Section 3 Electronic Configurations, Term Symbols, and States

Introductory Remarks- The Orbital, Configuration, and State Pictures of Electronic Structure

One of the goals of quantum chemistry is to allow practicing chemists to use knowledge of the electronic states of fragments (atoms, radicals, ions, or molecules) to predict and understand the behavior (i.e., electronic energy levels, geometries, and reactivities) of larger molecules. In the preceding Section, orbital correlation diagrams were introduced to connect the orbitals of the fragments along a 'reaction path' leading to the orbitals of the products. In this Section, analogous connections are made among the fragment and product electronic states, again labeled by appropriate symmetries. To realize such connections, one must first write down N-electron wavefunctions that possess the appropriate symmetry; this task requires combining symmetries of the occupied orbitals to obtain the symmetries of the resulting states.

Chapter 8

Electrons are Placed into Orbitals to Form Configurations, Each of Which Can be Labeled by its Symmetry. The Configurations May "Interact" Strongly if They Have Similar Energies.

I. Orbitals Do Not Provide the Complete Picture; Their Occupancy By the N Electrons Must Be Specified

Knowing the orbitals of a particular species provides one information about the sizes, shapes, directions, symmetries, and energies of those regions of space that are available to the electrons (i.e., the complete set of orbitals that are available). This knowledge does not determine into which orbitals the electrons are placed. It is by describing the electronic configurations (i.e., orbital occupancies such as $1s^2 2s^2 2p^2$ or $1s^2 2s^2 2p^1 3s^1$) appropriate to the energy range under study that one focuses on how the electrons occupy the orbitals. Moreover, a given configuration may give rise to several energy levels whose energies differ by chemically important amounts. for example, the $1s^2 2s^2 2p^2$ configuration of the Carbon atom produces nine degenerate ^3P states, five degenerate ^1D states, and a single ^1S state. These three energy levels differ in energy by 1.5 eV and 1.2 eV, respectively.

II. Even N-Electron Configurations Are Not Mother Nature's True Energy States

Moreover, even single-configuration descriptions of atomic and molecular structure (e.g., $1s^2 2s^2 2p^4$ for the Oxygen atom) do not provide fully correct or highly accurate representations of the respective electronic wavefunctions. As will be shown in this Section and in more detail in Section 6, the picture of N electrons occupying orbitals to form a configuration is based on a so-called "mean field" description of the coulomb interactions among electrons. In such models, an electron at **r** is viewed as interacting with an "averaged" charge density arising from the N-1 remaining electrons:

$$V_{\text{mean field}} = \int \rho_{N-1}(\mathbf{r}') \; e^2/|\mathbf{r}-\mathbf{r}'| \; \mathbf{dr}' \; .$$

Here $\rho_{N-1}(\mathbf{r}')$ represents the probability density for finding electrons at $\mathbf{r}'$, and $e^2/|\mathbf{r}-\mathbf{r}'|$ is the mutual coulomb repulsion between electron density at **r** and $\mathbf{r}'$. Analogous mean-field models arise in many areas of chemistry and physics, including electrolyte theory (e.g., the Debye-Hückel theory), statistical mechanics of dense gases (e.g., where the Mayer-Mayer cluster expansion is used to improve the ideal-gas mean field model), and chemical dynamics (e.g., the vibrationally averaged potential of interaction).

In each case, the mean-field model forms only a starting point from which one attempts to build a fully correct theory by effecting systematic corrections (e.g., using perturbation theory) to the mean-field model. The ultimate value of any particular mean-field model is related to its accuracy in describing experimental phenomena. If predictions of the mean-field model are far from the experimental observations, then higher-order corrections (which are usually difficult to implement) must be employed to improve its predictions. In such a case, one is motivated to search for a better model to use as a starting point so that lower-order perturbative (or other) corrections can be used to achieve chemical accuracy (e.g., ± 1 kcal/mole).

In electronic structure theory, the single-configuration picture (e.g., the $1s^2 2s^2 2p^4$ description of the Oxygen atom) forms the mean-field starting point; the configuration interaction (CI) or perturbation theory techniques are then used to systematically improve this level of description.

