

Molecules (and Related Topics)

Chemistry 3BB3

I. Electronegativity and Bond Strengths in Heteronuclear Diatomics (.9)

There are several “competing” definitions for electronegativity. Most prominent among these are the definitions of Mulliken, which relates the electronegativity to the ionization potential, I , and the electron affinity, A , of a species, via

$$\chi^{(M)} \equiv \frac{I+A}{2} \quad (1.1)$$

and the definition of Pauling, which relates the difference in the electronegativities of two atoms, A and B to the bond dissociation energies of the heteronuclear and homonuclear diatomics:

$$\chi_A^{(P)} - \chi_B^{(P)} \propto \sqrt{D_{AB} - \sqrt{D_{AA}D_{BB}}} . \quad (1.2)$$

Here D_{AB} is the bond dissociation energy for the molecule, that is, the energy change associated with the reaction



namely,

$$D_{AB} = E_A + E_B - E_{AB} . \quad (1.4)$$

The proportionality constant in Pauling’s electronegativity can be chosen so that the scale closely resembles that from Mulliken’s definition.

Some authors define the Pauling electronegativity using the arithmetic mean instead of the geometric mean, that is,

$$\Delta\tilde{\chi}_P \propto \sqrt{D_{AB} - \frac{D_{AA}+D_{BB}}{2}} . \quad (1.5)$$

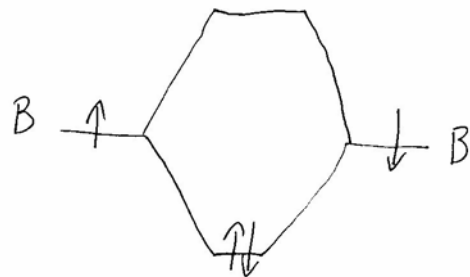
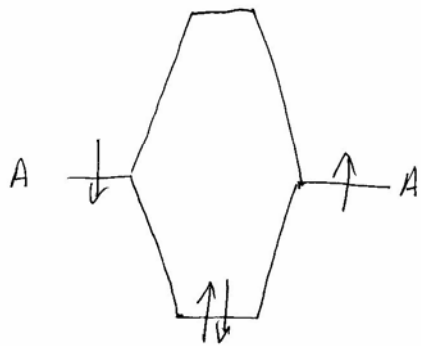
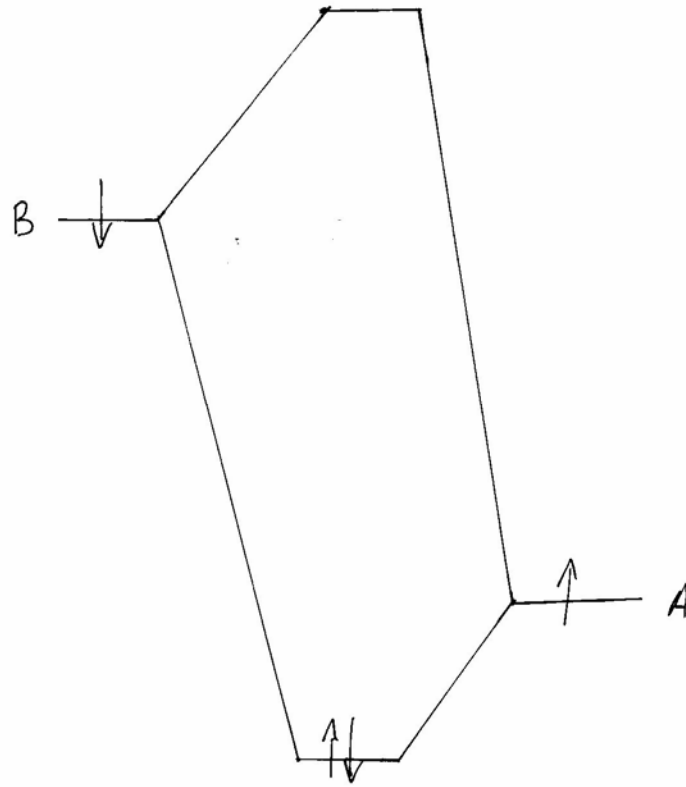
A. Show that the arithmetic mean, \bar{x} , and the geometric mean, $\langle x \rangle$, of two numbers, x_1 and x_2 , are related by the formula,

$$\langle x \rangle \approx \bar{x} - \frac{1}{8} \frac{(x_2 - x_1)^2}{|\bar{x}|} - \frac{1}{32} \frac{(x_2 - x_1)^4}{|\bar{x}|^3} \quad (1.6)$$

(Hint. Write $x_1 = \bar{x} - \frac{(x_2 - x_1)}{2}$ and $x_2 = \bar{x} + \frac{(x_2 - x_1)}{2}$ and use the binomial series.)

It follows from Eq. (1.6) that, for many purposes, the geometric mean and arithmetic mean are “almost the same.” From Eq. (1.6), we may surmise (though not prove) the true statement: the arithmetic mean is never less than the geometric mean ($\langle x \rangle \leq \bar{x}$).

