

# Set 2

**You must do problems I, II, V, VI. You can choose between III and IV. If you do an extra problem (from this set or from the “extra” problems available on the web site), then extra credit will be awarded in accord with the syllabus.**

## I. Term Symbols and Electron Coupling

- A. Show that if the operators  $\hat{A}$  and  $\hat{B}$  commute with one another, then the eigenfunctions of  $\hat{A}$  can be chosen so that they are also eigenfunctions of  $\hat{B}$ .**

Now, we prove the converse of the result.

- B. Similarly, show that if every eigenfunction of  $\hat{B}$  is also an eigenfunction of  $\hat{A}$ , then  $\hat{A}$  and  $\hat{B}$  commute.**

Because “A” and “B” are true, it follows that the following two statements are *equivalent*: “ $\hat{A}$  and  $\hat{B}$  have common eigenfunctions” and “ $\hat{A}$  and  $\hat{B}$  commute.”

In class we showed that for an atom,  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$  commute with the electronic Hamiltonian,

$$\hat{H}_{el} \equiv \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} + v(\mathbf{r}_i) + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \quad (1.1)$$

Since the components of the angular momentum do not commute with one another, the atomic wave function can only be an eigenfunction of one of these operators and, by convention, we chose to consider eigenfunctions of the Hamiltonian which are also eigenfunctions of  $\hat{L}_z$ . In addition, because the Hamiltonian does not depend on spin,

$$[\hat{H}_{el}, \hat{S}_x] = [\hat{H}_{el}, \hat{S}_y] = [\hat{H}_{el}, \hat{S}_z] = [\hat{H}_{el}, \hat{S}^2] = 0, \quad (1.2)$$

and so we can choose the eigenfunctions of the Hamiltonian to be eigenstates of  $\hat{S}^2$  and  $\hat{S}_z$  also.

A very useful result about commutators is that

$$\begin{aligned} [\hat{A}, \hat{B}\hat{C}] &\equiv \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} \\ &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} \\ &= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + \hat{B}\hat{A}\hat{C} - \hat{B}\hat{C}\hat{A} \\ &= [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \end{aligned} \quad (1.3)$$

- C. Show that**

$$[\hat{A}\hat{B}, \hat{C}] = [\hat{A}, \hat{C}]\hat{B} + \hat{A}[\hat{B}, \hat{C}] \quad (1.4)$$

- D. Show that  $\hat{H}_{el}$  and  $\hat{L}^2$  commute.**

(Hint, use Eq. (1.3) and/or Eq. (1.4))

Because  $\hat{H}_{el}$  and  $\hat{L}^2$  commute, we can choose the eigenfunctions of an atom to be eigenfunctions of  $\hat{L}^2$ ,  $\hat{L}_z$ ,  $\hat{S}^2$ , and  $\hat{S}_z$ . This is the basis of term symbols. Referring to a text (or to the notes on this material),

**E. What are the term symbols for a two p-electrons in an unfilled shell, but all other shells filled?**

**F. What are the term symbols for a  $p^2 f^1$  configuration?**

One of the complicating factors of the preceding analysis is that many Slater determinants are not eigenfunctions of  $\hat{L}^2$  and  $\hat{S}^2$  (though most are eigenfunctions of  $\hat{L}_z$  and  $\hat{S}_z$ ).

**G. Show that**

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{2p_1}(\mathbf{r}_1)\alpha(1) & \psi_{2p_1}(\mathbf{r}_2)\alpha(2) \\ \psi_{2p_{-1}}(\mathbf{r}_1)\beta(1) & \psi_{2p_{-1}}(\mathbf{r}_2)\beta(2) \end{vmatrix} \quad (1.5)$$

**is not an eigenfunction of  $\hat{L}^2$  or  $\hat{S}^2$  but is an eigenfunction of  $\hat{L}_z$  and  $\hat{S}_z$ .**

**H. For which specific values of  $M_L$  and  $M_S$  does the  $p^2$  configuration have a Slater determinantal wave function?**

## II. Zeeman Splitting

When an atom is put in a magnetic field, one observes a splitting of the spectral lines. To understand why, we need to recall that both the spin of the electron and its orbital angular momentum serve to give the atom a magnetic moment.

For an atom in an eigenstate of the Hamiltonian,  $\hat{L}^2, \hat{S}^2, \hat{J}^2$ , and  $\hat{J}_z$ ,  $\Psi^{L,S,J,M_J}$ , the magnetic moment from the orbital angular momentum and the spin multiplicity can be taken from Eqs. (3.47) and (3.48) of the third set of notes. That is,

$$\boldsymbol{\mu}_L \equiv -\frac{\beta_e}{\hbar} \hat{\mathbf{L}} \Psi^{L,S,J,M_J} \quad (\text{II.1})$$

and

$$\begin{aligned} \boldsymbol{\mu}_S &= -g \frac{\beta_e}{\hbar} \hat{\mathbf{S}} \Psi^{L,S,J,M_J} \\ &\approx -2 \frac{\beta_e}{\hbar} \hat{\mathbf{S}} \Psi^{L,S,J,M_J} \end{aligned} \quad (\text{II.2})$$

where  $\beta_e = \frac{e\hbar}{me}$  is the Bohr magneton and  $g$  denotes the anomalous (or Landé) spin factor.

What is the total magnetic moment? We can surmise, from analogy to Eqs. (II.1) and (II.2) that the total magnetic moment will be proportional to  $\hat{\mathbf{J}} \Psi^{L,S,J,M_J} = \hat{\mathbf{L}} \Psi^{L,S,J,M_J} + \hat{\mathbf{S}} \Psi^{L,S,J,M_J}$ ,

$$\begin{aligned} \boldsymbol{\mu}_J &\propto \frac{\beta_e}{\hbar} \hat{\mathbf{J}} \Psi^{L,S,J,M_J} \\ &= -g_J(L,S) \frac{\beta_e}{\hbar} \hat{\mathbf{J}} \Psi^{L,S,J,M_J} \end{aligned} \quad (\text{II.3})$$

but the anomalous spin factor forces the constant of proportionality,  $g_J(L,S)$  to depend on  $S$  and  $L$ . (To see this, consider that  $g_J = g \approx 2$  when  $L = 0$ , and  $g_J = 1$  when  $S = 0$ . Presumably when  $S > 0$  and  $L > 0$ , then  $1 \leq g_J(L,S) \lesssim 2$ .  $g_J(L,S)$  is called the generalized Landé  $g$ -factor, and the standard notation (wherein the same symbol, without the  $J$  subscript) is used for both the anomalous spin-factor of the electron and the description of atomic spectra in a magnetic field is unfortunate. Be careful.