The single-configuration mean-field theories of electronic structure neglect correlations among the electrons. That is, in expressing the interaction of an electron at **r** with the N-1 other electrons, they use a probability density $\rho_{N-1}(\mathbf{r'})$ that is independent of the fact that another electron resides at **r**. In fact, the so-called conditional probability density for finding one of N-1 electrons at **r'**, given that an electron is at **r** certainly depends on **r**. As a result, the mean-field coulomb potential felt by a $2p_x$ orbital's electron in the $1s^2 2s^2 2p_x 2p_y$ single-configuration description of the Carbon atom is:

$$V_{\text{mean field}} = 2\int |1s(\mathbf{r'})|^2 \; e^2/|\mathbf{r}-\mathbf{r'}| \; \mathbf{dr'}$$

$$+ 2\int |2s(\mathbf{r'})|^2 \; e^2/|\mathbf{r}-\mathbf{r'}| \; \mathbf{dr'}$$

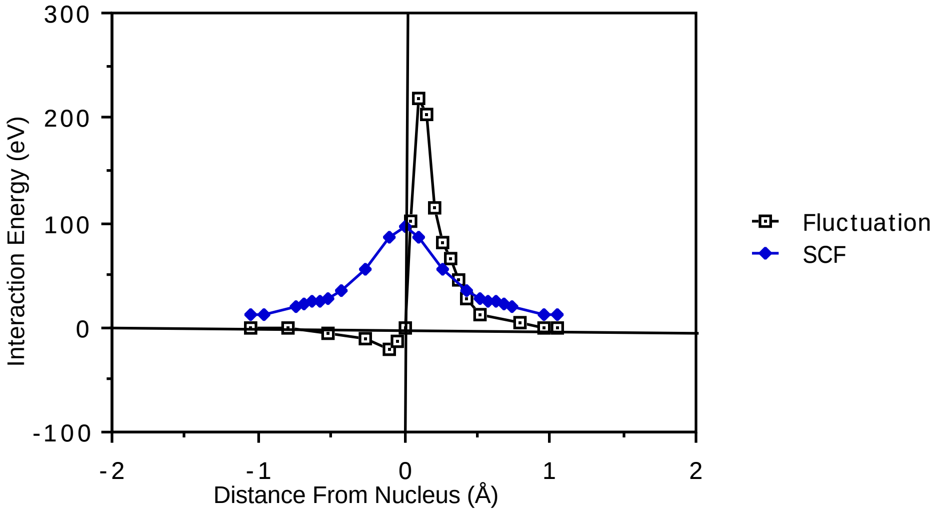
$$+ \int |2p_y(\mathbf{r'})|^2 \; e^2/|\mathbf{r}-\mathbf{r'}| \; \mathbf{dr'} \; .$$

In this example, the density $\rho_{N-1}(\mathbf{r'})$ is the sum of the charge densities of the orbitals occupied by the five other electrons
$2\,|1s(\mathbf{r'})|^2 + 2\,|2s(\mathbf{r'})|^2 + |2p_y(\mathbf{r'})|^2$, and is not dependent on the fact that an electron resides at **r**.

III. Mean-Field Models

The Mean-Field Model, Which Forms the Basis of Chemists' Pictures of Electronic Structure of Molecules, Is Not Very Accurate

The magnitude and "shape" of such a mean-field potential is shown below for the Beryllium atom. In this figure, the nucleus is at the origin, and one electron is placed at a distance from the nucleus equal to the maximum of the 1s orbital's radial probability density (near 0.13 Å). The radial coordinate of the second is plotted as the abscissa; this second electron is arbitrarily constrained to lie on the line connecting the nucleus and the first electron (along this direction, the inter-electronic interactions are largest). On the ordinate, there are two quantities plotted: (i) the Self-Consistent Field (SCF) mean-field potential $\int |1s(\mathbf{r'})|^2 \; e^2/|\mathbf{r}-\mathbf{r'}| \; \mathbf{dr'}$, and (ii) the so-called Fluctuation potential (F), which is the true coulombic $e^2/|\mathbf{r}-\mathbf{r'}|$ interaction potential minus the SCF potential.



As a function of the inter-electron distance, the fluctuation potential decays to zero more rapidly than does the SCF potential. For this reason, approaches in which F is treated as a perturbation and corrections to the mean-field picture are computed perturbatively might be expected to be rapidly convergent (whenever perturbations describing long-range interactions arise, convergence of perturbation theory is expected to be slow or not successful). However, the magnitude of F is quite large and remains so over an appreciable range of inter-electron distances.

The resultant corrections to the SCF picture are therefore quite large when measured in kcal/mole. For example, the differences ΔE between the true (state-of-the-art quantum chemical calculation) energies of interaction among the four electrons in Be and the SCF mean-field estimates of these interactions are given in the table shown below in eV (recall that 1 eV = 23.06 kcal/mole).

