. Indeed, in the limit of including all possible Slater determinants (i.e., all possible ways of choosing N spin-orbitals from a complete orthonormal set), the starting choice of orbitals becomes totally immaterial, and *any* complete orthonormal set of orbitals could serve equally well to describe Ψ . Thus, one might be led to the extreme conclusion that orbitals play *no* useful conceptual role except in the uncorrelated single-configuration HF limit. In this extreme view, the familiar atomic and molecular orbitals (MOs) of freshman chemistry seem to have lost significance, and the orbital concept itself is called into question.

Fortunately, the rigorous measurement theory of many-electron quantum mechanics justifies essential *retention* of orbital-type conceptions and their applications in bonding theory. As originally formulated by J. von Neumann in his *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, Princeton, NJ, 1955), the fundamental object underlying quantal measurement of a pure-state N -electron system is the “density matrix” $\Gamma^{(N)}$:

$$\Gamma^{(N)} = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi^*(\mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N) \quad (2.1)$$

K. Husimi (*Proc. Phys. Math. Soc. Jpn.* **22**, 264, 1940) subsequently showed that analogous measurable properties of smaller *subsystems* of the N -electron system are expressed most rigorously in terms of corresponding p th-order “reduced” density matrices $\Gamma^{(p)}$,

$$\Gamma^{(p)} = [N!/p!(N-p)!] \int \Gamma^{(N)} d\tau_N d\tau_{N-1} \cdots d\tau_{N-p+1} \quad (2.2)$$

in which the dependence on all but p subsystem electrons has been “averaged out” by spatial integration over electrons $p+1, p+2, \dots, N$ (after equating primed and unprimed coordinates in the integrand). This reduction permits a spectacular simplification for atomic or molecular systems, because the Hamiltonian operator depends only on one-electron (kinetic energy and nuclear attraction) and two-electron (interelectron repulsion) interactions. As a result, only the *first-* and *second-order* reduced density matrices $\Gamma^{(1)}, \Gamma^{(2)}$ are required to evaluate *any* measurable property of a pure-state atomic or molecular species. In effect, $\Gamma^{(1)}$ and $\Gamma^{(2)}$ condense *all* the information about Ψ that is relevant to chemical questions!

Of these two objects, $\Gamma^{(1)}$ (usually referred to as “the” density matrix) is far the more important. Indeed, $\Gamma^{(1)}$ would be completely adequate for chemical questions if electron correlation effects were completely negligible rather than a $\sim 1\%$ correction to total energy. Thus, about 99% of a chemist’s attention should focus on the information contained in the first-order reduced density matrix $\Gamma^{(1)}$, as is done throughout this book.

Because $\Gamma^{(1)}$ is inherently a *one*-electron operator, it is deeply connected to *orbital*-level description of the N -electron system. Indeed, it was recognized by P.-O. Löwdin (*Phys. Rev.* **97**, 1474, 1955) that the solutions $\{\theta_i\}$ of the characteristic “eigenvalue equation” for $\Gamma^{(1)}$

$$\Gamma^{(1)}\theta_i = n_i\theta_i, \quad i = 1, 2, \dots, \infty \quad (2.3)$$

provide the fundamental “natural” orbitals (intrinsic eigenorbitals of $\Gamma^{(1)}$) that underlie description of an N -electron system of arbitrary complexity. Each natural orbital (NO) θ_i has “occupancy” n_i

$$n_i = \int \theta_i^* \Gamma^{(1)} \theta_i d\tau = \langle \theta_i | \Gamma^{(1)} | \theta_i \rangle \quad (2.4)$$

that is *maximum possible* for ordered members of a complete orthonormal set as follows from general minmax properties of eigenvalue equations such as (2.3). Accordingly, natural orbitals $\{\theta_i\}$ are intrinsically optimal for providing the most compact and rapidly convergent description of *all* one-electron properties of the *exact* many-electron Ψ . In effect, “natural orbitals” can be defined as the orbitals selected by the wavefunction itself (through its reduced $\Gamma^{(1)}$) as optimal for its own description.

Unlike HF molecular orbitals, the natural orbitals are not restricted to a low-level approximation, but are rigorously defined for *any* theoretical level, up to and including the exact Ψ . As eigenfunctions of a physical (Hermitian) operator, the NOs automatically form a *complete* orthonormal set, able to describe every nuance of the exact Ψ and associated density distribution, whereas the occupied MOs are seriously *incomplete* without augmentation by virtual MOs. Furthermore, the occupancies n_i of NOs are not restricted to integer values (as are those of MOs), but can vary *continuously* within the limits imposed by the Pauli exclusion principle, namely, for closed-shell spatial orbitals,

$$0 \leq n_i \leq 2 \text{ (sum of } \alpha \text{ and } \beta \text{ occupancies)} \quad (2.5)$$

Nevertheless, the NOs are optimally chosen to give greatest possible condensation of electron density into the lowest few orbitals (most “HF-like” description of the exact Ψ in the maximum density sense), and they reduce back to conventional Hartree–Fock MOs in the uncorrelated limit $\Psi \rightarrow \Psi_{\text{HF}}$. Hence, familiar MO-type concepts are recovered intact when electron correlation effects are negligible, but the intrinsic NOs allow us to extend and generalize these orbital concepts for wavefunctions of *any* theoretical level.