We need to find the magnitude of  $\boldsymbol{\mu}_J$ , because then we can describe the effect of a magnetic field. Because

$$\hat{J}^2 \Psi^{L,S,J,M_J} \equiv \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} \Psi^{L,S,J,M_J} = \hbar^2 (J(J+1)) \Psi^{L,S,J,M_J} \quad (\text{II.4})$$

we know the magnitude of the total angular momentum of the atom is

$$\left| \left\langle \Psi^{L,S,J,M_J} \left| \hat{\mathbf{J}} \right| \Psi^{L,S,J,M_J} \right\rangle \right| = \hbar \sqrt{J(J+1)} \quad (\text{II.5})$$

with similar results for the total spin and orbital angular momenta,

$$\begin{aligned} \left| \left\langle \Psi^{L,S,J,M_J} \left| \hat{\mathbf{L}} \right| \Psi^{L,S,J,M_J} \right\rangle \right| &= \hbar \sqrt{L(L+1)} \\ \left| \left\langle \Psi^{L,S,J,M_J} \left| \hat{\mathbf{S}} \right| \Psi^{L,S,J,M_J} \right\rangle \right| &= \hbar \sqrt{S(S+1)} \end{aligned} \quad (\text{II.6})$$

The magnitude of  $\boldsymbol{\mu}_J$  clearly depends on the extent to which the spin and orbital angular momenta are aligned with one another and hence the total magnetic moment of the molecule. To find this, we start with the knowledge that the total magnetic moment is the sum of its orbital and spin contributions,

$$\begin{aligned} \boldsymbol{\mu}_J &= \boldsymbol{\mu}_S + \boldsymbol{\mu}_L \\ g_J(L,S) \hat{\mathbf{J}} \Psi^{L,S,J,M_J} &\approx 2 \hat{\mathbf{S}} \Psi^{L,S,J,M_J} + \hat{\mathbf{L}} \Psi^{L,S,J,M_J} \\ &\approx (2\hat{\mathbf{S}} + \hat{\mathbf{L}}) \Psi^{L,S,J,M_J} \\ &\approx (\hat{\mathbf{J}} + \hat{\mathbf{S}}) \Psi^{L,S,J,M_J} \end{aligned} \quad (\text{II.7})$$

If we operate on both sides of this expression with  $\hat{\mathbf{J}}$  and use Eq. (III.8), we obtain

$$g_J(L, S) \approx 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \quad (\text{II.8})$$

**A. Derive Eq. (II.8).**

Since the interaction between a magnetic moment and a magnetic field is given by

$$\mathbf{E} = -\boldsymbol{\mu} \cdot \mathbf{B} \quad (\text{II.9})$$

we see, from Eq. (II.3) that the effect of placing an atom in a magnetic field is to add a term,

$$\hat{H}_B = g_J(L, S) \frac{\beta_e}{\hbar} \hat{\mathbf{J}} \cdot \hat{\mathbf{B}}, \quad (\text{II.10})$$

to the Hamiltonian. If the magnetic field is uniform and directed along the z-direction, then

$$\begin{aligned} \hat{H}_B &= g_J(L, S) \frac{\beta_e}{\hbar} \hat{\mathbf{J}} \cdot B_z \hat{\mathbf{z}} \\ &= g_J(L, S) \frac{\beta_e B_z}{\hbar} \hat{J}_z \end{aligned} \quad (\text{II.11})$$

**B. Using Eq. (II.11), explain why the energy of the atomic state with quantum numbers  $L$ ,  $S$ ,  $J$ , and  $M_J$  is shifted by**

$$\Delta E_B = g_J(L, S) \beta_e B_z M_J \quad (\text{II.12})$$

**in the presence of a uniform magnetic field with strength  $B_z$ .**

The ground state term for Oxygen is  $^3P$ .

**C. Write out the values of  $J$  for the Oxygen atom.**

**D. For each term associated with the  $^3P$  symbol (that is, all the values of  $J$  from part B), sketch the spectrum in the presence of a magnetic field. Use Hund's third rule to order states with different  $J$  correctly.**

**E. The first excited-state term for the Oxygen atom is  $^1D$ . As in part D, sketch the spectrum.**

**F. In class I stated that, in a magnetic field, the "natural eigenstates" are not the conventional "Cartesian" p-orbitals,  $2p_{x,y,z}$ , but those depending on the spherical harmonics,  $2p_0; 2p_{\pm 1}$ . Using the ideas from part E, justify the preceding assertion.**

The sort of term diagram you sketched in part D is called the anomalous Zeeman effect, which is the term used to describe the splitting of a non-singlet state in a magnetic field. By contrast, the splitting of the  $^1D$  term is the "normal" Zeeman splitting. The anomalous splitting is called that for precisely the same reason as the "anomalous" g-factor for the electron was so named: there was a long gap between the laying of the foundations of quantum mechanics (ca. 1913 by Bohr) and the explanation of the unexpected complexity of atomic spectra in magnetic fields (ca. 1928 by Dirac). Imagine being a spectroscopist in the early days, expecting that there would only be 5 states TOTAL in the spectrum of a  $2p^2$  atom. Anomalous indeed.

### III. Spin-Orbit Coupling (1.0)

Because of the electron's spin, it has a magnetic moment. Similarly, referring to Eq. (3.44) in the third set of notes, we observe that the orbital angular momentum of the electron imparts a magnetic moment to the atom. These two magnetic moments interact and can either be aligned with each other or opposed to one another, which causes terms with the same value of  $L$  and  $S$  but different values of  $J$  (reflecting different degrees of "alignment" between the vectors) to split. Typically the state of lowest energy

is the one with the smallest value of  $J$  when an orbital subshell is less than half-filled, and the state with the highest value of  $J$  when the orbital subshell is more than half-filled.<sup>1</sup>

The form of the spin-orbital interaction is

$$\begin{aligned}\hat{H}_{S.O.} &= \sum_{i=1}^N \frac{Z}{4\pi\epsilon_0 r_i^3} \left( \frac{-e}{2mc} \hat{\mathbf{L}}(\mathbf{r}_i) \cdot -g \frac{e}{2mc} \hat{\mathbf{S}}(i) \right) \\ &\approx \sum_{i=1}^N \frac{Ze^2}{8\pi\epsilon_0 m^2 c^2 r_i^3} (\hat{\mathbf{L}}(\mathbf{r}_i) \cdot \hat{\mathbf{S}}(i))\end{aligned}\quad (\text{III.1})$$

Recalling the first problem on the second homework set, you will be unsurprised that, in general,

$$\left\langle \frac{Z}{r^n} \right\rangle \propto Z^{n+1} \quad (\text{III.2})$$

which leads us to conclude that the size of the spin-orbit interaction grows with atomic number,  $Z$ , as  $Z^4$ . Thus, while spin-orbit effects are not very important for first row atoms, they rapidly increase in importance as we move down the periodic table, until they become much more important than the electrostatic effects that drove light atoms to form states with easily identified values of  $\hat{L}_z$  and  $\hat{S}_z$ .

The total atomic Hamiltonian, including spin-orbit effects, is

$$\begin{aligned}\hat{H}_{atom} &= \hat{H}_{el} + \hat{H}_{S.O.} \\ &= \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} + v(\mathbf{r}_i) + \frac{Z}{2c^2 r_i^3} (\hat{\mathbf{L}}(\mathbf{r}_i) \cdot \hat{\mathbf{S}}(i)) + \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right)\end{aligned}\quad (\text{III.3})$$

In Eq. (III.3) we introduced atomic units into the spin-orbit term.

**A. Show that**  $[\hat{L}_z, \hat{H}_{S.O.}] = \left( \frac{Z}{2c^2 r_i^3} \right) \{ \hat{S}_x (i\hat{L}_y) - \hat{S}_y (i\hat{L}_x) \} \neq 0$ .