Orb. Pair	1sα1sβ	1sα2sα	1sα2sβ	1sβ2sα	1sβ2sβ	2sα2sβ
ΔE in eV	1.126	0.022	0.058	0.058	0.022	1.234

To provide further insight why the SCF mean-field model in electronic structure theory is of limited accuracy, it can be noted that the average value of the kinetic energy plus the attraction to the Be nucleus plus the SCF interaction potential for one of the 2s orbitals of Be with the three remaining electrons in the $1s^2 2s^2$ configuration is:

$$< 2s| -\hbar^2/2m_e \quad {}^2 - 4e^2/r + V_{SCF} |2s> = -15.4 \text{ eV};$$

the analogous quantity for the 2p orbital in the $1s^22s2p$ configuration is:

$$< 2p| -\hbar^2/2m_e \nabla^2 - 4e^2/r + V'_{SCF} |2p> = -12.28 \text{ eV};$$

the corresponding value for the 1s orbital is (negative and) of even larger magnitude. The SCF average coulomb interaction between the two 2s orbitals of $1s^22s^2$ Be is:

$$\int |2s(\mathbf{r})|^2 \, |2s(\mathbf{r'})|^2 \, e^2/|\mathbf{r}-\mathbf{r'}| \; \mathbf{dr} \; \mathbf{dr'} = 5.95 \text{ eV}.$$

This data clearly shows that corrections to the SCF model (see the above table) represent significant fractions of the inter-electron interaction energies (e.g., 1.234 eV compared to 5.95- 1.234 = 4.72 eV for the two 2s electrons of Be), and that the inter-electron interaction energies, in turn, constitute significant fractions of the total energy of each orbital (e.g., 5.95 -1.234 eV = 4.72 eV out of -15.4 eV for a 2s orbital of Be).

The task of describing the electronic states of atoms and molecules from first principles and in a chemically accurate manner (± 1 kcal/mole) is clearly quite formidable. The orbital picture and its accompanying SCF potential take care of "most" of the interactions among the N electrons (which interact via long-range coulomb forces and whose dynamics requires the application of quantum physics and permutational symmetry). However, the residual fluctuation potential, although of shorter range than the bare coulomb potential, is large enough to cause significant corrections to the mean-field picture. This, in turn, necessitates the use of more sophisticated and computationally taxing techniques (e.g., high order perturbation theory or large variational expansion spaces) to reach the desired chemical accuracy.

Mean-field models are obviously approximations whose accuracy must be determined so scientists can know to what degree they can be "trusted". For electronic structures of atoms and molecules, they require quite substantial corrections to bring them into line with experimental fact. Electrons in atoms and molecules undergo dynamical motions in which their coulomb repulsions cause them to "avoid" one another at every instant of time, not only in the average-repulsion manner that the mean-field models embody. The inclusion of instantaneous spatial correlations among electrons is necessary to achieve a more accurate description of atomic and molecular electronic structure.

IV. Configuration Interaction (CI) Describes the Correct Electronic States

The most commonly employed tool for introducing such spatial correlations into electronic wavefunctions is called configuration interaction (CI); this approach is described briefly later in this Section and in considerable detail in Section 6.

Briefly, one employs the (in principle, complete as shown by P. O. Löwdin, Rev. Mod. Phys. 32, 328 (1960)) set of N-electron configurations that (i) can be formed by placing the N electrons into orbitals of the atom or molecule under study, and that (ii) possess the spatial, spin, and angular momentum symmetry of the electronic state of interest. This set of functions is then used, in a linear variational function, to achieve, via the CI technique, a more accurate and dynamically correct description of the electronic structure of that state. For example, to describe the ground ^1S state of the Be atom, the $1s^2 2s^2$ configuration (which yields the mean-field description) is augmented by including other configurations such as $1s^2 3s^2$, $1s^2 2p^2$, $1s^2 3p^2$, $1s^2 2s3s$, $3s^2 2s^2$, $2p^2 2s^2$, etc., all of which have overall ^1S spin and angular momentum symmetry. The excited ^1S states are also combinations of all such configurations. Of course, the ground-state wavefunction is dominated by the $|1s^2 2s^2|$ and excited states contain dominant contributions from $|1s^2 2s3s|$, etc. configurations. The resultant CI wavefunctions are formed as shown in Section 6 as linear combinations of all such configurations.