As mentioned above, the maximum-occupancy property of NOs is a necessary and sufficient condition for satisfying the eigenvalue equation (2.3). We can therefore use the maximum-occupancy criterion to search for localized (i.e., 1- or 2-center) regions that contain high-occupancy “*local* NOs,” consistent with the Pauli restriction (2.5). From elementary bonding principles, we can expect that such high-occupancy 1-center (lone pair) or 2-center (bond) local NOs are primarily located in the regions associated with electron pairs in the Lewis dot diagram. Accordingly, it turns out (J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.* **102**, 7211, 1980) that density matrix and natural orbital concepts can be generalized to identify the optimal *local* bonding patterns

envisioned in the chemist's Lewis structure diagram, leading to the "natural bond orbitals" that optimally correspond to such localized description of electron density. Because the forms of 1c/2c NBOs are more restrictive than those of delocalized multicenter NOs, the NBO occupancies are typically less than those of delocalized NOs, even in the single-configuration MO limit. However, as the success of Lewis structural concepts leads us to expect, the NBOs are commonly exhibit *near* double-occupancy, with slight deviations that reflect the subtle resonance effects of the molecular bonding pattern. The NBO occupancy variations also guarantee the *uniqueness* of NBO forms, whereas the exact double-occupancy of MOs (or NOs) leads to a type of unitary indeterminacy that prevents their unique definition (cf. Sidebar 11.5).

For further details, see the "What Are 'Natural' Orbitals" link on the NBO website or Chapter 1 of *Valency and Bonding* and references therein.

2.2 ATOMIC ORBITALS AND THEIR GRAPHICAL REPRESENTATION

Getting acquainted with the shapes and sizes of atomic orbitals is one of the first important skills for a chemistry student to master. Figure 2.1a–c depicts the occupied 1s atomic orbital of the ground-state hydrogen (H) atom in three different graphical representations (all obtained from PLOT output using the NBOView orbital plotter, as described in Appendix B).

Figure 2.1a shows the one-dimensional (1D) orbital amplitude profile $\varphi(r)$ as a function of distance r from the nucleus (positioned at the cross-hair symbol at the midpoint of the profile axis). As shown, the orbital amplitude "peaks" at the nucleus, but decays steeply as r increases in either direction along the chosen one-dimensional profile axis. Note that no particular "electron radius" about the nucleus is evident in such a plot. Indeed, we must begin thinking in completely nonclassical fashion when attempting to envision electrons in orbital terms, because the proper quantum mechanical description bears only remote connection to the classical-type

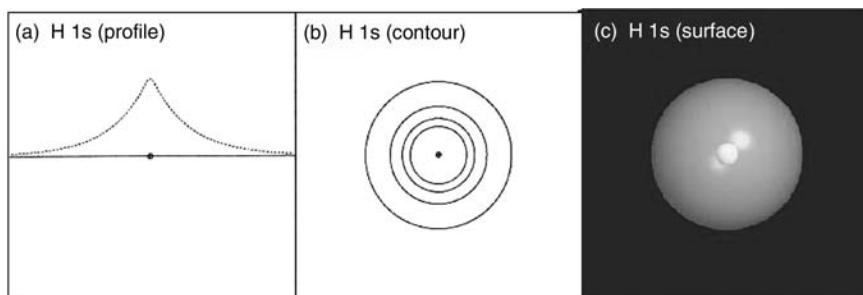


Figure 2.1 Hydrogen atom 1s orbital in (a) 1D profile, (b) 2D contour, and (c) 3D surface plot. (See the color version of this figure in Color Plates section.)

“Bohr orbit” model that students are first told about in beginning chemistry classes. (Such oversimplified models create a superficial sense of “understanding” the quantum mechanical behavior that is aptly characterized as “weirder than you think, and weirder than you *can* think!”)

Figure 2.1b shows a corresponding 2D contour plot of orbital amplitude in a plane around the nucleus, centered at the middle of the contour plane. This plot shows the circular contour lines of equal “elevation” (amplitude), widely spaced over the gentle outer slopes of the orbital, but tightly bunched around the nucleus (where only the first few contours are shown approaching the cross-hair nucleus symbol). The circular contour lines clearly exhibit the spherical symmetry of the 1s hydrogenic orbital, which is not so apparent in Fig. 2.1a.