Similar to the result in part **A**, we have that

$$[\hat{S}_z, \hat{H}_{S.O.}] = \left( \frac{Z}{2c^2 r_i^3} \right) \{ \hat{L}_x (i\hat{S}_y) - \hat{L}_y (i\hat{S}_x) \} \neq 0 \quad (\text{III.4})$$

It follows from Eq. (III.4) and its analogue for  $\hat{L}_z$  that for small atoms (where the size of the spin-orbit term in the Hamiltonian is small)

$$\begin{aligned}\langle \Psi | [\hat{H}_{atom}, \hat{L}_z] | \Psi \rangle &\approx 0 \\ \langle \Psi | [\hat{H}_{atom}, \hat{S}_z] | \Psi \rangle &\approx 0.\end{aligned}\quad (\text{III.5})$$

and so the eigenstates of the atomic Hamiltonian, Eq. (III.3), are approximate eigenfunctions of  $\hat{L}_z$  and  $\hat{S}_z$  for small atoms.

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<sup>1</sup> The reason for this is related to the term symbols for the atom. Recall that the terms for a subshell with  $p$  electrons is the same as that for the subshell occupied with  $h$  electron holes (or electron vacancies)—or the lack of particles. This is why, for instance, the term symbols for  $p^1$  and  $p^5$ ,  $p^2$  and  $p^4$ ,  $d^1$  and  $d^9$ ,  $d^2$  and  $d^8$ , etc. are the same. The hole is exactly a “negative electron”, since the sum of an electron and a hole must be zero. Thus the electron hole will have the same Landé  $g$  factor as the electron but opposite charge. Thus, while the magnetic moment of the electron is  $\boldsymbol{\mu}_S^e \equiv -g \cdot \frac{e}{mc} \hat{\mathbf{S}}$ , the magnetic moment of the hole is  $\boldsymbol{\mu}_S^h \equiv -g \cdot \frac{-e}{mc} \hat{\mathbf{S}} = g \cdot \frac{e}{mc} \hat{\mathbf{S}} = -\boldsymbol{\mu}_S^e$ . It follows that what is a favorable effect for a shell that is less than half-filled (which is to have the orbital and spin magnetic moments opposite one another, so that  $J$  is small) is an unfavorable effect for a shell that is more than half-filled, where having the orbital and spin-magnetic moments of the electron holes opposed to one another requires that the orbital and spin magnetic moments of the electrons be aligned.

Using perturbation theory, we can approximate the energy splitting induced by spin-orbit coupling. Let  $\Psi^{L,S,J}$  be an eigenstate of the electronic Hamiltonian, Eq. (I.1), and an eigenstate of  $\hat{L}^2$ ,  $\hat{S}^2$ , and  $\hat{J}^2$ . From first-order perturbation theory, we find that the spin-orbit interaction gives different energies to states with the same value of  $S$  and  $L$  but different values of  $J$ . In particular we predict that the energy of the  $^{2S+1}A(L)_J$  term will be given by

$$E_{^{2S+1}A(L)_J} \equiv A(L, S) \cdot (J(J+1) - L(L+1) - S(S+1)) \quad (\text{III.6})$$

where  $A(L, S) \equiv \frac{\hbar^2}{2} \cdot \left\langle \Psi^{L,S,J} \left| \left( \frac{Z}{2c^2 r_i^3} \right) \right| \Psi^{L,S,J} \right\rangle$ . Because  $\left( \frac{Z}{2c^2 r_i^3} \right) > 0$ ,  $A(L, S)$  is usually greater than zero for shells that are less than half-filled. Referring to the first footnote, we note that for shells that are more than half-filled it is more appropriate to use the spin-magnetic of the hole than that of the electron in the first line of Eq. (III.1), which changes the sign of the perturbation, and thus the sign of  $A(L, S)$ . Summarizing

$$\begin{aligned} A(L, S) &\gtrsim 0 && \text{(less than half-filled shells)} \\ A(L, S) &\lesssim 0 && \text{(more than half-filled shells)} \end{aligned} \quad (\text{III.7})$$

where the odd-looking inequality is used to stress the fact that Hund's third rule is not infrequently violated, especially for excited states.

**B. Derive Eq. (III.6). You will find it helpful to use the result**

$$\begin{aligned} \hat{J}^2 &= (\hat{\mathbf{J}} \cdot \hat{\mathbf{J}}) = (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}}) \\ &= \hat{L}^2 + \hat{S}^2 + 2(\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}) \end{aligned} \quad (\text{III.8})$$

**C. Using Eq. (III.7), derive Hund's third rule (that small values of  $J$  are energetically favorable when subshells that are less than half-filled, but large values of  $J$  for shells that are more than half-filled).**

As established in part I, because  $\hat{L}_z$  and  $\hat{S}_z$  do not commute with the atomic Hamiltonian, Eq. (III.3), when the spin-orbit interaction is included, we should not use  $M_L$  and  $M_S$  to label states atoms with large atomic number. However, we can still use  $\hat{L}^2$ ,  $\hat{S}^2$ ,  $\hat{J}^2$ , and  $\hat{J}_z$  to describe these states.

**D. Show that  $[\hat{L}^2, \hat{H}_{s.o.}] = [\hat{J}^2, \hat{H}_{s.o.}] = [\hat{J}_z, \hat{H}_{s.o.}] = 0$ . You may find it helpful to use your result from part A and Eq. (III.4).**

## IV. The Form of the Wave Function Close to the Nucleus of an Atom

Suppose we are given an  $N$ -electron  $P$ -atom molecule. The electronic Hamiltonian is

$$\hat{H} = \sum_{i=1}^N \left( \frac{-\nabla_i^2}{2} - \sum_{\alpha=1}^P \frac{Z}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right) + \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (\text{IV.1})$$

Now, suppose that

$$\begin{aligned} |\mathbf{r}_1 - \mathbf{R}_1| &\ll |\mathbf{r}_k - \mathbf{R}_\alpha| && k \text{ and } \alpha \text{ are not both equal to } 1. \\ |\mathbf{r}_1 - \mathbf{R}_1| &\ll |\mathbf{r}_i - \mathbf{r}_j| && 1 \leq i, j \leq N \end{aligned} \quad (\text{IV.2})$$

That is, electron one and nucleus one are closer to coalescence than any other pairing of electrons and nuclei or electrons and electrons. Then we have that

$$\begin{aligned} \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} &\gg \frac{1}{|\mathbf{r}_k - \mathbf{R}_\alpha|} & k, \alpha \neq 1 \\ \frac{1}{|\mathbf{r}_1 - \mathbf{R}_1|} &\gg \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} & 1 \leq i, j \leq N \end{aligned} \quad (\text{IV.3})$$

Choose the origin of the coordinate system to be at  $\mathbf{R}_1$ . That is, choose  $\mathbf{R}_1 = \mathbf{0}$ .