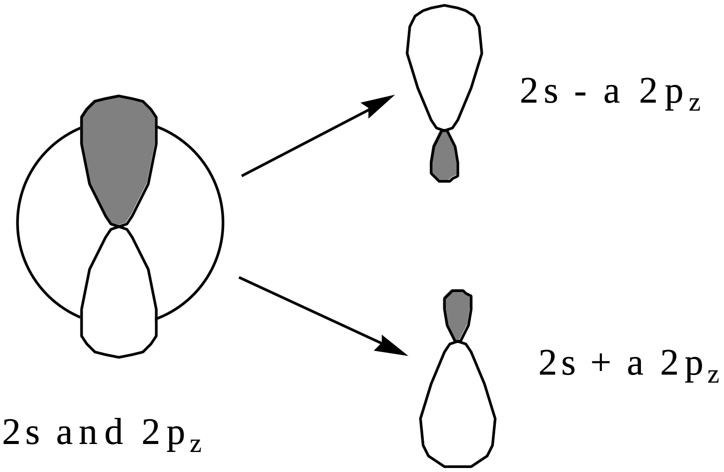
To clarify the physical significance of mixing such configurations, it is useful to consider what are found to be the two most important such configurations for the ground ^1S state of the Be atom:

$$\Psi \quad C_1 |1s^2 2s^2| - C_2 [|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2 |].$$

As proven in Chapter 13.III, this two-configuration description of Be's electronic structure is equivalent to a description is which two electrons reside in the 1s orbital (with opposite, α and β spins) while the other pair reside in 2s-2p hybrid orbitals (more correctly, polarized orbitals) in a manner that instantaneously correlates their motions:

$$\begin{aligned}\Psi \quad 1/6\ C_1 |1s^2 \{&[(2s-a2p_x)\alpha(2s+a2p_x)\beta - (2s-a2p_x)\beta(2s+a2p_x)\alpha] \\ &+[(2s-a2p_y)\alpha(2s+a2p_y)\beta - (2s-a2p_y)\beta(2s+a2p_y)\alpha] \\ &+[(2s-a2p_z)\alpha(2s+a2p_z)\beta - (2s-a2p_z)\beta(2s+a2p_z)\alpha]\}|,\end{aligned}$$

where a = $\sqrt{3C_2/C_1}$. The so-called polarized orbital pairs ($2s \pm a\, 2p_{x,y,\text{ or } z}$) are formed by mixing into the 2s orbital an amount of the $2p_{x,y,\text{ or } z}$ orbital, with the mixing amplitude determined by the ratio of C_2 to C_1 . As will be detailed in Section 6, this ratio is proportional to the magnitude of the coupling $<|1s^22s^2 |H|1s^22p^2| >$ between the two configurations and inversely proportional to the energy difference $[<|1s^22s^2|H|1s^22s^2|> - <|1s^22p^2|H|1s^22p^2|>]$ for these configurations. So, in general, configurations that have similar energies (Hamiltonian expectation values) and couple strongly give rise to strongly mixed polarized orbital pairs. The result of forming such polarized orbital pairs are described pictorially below.



Polarized Orbital 2s and 2p $_z$ Pairs

In each of the three equivalent terms in this wavefunction, one of the valence electrons moves in a 2s+a2p orbital polarized in one direction while the other valence electron moves in the 2s-a2p orbital polarized in the opposite direction. For example, the first term $[(2s-a2p_x)\alpha(2s+a2p_x)\beta - (2s-a2p_x)\beta(2s+a2p_x)\alpha]$ describes one electron occupying a $2s-a2p_x$ polarized orbital while the other electron occupies the $2s+a2p_x$ orbital. In this picture, the electrons reduce their mutual coulomb repulsion by occupying different regions of space; in the SCF mean-field picture, both electrons reside in the same 2s region of space. In this particular example, the electrons undergo angular correlation to "avoid" one another. The fact that equal amounts of x, y, and z orbital polarization appear in Ψ is what preserves the ^1S symmetry of the wavefunction.

The fact that the CI wavefunction

$$\Psi \quad C_1 |1s^2 2s^2| - C_2 [|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2|]$$

mixes its two configurations with <u>opposite sign</u> is of significance. As will be seen later in Section 6, solution of the Schrödinger equation using the CI method in which two configurations (e.g., $|1s^2 2s^2|$ and $|1s^2 2p^2|$) are employed gives rise to two solutions. One approximates the ground state wave function; the other approximates an excited state. The former is the one that mixes the two configurations with opposite sign.