Finally, Fig. 2.1c shows the same hydrogenic 1s orbital as a 3D surface plot, which resembles a photograph of a space-filling object. The “surface” of this orbital object corresponds to the outermost contour line of Fig. 2.1b, chosen as 0.0136 a.u. to roughly match the empirical van der Waals radius of the atom. Of course, the orbital $\phi(\mathbf{r})$ exhibits no sharp discontinuity or “surface” at any distance (as shown in Fig. 2.1a). But with a consistent cutoff amplitude, one can gain an informative visual impression of both shape and size of the orbital, i.e., the spatial region in which its amplitude contours are most highly concentrated. When the orbital is occupied, its square $|\phi(\mathbf{r})|^2$ gives the contribution to *electron density* at point \mathbf{r} , which allows us to “find the electron” as nearly as that phrase makes sense in the quantum world.

With this background, we can also consider atomic orbitals of more varied shapes and sizes. Figure 2.2 shows the corresponding profile, contour, and surface plots of fluorine (F) atom 2s, 2p, and 3d orbitals. As seen in Fig. 2.2, all three orbitals now have regions of both positive and negative sign (phase), separated by *nodes* (surfaces of zero amplitude). The contour plots (middle) show contours of positive or negative phase as solid lines or dashed lines, respectively, while the corresponding phases in the surface plots (right) are shown as blue or yellow, respectively. The contour plots clearly show both the angular shape (e.g., the “dumbbell” shape of the 2p orbital or “four-leaf clover” shape of the 3d orbital) and the radial “strength” of each orbital. Because the orbital phase patterns play an important role in understanding chemical behavior, the 2D contour or 3D surface plots usually provide the more useful orbital visualization, but the 1D radial profiles may also be useful in showing orbital details that are relevant to chemical behavior.

The qualitative orbital forms shown in Fig. 2.2 are *modulated* by subtle variations of overall electronic configuration and charge state. These variations are shown in greater detail for the $2p_z$ orbital in Fig. 2.3. Slight variations in $2p_z$ spin-orbital size (diffuseness) are seen to distinguish the occupied $2p_z^\uparrow$ (a) from the vacant $2p_z^\downarrow$ spin-orbital (b) of neutral fluorine atom, or from the corresponding doubly occupied orbital of the F^- anion (c). In the 1D amplitude profiles, the subtle differences can be seen most clearly in the slightly lower “peak” heights and correspondingly expanded “wing” spans of anionic fluoride (c) compared to that of neutral fluorine (a and b). Such anionic orbital expansion might be expected from the weakened attractive forces

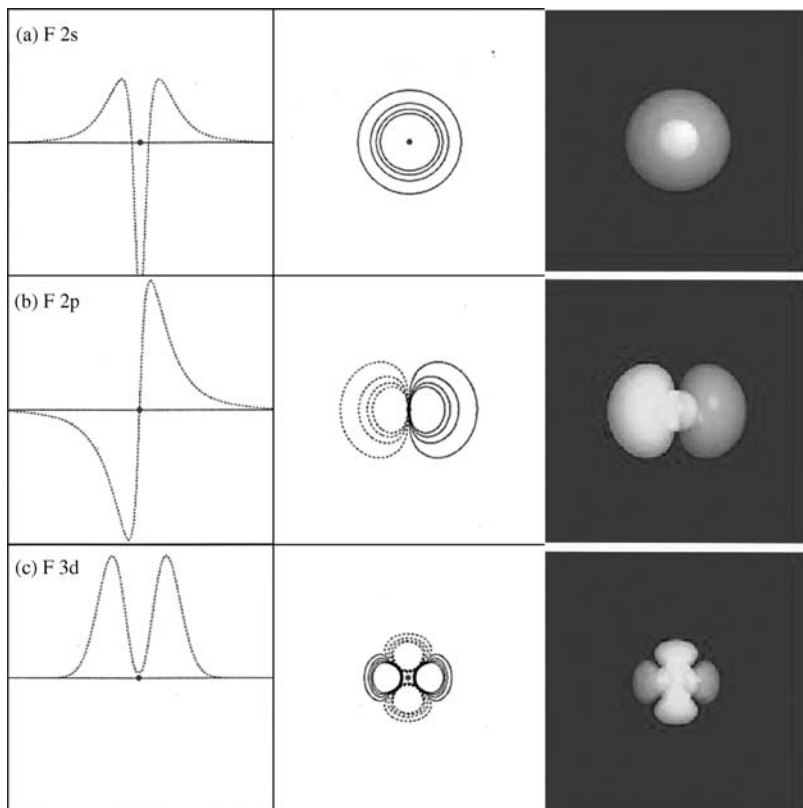


Figure 2.2 Fluorine atom (a) 2s, (b) 2p, and (c) 3d orbitals in 1D profile (left), 2D contour (middle), and 3D surface plot (right). The depicted orbitals have respective occupancies of 2, 1, and 0 in the F atom ground state. (Note that the four outermost contour lines of default *NBOView* contour output do not include the negative 2s “inner spike” near the nucleus, which is better seen in the 1D profile plot.) (See the color version of this figure in Color Plates section.)