**A. Show that the electronic Schrödinger equation can be written as**

$$\left( -\frac{\nabla_1^2}{2} - \frac{Z_1}{r_1} - \sum_{\alpha=2}^P \frac{Z_\alpha}{|\mathbf{r}_1 - \mathbf{R}_\alpha|} + \sum_{j=2}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_1|} + \sum_{i=2}^N \left( -\frac{\nabla_i^2}{2} - \sum_{\alpha=1}^P \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right) + \sum_{i=2}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (\text{IV.4})$$

**B. Derive the next two equations:**

$$\left( -\frac{\nabla_1^2}{2} - \frac{Z_1}{r_1} - \sum_{\alpha=2}^P \frac{Z_\alpha}{R_\alpha} + \sum_{j=2}^N \frac{1}{r_j} + \sum_{\alpha=2}^P \mathcal{O}\left(\frac{r_1}{R_\alpha}\right) + \sum_{j=2}^N \mathcal{O}\left(\frac{r_1}{r_j}\right) + \sum_{i=2}^N \left( -\frac{\nabla_i^2}{2} - \sum_{\alpha=1}^P \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right) + \sum_{i=2}^N \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \quad (\text{IV.5})$$

$$\left( -\frac{\nabla_1^2}{2} - \frac{Z_1}{r_1} - \mathcal{O}(r_1^0) + \mathcal{O}(r_1) \right) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0$$

When  $r_1$  is small, the higher order terms in Eq. (IV.5) are very small compared to the terms we are including. Expanding  $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  in a power series about  $\mathbf{r}_1 = \mathbf{0}$  we have

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{n=0}^{\infty} \frac{r_1^n}{n!} \frac{\partial^n \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}{\partial r_1^n} \bigg|_{r_1=0} \quad (\text{IV.6})$$

**C. Show that Eq. (IV.5) is solved (up to constant terms) by**

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(0, \mathbf{r}_2, \dots, \mathbf{r}_N) (1 - Z_1 r_1 + \mathcal{O}(r_1^2)). \quad (\text{IV.7})$$

**D. Show that Eq. (IV.7) can be rewritten as**

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(0, \mathbf{r}_2, \dots, \mathbf{r}_N) (e^{-Z_1 r_1} + \mathcal{O}(r_1^2)). \quad (\text{IV.8})$$

Equation (IV.8) indicates that, very near an atomic nucleus, electrons behave very much like electrons in the hydrogen atom. This, of course, is because when the dominant force on the electron is from a single nucleus, it *feels* a force very much like the force it feels in the hydrogen atom. Note that the form of the solution is *forced* by the fact that in order for Eq. (IV.5) to hold, the kinetic energy term must “cancel out” the potential term. (That is the secret to making this derivation more rigorous.)<sup>2</sup>

**E. Show that**

$$Z_1 = - \frac{d \ln \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)}{dr_1} \bigg|_{r_1=0} \quad (\text{IV.9})$$

<sup>2</sup> There is a much more rigorous way, due to Kato, to derive these results. However, here I want to stress how “reasonable” the result is, rather than the high-powered mathematics required to prove it properly.

**F. Explain why Eq. (IV.9) is often called the coalescence cusp condition.**

## V. Orbital Hybridization and Resonance

To elaborate on the concept of orbital hybridization and resonance we treat, in detail, the hydrogen fluoride molecule,  $HF$ . We start our treatment by writing down an “electron configuration” for the molecule in a “general chemistry” way, for instance,

$$HF : 1s_F^2 2s_F^2 2p_F^5 1s_H^1 \quad (V.1)$$

which suggests the valence-bond wave function

$$\begin{aligned} \Psi_{HF}^{VB} &\equiv \left| \psi_{1s}^F \alpha \quad \psi_{1s}^F \beta \quad \psi_{2s}^F \alpha \quad \psi_{2s}^F \beta \quad \psi_{2p_x}^F \alpha \quad \psi_{2p_x}^F \beta \quad \psi_{2p_y}^F \alpha \quad \psi_{2p_y}^F \beta \quad \begin{pmatrix} \psi_{2p_z}^F \alpha \psi_{1s}^H \beta \\ + \psi_{2p_z}^F \beta \psi_{1s}^H \alpha \end{pmatrix} \right| \\ &= \mathcal{A} \left( \begin{aligned} &\psi_{1s}^F(\mathbf{r}_1) \alpha(1) \psi_{1s}^F(\mathbf{r}_2) \beta(2) \psi_{2s}^F(\mathbf{r}_3) \alpha(3) \psi_{2s}^F(\mathbf{r}_4) \beta(4) \\ &\times \psi_{2p_x}^F(\mathbf{r}_5) \alpha(5) \psi_{2p_x}^F(\mathbf{r}_6) \beta(6) \psi_{2p_y}^F(\mathbf{r}_7) \alpha(7) \psi_{2p_y}^F(\mathbf{r}_8) \beta(8) \\ &\times (\psi_{2p_z}^F(\mathbf{r}_9) \alpha(9) \psi_{1s}^H(\mathbf{r}_{10}) \beta(10) + \psi_{2p_z}^F(\mathbf{r}_{10}) \beta(10) \psi_{1s}^H(\mathbf{r}_9) \alpha(9)) \end{aligned} \right) \quad (V.2) \end{aligned}$$

where  $\mathcal{A}$  denotes the antisymmetrizer, which permutes all the electrons in the right-hand side of Eq. (V.2) and “permutes them” so that we obtain the appropriately antisymmetric wave function. For example, we can write the Heitler-London wave function for the hydrogen molecule as:

$$\begin{aligned} \Psi_{H_2} &\equiv \left| \psi_{1s}^{(l)} \alpha \psi_{1s}^{(r)} \beta + \psi_{1s}^{(l)} \beta \psi_{1s}^{(r)} \alpha \right| \\ &= \mathcal{A} \left( \psi_{1s}^{(l)}(\mathbf{r}_1) \alpha(1) \psi_{1s}^{(r)}(\mathbf{r}_2) \beta(2) + \psi_{1s}^{(l)}(\mathbf{r}_1) \beta(1) \psi_{1s}^{(r)}(\mathbf{r}_2) \alpha(2) \right) \\ &= \psi_{1s}^{(l)}(\mathbf{r}_1) \alpha(1) \psi_{1s}^{(r)}(\mathbf{r}_2) \beta(2) + \psi_{1s}^{(l)}(\mathbf{r}_1) \beta(1) \psi_{1s}^{(r)}(\mathbf{r}_2) \alpha(2) \\ &\quad - \psi_{1s}^{(l)}(\mathbf{r}_2) \alpha(2) \psi_{1s}^{(r)}(\mathbf{r}_1) \beta(1) + \psi_{1s}^{(l)}(\mathbf{r}_2) \beta(2) \psi_{1s}^{(r)}(\mathbf{r}_1) \alpha(1) \\ &= (\psi_{1s}^{(l)}(\mathbf{r}_1) \psi_{1s}^{(r)}(\mathbf{r}_2) + \psi_{1s}^{(l)}(\mathbf{r}_2) \psi_{1s}^{(r)}(\mathbf{r}_1)) (\alpha(1) \beta(2) - \alpha(2) \beta(1)) \end{aligned} \quad (V.3)$$

where  $\psi_{1s}^{(l)}(\mathbf{r})$  and  $\psi_{1s}^{(r)}(\mathbf{r})$  denote the 1s-orbitals centered on the “left-hand” and “right-hand” hydrogen atoms, respectively.