To understand why the latter is of higher energy, it suffices to analyze a function of the form

$$\Psi' \quad C_1 |1s^2 2s^2| + C_2 [|1s^2 2p_x^2| + |1s^2 2p_y^2| + |1s^2 2p_z^2|]$$

in a manner analogous to above. In this case, it can be shown that

$$\begin{aligned}\Psi' \quad 1/6\, C_1 |1s^2\{&[(2s-ia2p_x)\alpha(2s+ia2p_x)\beta - (2s-ia2p_x)\beta(2s+ia2p_x)\alpha] \\ &+[(2s-ia2p_y)\alpha(2s+ia2p_y)\beta - (2s-ia2p_y)\beta(2s+ia2p_y)\alpha] \\ &+[(2s-ia2p_z)\alpha(2s+ia2p_z)\beta - (2s-ia2p_z)\beta(2s+ia2p_z)\alpha]|\}.\end{aligned}$$

There is a fundamental difference, however, between the polarized orbital pairs introduced earlier $\varphi_\pm = (2s \pm a2p_{x,y,\text{or } z})$ and the corresponding functions $\varphi'_\pm = (2s \pm ia2p_{x,y,\text{or } z})$ appearing here. The probability densities embodied in the former

$$|\varphi_\pm|^2 = |2s|^2 + a^2 |2p_{x,y,\text{or } z}|^2 \pm 2a(2s\ 2p_{x,y,\text{or } z})$$

describe constructive (for the + case) and destructive (for the - case) superposition of the probabilities of the 2s and 2p orbitals. The probability densities of $\varphi'_\pm$ are

$$\begin{aligned}|\varphi'_\pm|^2 &= (2s \pm ia2p_{x,y,\text{or } z})^*(2s \pm ia2p_{x,y,\text{or } z}) \\ &= |2s|^2 + a^2 |2p_{x,y,\text{or } z}|^2 .\end{aligned}$$

These densities are identical to one another and do not describe polarized orbital densities. Therefore, the CI wavefunction which mixes the two configurations with like sign, when analyzed in terms of orbital pairs, places the electrons into orbitals $\varphi_{\pm}=(2s \pm ia2p_{x,y,\text{or } z})$ whose densities do not permit the electrons to avoid one another. Rather, both orbitals have the same spatial density $|2s|^2 + a^2$ $|2p_{x,y,\text{or } z}|^2$, which gives rise to higher coulombic interaction energy for this state.

V. Summary

In summary, the dynamical interactions among electrons give rise to instantaneous spatial correlations that must be handled to arrive at an accurate picture of atomic and molecular structure. The simple, single-configuration picture provided by the mean-field model is a useful starting point, but improvements are often needed.
In Section 6, methods for treating electron correlation will be discussed in greater detail.

For the remainder of this Section, the primary focus is placed on forming proper N-electron wavefunctions by occupying the orbitals available to the system in a manner that guarantees that the resultant N-electron function is an eigenfunction of those operators that commute with the N-electron Hamiltonian.

For polyatomic molecules, these operators include point-group symmetry operators (which act on all N electrons) and the spin angular momentum (S^2 and S_z) of all of the electrons taken as a whole (this is true in the absence of spin-orbit coupling which is treated later as a perturbation). For linear molecules, the point group symmetry operations involve rotations R_z of all N electrons about the principal axis, as a result of which the total angular momentum L_z of the N electrons (taken as a whole) about this axis commutes with the Hamiltonian, H. Rotation of all N electrons about the x and y axes does not leave the total coulombic potential energy unchanged, so L_x and L_y do not commute with H. Hence for a linear molecule, L_z , S^2, and S_z are the operators that commute with H. For atoms, the corresponding operators are L^2, L_z, S^2, and S_z (again, in the absence of spin-orbit coupling) where each operator pertains to the total orbital or spin angular momentum of the N electrons.

To construct N-electron functions that are eigenfunctions of the spatial symmetry or orbital angular momentum operators as well as the spin angular momentum operators, one has to "couple" the symmetry or angular momentum properties of the individual spin-orbitals used to construct the N-electrons functions. This coupling involves forming direct product symmetries in the case of polyatomic molecules that belong to finite point groups, it involves vector coupling orbital and spin angular momenta in the case of atoms, and it involves vector coupling spin angular momenta and axis coupling orbital angular momenta when treating linear molecules. Much of this Section is devoted to developing the tools needed to carry out these couplings.