when the nuclear charge is further “screened” by the added electron. (Corresponding orbital contraction is found when electrons are removed from other orbitals to form cations.) Such “breathing” size changes that accompany gain or loss of electrons are among the most important physical effects to be captured in accurate orbital visualizations.

A similar, but weaker, form of orbital-breathing variation can be found even in neutral atoms. The spin-orbital plotted in Fig. 2.3a is the *singly* occupied $2p_z^\uparrow$ of the atomic fluorine radical, whereas that in (b) is the corresponding $2p_z^\downarrow$ (“down”) spin-orbital that is vacant in this formal configurational assignment and slightly less tightly attracted to the nucleus. Comparison of the singly occupied $2p_z^\uparrow$ with the doubly occupied $2p_{x,y}^\uparrow$ or $2p_{x,y}^\downarrow$ spin-orbitals would reveal still more subtle size variations, corresponding to the differing

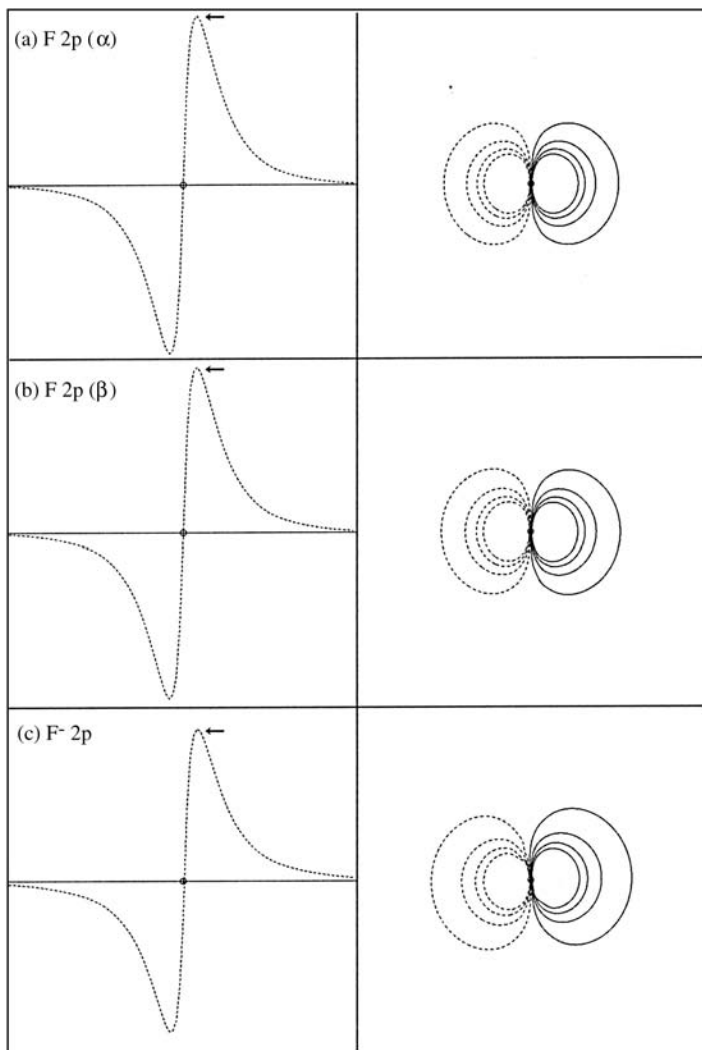


Figure 2.3 Fluorine valence $2p_z$ natural spin-orbital in profile (left) and contour (right) plots for F atom: (a) α spin, (b) β spin, and (c) F^- anion, showing subtle variations of diffuseness with differences in electron configuration and overall charge. (The small arrows in the left panels call attention to variations in maximum lobe amplitude, which are among the most “obvious” of the virtually imperceptible graphical differences.)

electronic environments in doubly occupied versus singly occupied orbital regions. Thus, we should anticipate that accurate representations of atomic orbitals (in contrast to cartoon-like textbook representations) should depict the subtle size variations resulting from altered Coulomb and exchange forces in electronic states of differing charge or spin multiplicity.