It is convenient to introduce a shorthand for the “electron pairing” behavior that dominates the valence-bond treatment. For this purpose, we introduce the notation

$$\Psi_{HF}^{VB} \equiv \overbrace{\psi_{1s}^F \alpha \psi_{1s}^F \beta} \overbrace{\psi_{2s}^F \alpha \psi_{2s}^F \beta} \overbrace{\psi_{2p_x}^F \alpha \psi_{2p_x}^F \beta} \overbrace{\psi_{2p_y}^F \alpha \psi_{2p_y}^F \beta} \overbrace{\psi_{2p_z}^F \alpha \psi_{2p_z}^F \beta} \overbrace{\psi_{1s}^H \alpha} \quad (V.4)$$

which we usually abbreviate to simply

$$\Psi_{HF}^{VB} \equiv \overbrace{\psi_{1s}^F} \overbrace{\psi_{2s}^F} \overbrace{\psi_{2p_x}^F} \overbrace{\psi_{2p_y}^F} \overbrace{\psi_{2p_z}^F} \overbrace{\psi_{1s}^H} \quad (V.5)$$

Returning to Eq. (V.2), we recognize that we might find it preferable to “mix” the 2s - and 2p - orbitals together to form a “hybrid orbital”, something like  $\psi_{2sp}^F(\mathbf{r}) \propto \mu_p \cdot \psi_{2p_z}^F(\mathbf{r}) + \mu_s \cdot \psi_{2s}^F(\mathbf{r})$ , where  $\mu_s$  and  $\mu_p$  are mixing coefficients. In particular, if we “mix” in a fraction,  $\mathcal{F}$ , of s character, we have the hybrid orbitals,

$$\begin{aligned} \psi_{sp}^+(\mathbf{r}) &\equiv \sqrt{1 - \mathcal{F}} \psi_{2s}^F(\mathbf{r}) + \sqrt{\mathcal{F}} \psi_{2p_z}^F(\mathbf{r}) \\ \psi_{sp}^-(\mathbf{r}) &\equiv \sqrt{\mathcal{F}} \psi_{2s}^F(\mathbf{r}) - \sqrt{1 - \mathcal{F}} \psi_{2p_z}^F(\mathbf{r}) \end{aligned} \quad (V.6)$$

Based on the physical interpretation, clearly we must restrict the fraction of s-character,  $\mathcal{F}$ , to  $0 \leq \mathcal{F} \leq 1$ .

### A. Show that the orbitals in Eq. (V.6) are orthonormal.

In terms of the hybrid orbitals, then we can write, instead of Eq. (V.2),



$$\begin{aligned}
\Psi_{HF}^{sp} &\equiv \left| \psi_{1s}^F \alpha \quad \psi_{1s}^F \beta \quad \psi_{sp}^- \alpha \quad \psi_{sp}^- \beta \quad \psi_{2p_x}^F \alpha \quad \psi_{2p_x}^F \beta \quad \psi_{2p_y}^F \alpha \quad \psi_{2p_y}^F \beta \quad \begin{pmatrix} \psi_{sp}^+ \alpha \psi_{1s}^H \beta \\ + \psi_{sp}^+ \beta \psi_{1s}^H \alpha \end{pmatrix} \right| \\
&= \mathcal{A} \left[ \begin{aligned} &\psi_{1s}^F(\mathbf{r}_1) \alpha(1) \psi_{1s}^F(\mathbf{r}_2) \beta(2) \psi_{sp}^-(\mathbf{r}_3) \alpha(3) \psi_{sp}^-(\mathbf{r}_4) \beta(4) \\ &\times \psi_{2p_x}^F(\mathbf{r}_5) \alpha(5) \psi_{2p_x}^F(\mathbf{r}_6) \beta(6) \psi_{2p_y}^F(\mathbf{r}_7) \alpha(7) \psi_{2p_y}^F(\mathbf{r}_8) \beta(8) \\ &\times (\psi_{sp}^+(\mathbf{r}_9) \alpha(9) \psi_{1s}^H(\mathbf{r}_{10}) \beta(10) + \psi_{sp}^+(\mathbf{r}_{10}) \beta(9) \psi_{1s}^H(\mathbf{r}_9) \alpha(10)) \end{aligned} \right] \quad (V.7) \\
&= \widehat{\psi_{1s}^F} \widehat{\psi_{sp}^-} \widehat{\psi_{2p_x}^F} \widehat{\psi_{2p_y}^F} \widehat{\psi_{sp}^+} \widehat{\psi_{1s}^H}
\end{aligned}$$

The energy would then be optimized so that the best possible value of  $\mathcal{F}$  was found.

In Eq. (V.7) the lone pair orbitals are not equivalent—two of the “lone pairs” are in  $p$ -type orbitals perpendicular to the bonding axis and one of the “lone pairs” lies at lower energy, in an  $sp$ -hybrid orbital. To get a symmetric description we can introduce the  $sp$  hybrids. The most important cases are the  $sp$ -hybrid orbitals

$$\begin{aligned}
\psi_{sp}^+(\mathbf{r}) &\equiv \frac{\psi_{2s}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r})}{\sqrt{2}} \\
\psi_{sp}^-(\mathbf{r}) &\equiv \frac{\psi_{2s}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})}{\sqrt{2}}, \quad (V.8)
\end{aligned}$$

which is a special case of Eq. (V.6). Similarly, we have that the  $sp^2$  hybrids are given by

$$\begin{aligned}
\psi_{sp^2}^{(1)}(\mathbf{r}) &\equiv \frac{1}{\sqrt{3}} \psi_{2s}(\mathbf{r}) + \frac{2}{\sqrt{3}} \psi_{2p_z}(\mathbf{r}) \\
\psi_{sp^2}^{(2)}(\mathbf{r}) &\equiv \frac{1}{\sqrt{3}} \psi_{2s}(\mathbf{r}) - \frac{1}{\sqrt{6}} \psi_{2p_x}(\mathbf{r}) + \frac{1}{\sqrt{2}} \psi_{2p_y}(\mathbf{r}) \\
\psi_{sp^2}^{(3)}(\mathbf{r}) &\equiv \frac{1}{\sqrt{3}} \psi_{2s}(\mathbf{r}) - \frac{1}{\sqrt{6}} \psi_{2p_x}(\mathbf{r}) - \frac{1}{\sqrt{2}} \psi_{2p_y}(\mathbf{r}) \quad (V.9)
\end{aligned}$$

The most important case, beloved of organic chemists, are the  $sp^3$  hybrids

$$\begin{aligned}
\psi_{sp^3}^{(1)}(\mathbf{r}) &\equiv \frac{\psi_{2s}(\mathbf{r}) + \psi_{2p_x}(\mathbf{r}) + \psi_{2p_y}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r})}{2} \\
\psi_{sp^3}^{(2)}(\mathbf{r}) &\equiv \frac{\psi_{2s}(\mathbf{r}) - \psi_{2p_x}(\mathbf{r}) - \psi_{2p_y}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r})}{2} \\
\psi_{sp^3}^{(3)}(\mathbf{r}) &\equiv \frac{\psi_{2s}(\mathbf{r}) + \psi_{2p_x}(\mathbf{r}) - \psi_{2p_y}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})}{2} \\
\psi_{sp^3}^{(4)}(\mathbf{r}) &\equiv \frac{\psi_{2s}(\mathbf{r}) - \psi_{2p_x}(\mathbf{r}) + \psi_{2p_y}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})}{2} \quad (V.10)
\end{aligned}$$

Using the  $sp^3$  hybrids, we can write an approximate wave function for  $HF$  as

$$\begin{aligned}
\Psi_{HF}^{sp^3} &\equiv \left| \psi_{1s}^F \alpha \quad \psi_{1s}^F \beta \quad \psi_{sp^3}^{(1)} \alpha \quad \psi_{sp^3}^{(1)} \beta \quad \psi_{sp^3}^{(2)} \alpha \quad \psi_{sp^3}^{(2)} \beta \quad \psi_{sp^3}^{(3)} \alpha \quad \psi_{sp^3}^{(3)} \beta \quad \begin{pmatrix} \psi_{sp^3}^{(4)} \alpha \psi_{1s}^H \beta \\ + \psi_{sp^3}^{(4)} \beta \psi_{1s}^H \alpha \end{pmatrix} \right| \\
&= \mathcal{A} \left[ \begin{aligned} &\psi_{1s}^F(\mathbf{r}_1) \alpha(1) \psi_{1s}^F(\mathbf{r}_2) \beta(2) \psi_{sp^3}^{(1)}(\mathbf{r}_3) \alpha(3) \psi_{sp^3}^{(1)}(\mathbf{r}_4) \beta(4) \\ &\times \psi_{sp^3}^{(2)}(\mathbf{r}_5) \alpha(5) \psi_{sp^3}^{(2)}(\mathbf{r}_6) \beta(6) \psi_{sp^3}^{(3)}(\mathbf{r}_7) \alpha(7) \psi_{sp^3}^{(3)}(\mathbf{r}_8) \beta(8) \\ &\times (\psi_{sp^3}^{(4)}(\mathbf{r}_9) \alpha(9) \psi_{1s}^H(\mathbf{r}_{10}) \beta(10) + \psi_{sp^3}^{(4)}(\mathbf{r}_{10}) \beta(9) \psi_{1s}^H(\mathbf{r}_9) \alpha(10)) \end{aligned} \right] \quad (V.11) \\
&= \widehat{\psi_{1s}^F} \widehat{\psi_{sp^3}^{(1)}} \widehat{\psi_{sp^3}^{(2)}} \widehat{\psi_{sp^3}^{(3)}} \widehat{\psi_{sp^3}^{(4)}} \widehat{\psi_{1s}^H}
\end{aligned}$$

**B. After minimizing the energy of the wave function in Eq. (V.7) with respect to  $\mathcal{F}$ , will the energy be greater or less than the energy of the wave function in Eq. (V.11)?**

In each of these wave functions, the binding electrons are shared equally between Hydrogen and Fluorine. Of course, we know that  $HF$  has a substantial dipole moment. We can accommodate this observation using resonance, namely,

$$HF \leftrightarrow H^+F^- \quad (V.12)$$

Resonance is similar to configuration interaction in molecular-orbital theory, and is performed by adding together two Slater determinants and optimizing their coefficients (based on their perceived relative importance). We can write

$$\Psi_{H^+F^-} \equiv \begin{vmatrix} \psi_{1s}^F \alpha & \psi_{1s}^F \beta & \psi_{2s}^F \alpha & \psi_{2s}^F \beta & \psi_{2p_x}^F \alpha & \psi_{2p_x}^F \beta & \psi_{2p_y}^F \alpha & \psi_{2p_y}^F \beta & \psi_{2p_z}^F \alpha & \psi_{2p_z}^F \beta \end{vmatrix} \quad (V.13)$$

and then the resonance-hybrid wave function will be

$$\Psi_{HF}^{resonance}(\mathbf{r}_1, \mathbf{r}_2) \approx c_1 \Psi_{HF}^{sp^3}(\mathbf{r}_1, \mathbf{r}_2) + c_2 \Psi_{H^+F^-}(\mathbf{r}_1, \mathbf{r}_2) \quad (V.14)$$

where  $c_1$  and  $c_2$  are chosen to minimize the energy. Note that  $\Psi_{HF}^{sp^3}(\mathbf{r}_1, \mathbf{r}_2)$  and  $\Psi_{H^+F^-}(\mathbf{r}_1, \mathbf{r}_2)$  are not orthogonal. This complicates valence bond calculations substantially, and may be considered the primary reason “conventional” valence bond theory has only rarely been used for quantitative chemical calculations in recent years.

### C. Write the resonance structures for the nitrite ion $NO_2^-$ .

Without using hybrid orbitals, we might write the electron configuration for the molecule (which we place in the  $xy$ -plane) as

$$\begin{array}{c} NO_2^- : 1s_{O1}^2 1s_{O2}^2 1s_N^2 2s_{O1}^2 2s_{O2}^2 2s_N^2 2p_{x;O1}^1 2p_{x;N}^1 2p_{y;O2}^1 2p_{y;N}^1 2p_{z;O1}^1 2p_{z;N}^1 2p_{x;O2}^2 2p_{z;O2}^2 2p_{y;O1}^2 \\ \updownarrow \\ 1s_{O1}^2 1s_{O2}^2 1s_N^2 2s_{O1}^2 2s_{O2}^2 2s_N^2 2p_{x;O1}^1 2p_{x;N}^1 2p_{y;O2}^1 2p_{y;N}^1 2p_{z;O2}^1 2p_{z;N}^1 2p_{x;O2}^2 2p_{z;O1}^2 2p_{y;O1}^2 \end{array} \quad (V.15)$$

- D. Write a valence-bond wave function for one of these resonance structures. What would you predict the bond angle to be?
- E. Write a valence-bond wave function for each of the resonance states using hybrid orbitals.
- F. What linear combination of these two wave functions gives the resonance-corrected valence-bond description?

## VI. The Electrostatic Theorem

What holds the atoms together in a molecule? Said differently: What, exactly, is a chemical bond? One of the most useful tools for this purpose is the electrostatic theorem, which is what we derive here. We consider the special of a diatomic molecule with bond length  $l$ , with one nucleus at  $\mathbf{R}_A = [0, 0, -\frac{l}{2}]$  and the other at  $\mathbf{R}_B = [0, 0, \frac{l}{2}]$ .

Let's start with the nuclear Schrödinger equation in the Born-Oppenheimer approximation

$$(\hat{T}_n + U^{BO}(\mathbf{R}_A, \mathbf{R}_B)) \chi_n^{BO}(\mathbf{R}_A, \mathbf{R}_B) = E^{BO} \chi_n^{BO}(\mathbf{R}_A, \mathbf{R}_B) \quad (VI.1)$$

Recall that  $U^{BO}(\mathbf{R}_1, \mathbf{R}_2)$  is the potential energy surface on which the nuclei move, and that

$$U^{BO}(\mathbf{R}_A, \mathbf{R}_B) = \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} + \left\langle \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \left| \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} - \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} - \frac{Z_B}{|\mathbf{r}_i - \mathbf{R}_B|} \right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \right\rangle_{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N} \quad (\text{VI.2})$$

Recall that the force on nucleus  $A$  is defined as

$$\mathbf{F}_A \equiv -\nabla_A U^{BO}(\mathbf{R}_A, \mathbf{R}_B) \quad (\text{VI.3})$$

Clearly a force on nucleus  $A$  in the the  $z$ -direction is associated with chemical binding. So the “binding force” on the nucleus is

$$\begin{aligned} \mathbf{F}_A \cdot \hat{z} &= -\nabla_A U^{BO}(\mathbf{R}_A, \mathbf{R}_B) \cdot \hat{z} \\ &= -\left[ \frac{\partial U^{BO}}{\partial x_A}, \frac{\partial U^{BO}}{\partial y_A}, \frac{\partial U^{BO}}{\partial z_A} \right] \cdot \hat{z} \\ &= -\frac{\partial U^{BO}}{\partial z_A} \end{aligned} \quad (\text{VI.4})$$

where  $\hat{z}$  is the unit vector in the  $z$ -direction. To evaluate (VI.4), we need to remember that

$$\begin{aligned} \frac{\partial \frac{1}{|\mathbf{r} - \mathbf{R}_A|}}{\partial z_A} &= \frac{\partial \left( \frac{1}{\sqrt{(x - x_A)^2 + (y - y_A)^2 + (z - z_A)^2}} \right)}{\partial z_A} \\ &= \frac{\partial \left( \left( (x - x_A)^2 + (y - y_A)^2 + (z - z_A)^2 \right)^{-1/2} \right)}{\partial z_A} \\ &= -\frac{1}{2} (2(z - z_A)) \left( (x - x_A)^2 + (y - y_A)^2 + (z - z_A)^2 \right)^{-3/2} \\ &= (z - z_A) (|\mathbf{r} - \mathbf{R}_A|)^{-3} \\ &= \frac{(z - z_A)}{|\mathbf{r} - \mathbf{R}_A|^3} \end{aligned} \quad (\text{VI.5})$$

**A. Explain why we use Eq. (VI.5) instead of**

$$\frac{\partial \frac{1}{|\mathbf{r} - \mathbf{R}_A|}}{\partial z_A} = -\frac{(z - z_A)}{|\mathbf{r} - \mathbf{R}_A|^3} \quad (\text{VI.6})$$

(We have to choose between Eqs. (VI.5) and (VI.6) because  $\frac{1}{|\mathbf{r} - \mathbf{R}_A|} = \frac{1}{|\mathbf{R}_A - \mathbf{r}|}$ .)

We use the Hellmann-Feynman theorem,

$$\frac{\partial E}{\partial z_A} = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial z_A} \right| \psi \right\rangle, \quad (\text{VI.7})$$

to write,

$$\begin{aligned}
 \frac{\partial U^{BO}(\mathbf{R}_A, \mathbf{R}_B)}{\partial z_A} &= \frac{\partial \left( \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \right)}{z_A} \\
 &+ \left\langle \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \left| \frac{\partial \left( \sum_{i=1}^N \left( -\frac{\nabla_i^2}{2} - \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \right) - \frac{Z_B}{|\mathbf{r}_i - \mathbf{R}_B|} \right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}{\partial z_A} \right| \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \right\rangle_{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N}
 \end{aligned} \tag{VI.8}$$

and so

$$\begin{aligned}
 \frac{\partial U^{BO}(\mathbf{R}_A, \mathbf{R}_B)}{\partial z_A} &= Z_A Z_B \frac{(z_B - z_A)}{|\mathbf{R}_B - \mathbf{R}_A|^3} \\
 &+ \left\langle \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \left| \sum_{i=1}^N -Z_A \left( \frac{z_i - z_A}{|\mathbf{r}_i - \mathbf{R}_A|^3} \right) \right| \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \right\rangle_{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N}
 \end{aligned} \tag{VI.9}$$

**B. Show that Eq. (VI.9) gives that**

$$\begin{aligned}
 \mathbf{F}_A \cdot \hat{\mathbf{z}} &= - \frac{\partial U^{BO}(\mathbf{R}_A, \mathbf{R}_B)}{\partial z_A} \\
 &= \int \rho(\mathbf{r}) \left( Z_A \left( \frac{z - z_A}{|\mathbf{r} - \mathbf{R}_A|^3} \right) \right) d\mathbf{r} - \frac{Z_A Z_B}{R^2}
 \end{aligned} \tag{VI.10}$$

where  $\rho(\mathbf{r})$  is the electron density of the system. What is the interpretation of the first term in Eq. (VI.10)? What is the interpretation of the second term in Eq. (VI.10)?

A “binding” force on atom  $B$  corresponds to a force in the  $-z$  direction. We have, then, that

$$\begin{aligned}
\mathbf{F}_B \cdot -\hat{z} &= -\nabla_B U^{BO}(\mathbf{R}_A, \mathbf{R}_B) \cdot -\hat{z} \\
&= \frac{\partial U^{BO}(\mathbf{R}_A, \mathbf{R}_B)}{\partial z_B} \\
&= \frac{\partial \left( \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} \right)}{\partial z_B} \\
&+ \left\langle \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \left| \sum_{i=1}^N -Z_B \frac{\partial \left( \frac{1}{|\mathbf{r}_i - \mathbf{R}_B|} \right)}{\partial z_B} \right| \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \right\rangle_{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N} \\
&= \frac{Z_A Z_B (z_A - z_B)}{|\mathbf{R}_A - \mathbf{R}_B|^3} \\
&+ \left\langle \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \left| \sum_{i=1}^N -Z_B \frac{(z_i - z_B)}{|\mathbf{r}_i - \mathbf{R}_B|^3} \right| \psi_e(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_A, \mathbf{R}_B) \right\rangle_{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N} \\
&= -\frac{Z_A Z_B}{R^2} - Z_B \int \rho(\mathbf{r}) \left( \frac{z - z_B}{|\mathbf{r} - \mathbf{R}_B|^3} \right) d\mathbf{r}
\end{aligned} \tag{VI.11}$$

It is not obvious, perhaps, but  $\mathbf{F}_A \cdot \hat{z} = \mathbf{F}_B \cdot -\hat{z}$ .

The *electrostatic theorem* notes that in both Eqs. (VI.10) and (VI.11), the forces on the nuclei are simply electrostatic: attraction to the negative electrons and repulsion from the positive nuclei. We conclude that molecules are held together by simple attractions between the nuclei and the electrons.

A useful application of the electrostatic theorem is Berlin's binding theorem. The idea is the following: at what points in space does the accumulation of electron density serve to "bind the molecule together" and where does the accumulation of electric charge serve to "push molecules apart"?

**C. Using Eq. (VI.10), argue the force on nucleus  $A$  due to the electron density at  $\mathbf{r}$ ,  $\rho(\mathbf{r}) d\mathbf{r}$ , is just**

$$F_A(\mathbf{r}) = Z_A \left( \frac{z - z_A}{|\mathbf{r} - \mathbf{R}_A|^3} \right) \rho(\mathbf{r}) d\mathbf{r}. \tag{VI.12}$$

Similarly, the force pushing on nucleus  $B$  toward atom  $A$  is:

$$F_B(\mathbf{r}) = -Z_B \left( \frac{z - z_B}{|\mathbf{r} - \mathbf{R}_B|^3} \right) \rho(\mathbf{r}) d\mathbf{r}. \tag{VI.13}$$

When  $F_A(\mathbf{r})$  and  $F_B(\mathbf{r})$  are both greater than zero, charge density at  $\mathbf{r}$  tends to "force" the two nuclei together. Similarly, if  $F_A(\mathbf{r})$  and  $F_B(\mathbf{r})$  were both less than zero, then charge density at  $\mathbf{r}$  would tend to "force" the nuclei apart. There is another possibility: if atom  $A$  is pushed toward atom  $B$  more strongly than atom  $B$  is pushed away from atom  $A$ , so that  $F_A(\mathbf{r}) > -F_B(\mathbf{r})$ , then the net effect of electron density at  $\mathbf{r}$  is to bind the nuclei together. Similarly, if atom  $B$  is pushed toward atom  $A$  more strongly than atom  $A$  is pushed away from atom  $B$ , then  $F_B(\mathbf{r}) > -F_A(\mathbf{r})$ , and charge density at  $\mathbf{r}$  is favorable for binding. We surmise that

$$\begin{aligned}
F_A(\mathbf{r}) + F_B(\mathbf{r}) &> 0 && \text{electron density at } \mathbf{r} \text{ pushes the nuclei together} \\
F_A(\mathbf{r}) + F_B(\mathbf{r}) &< 0 && \text{electron density at } \mathbf{r} \text{ pushes the nuclei apart}
\end{aligned}
\tag{VI.14}$$

**D. Using Eqs. (VI.12) and (VI.13), show that**

$$Z_A \left( \frac{z - z_A}{|\mathbf{r} - \mathbf{R}_A|^3} \right) > Z_B \left( \frac{z - z_B}{|\mathbf{r} - \mathbf{R}_B|^3} \right) \tag{VI.15}$$

indicates that electron density at  $\mathbf{r}$  is favorable for chemical binding.

Equation (VI.15) is often cited as Berlin's binding theorem.

In order to understand Eq. (VI.15), we should plot the “binding region”—the region of space where the build-up of electron density during molecule formation contributes to chemical binding. The general case is quite complicated, but several “special cases” can be considered, of which the simplest is to consider the effects of charge accumulation and depletion along the bonding axis. For simplicity, we choose our units and rotate the molecule so that the nuclei are on the  $z$ -axis, at  $z = \pm 1$ . Then Eq. (VI.15) becomes

$$Z_A \left( \frac{z + 1}{\left( \sqrt{x^2 + y^2 + (z + 1)^2} \right)^3} \right) > Z_B \left( \frac{z - 1}{\left( \sqrt{x^2 + y^2 + (z - 1)^2} \right)^3} \right) \tag{VI.16}$$

We examine what occurs along the internuclear axis, where  $x = y = 0$ .

**E. Show that along the  $z$ -axis, the condition for bonding is,**

$$Z_A \left( \frac{\text{sgn}(z + 1)}{(z + 1)^2} \right) > Z_B \left( \frac{\text{sgn}(z - 1)}{(z - 1)^2} \right) \tag{VI.17}$$

**F. Explain why this gives the condition**

$$\begin{aligned}
\sqrt{\frac{Z_A}{Z_B}} &> \frac{(z + 1)}{(z - 1)} && z > -1 \\
\sqrt{\frac{Z_A}{Z_B}} &< \frac{(z + 1)}{(z - 1)} && z < -1
\end{aligned}
\tag{VI.18}$$

**G. In a homonuclear diatomic molecule, where do you expect the buildup of electrons to be favorable for bonding? Is this consistent with Eq. (VI.18)?**

**H. Suppose  $Z_B > Z_A$ . Derive the fact that electron density where**

$$\frac{\sqrt{\frac{Z_A}{Z_B}} + 1}{\sqrt{\frac{Z_A}{Z_B}} - 1} > z \tag{VI.19}$$

is favorable for binding.

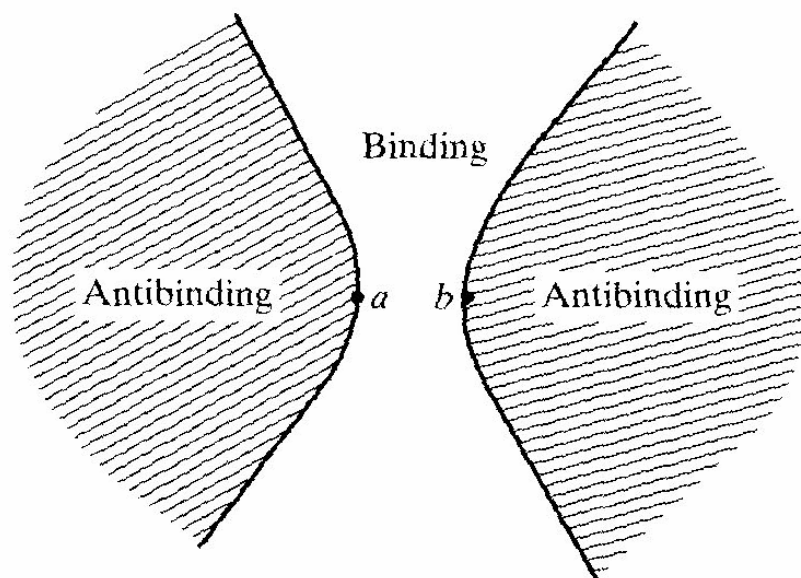


FIGURE 14.5 Cross section of binding and antibinding regions in a homonuclear diatomic molecule. To obtain the three-dimensional regions, rotate the figure about the internuclear axis.

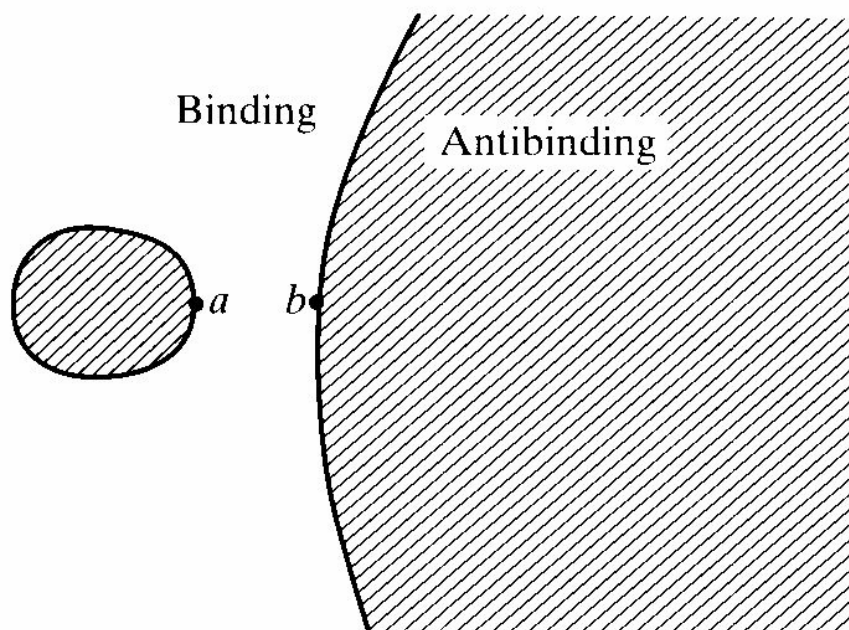


FIGURE 14.6 Binding and antibinding regions for a heteronuclear diatomic molecule with  $Z_b > Z_a$ .

**Figure.** From Ira N. Levine; Quantum Chemistry, 5<sup>th</sup> ed., (Prentice Hall, New Jersey, 2000).