We want to establish a link between the electronegativities of Mulliken and Pauling. To do this, consider a simple heteronuclear diatomic molecule, and assume that the bond between A and B is a single bond. The molecular orbital diagrams are sketched on the next page.



We start with Mulliken's definition. We define the chemical hardness (the same entity that enters in hard/soft acid/base theory) as

$$\eta \equiv I - A \quad (1.7)$$

We can formulate a quadratic model for the dependence of the energy on the charge of a system in terms of the Mulliken electronegativity and the chemical hardness, namely,

$$E(q) = E(0) + q\chi^{(M)} + \frac{\eta}{2}q^2 \quad (1.8)$$

B. Show that Eq. (1.8) is correct for the cation, anion, and neutral species.

C. Show that $\frac{\partial E}{\partial q} = \chi^{(M)}$.

Next, suppose we have two atoms, A , and B . We can approximate the energy of the diatomic molecule, AB , as the sum of the atomic energies,

$$E_{AB} = E_A(q_A) + E_B(q_B). \quad (1.9)$$

Because charge is neither created or destroyed,

$$q_A + q_B = 0 \quad (1.10)$$

and then

$$E_{AB} = E_A(q_A) + E_B(-q_A) \quad (1.11)$$

D. Using the expansion in Eq. (1.8), show that the minimum energy is

$$E_A + E_B - E_{AB} = \frac{(\chi_A^{(M)} - \chi_B^{(M)})^2}{2(\eta_A + \eta_B)} \quad (1.12)$$

E. Similarly, show that, at the minimum,

$$q_A = \frac{(\chi_B^{(M)} - \chi_A^{(M)})}{(\eta_A + \eta_B)} \quad (1.13)$$

Let $\psi_A(\mathbf{r})$ be the bonding orbital of the Lewis acid, A , and $\psi_B(\mathbf{r})$ be the bonding orbital on the Lewis base, B . In order to approximate the molecular orbitals, we find the eigenvalues of the Hamiltonian matrix, namely,

$$\begin{bmatrix} \langle \psi_A^{(r)} | \hat{h} | \psi_A^{(r)} \rangle & \langle \psi_A^{(r)} | \hat{h} | \psi_B^{(l)} \rangle \\ \langle \psi_A^{(r)} | \hat{h} | \psi_B^{(l)} \rangle^* & \langle \psi_B^{(l)} | \hat{h} | \psi_B^{(l)} \rangle \end{bmatrix} \quad (1.14)$$

where \hat{h} is the one-electron Hamiltonian—e.g., the Fock operator, $\hat{f}(\mathbf{r})$ or the operator in the Kohn-Sham equations. I've assumed the “right” atom is the acid and the “left” atom is the base, consistent with the above figure.

We define

$$\begin{aligned} \langle \psi_A^{(r)} | \hat{h}_{AB} | \psi_A^{(r)} \rangle &= \alpha_A \\ \langle \psi_B^{(l)} | \hat{h}_{AB} | \psi_B^{(l)} \rangle &= \alpha_B \end{aligned} \quad (1.15)$$

and use the Wolfsberg-Helmoltz relationship to approximate the off-diagonal terms in the Hamiltonian, so

$$\beta_{AB} \equiv \langle \psi_A^{(r)} | \hat{h}_{AB} | \psi_B^{(l)} \rangle \propto \sqrt{\alpha_A \alpha_B} \langle \psi_A^{(r)} | \psi_B^{(l)} \rangle = \sqrt{\alpha_A \alpha_B} \cdot S_{AB} \quad (1.16)$$

In order to calculate Pauling's electronegativity, we need to compute the binding energy of the molecule, which is usually defined using Eq. (1.4) or as the heat of reaction for the dissociation reaction,



We also need to compute the dissociation energy of the homonuclear species,



and



To proceed, we make some simplifying assumptions. We assume that because $\psi_A^{(r)}(\mathbf{r}) \approx 0$ near the “left” nucleus, that

$$\alpha_A = \langle \psi_A^{(r)} | \hat{h}_{AB} | \psi_A^{(r)} \rangle = \langle \psi_A^{(r)} | \hat{h}_{A_2} | \psi_A^{(r)} \rangle = \langle \psi_A^{(l)} | \hat{h}_{A_2} | \psi_A^{(l)} \rangle = \langle \psi_A | \hat{h}_A | \psi_A \rangle \quad (1.20)$$

That is, we assume that the energy of $\psi_A(\mathbf{r})$ is the same regardless of whether the atomic orbital is in the homonuclear diatomic molecule, A_2 , the heteronuclear diatomic molecule, AB , or the free atom. This is often an reasonable approximation. Similarly, we assume that

$$\alpha_B = \langle \psi_B^{(l)} | \hat{h}_{AB} | \psi_B^{(l)} \rangle = \langle \psi_B^{(r)} | \hat{h}_{B_2} | \psi_B^{(r)} \rangle = \langle \psi_B^{(l)} | \hat{h}_{B_2} | \psi_B^{(l)} \rangle = \langle \psi_B | \hat{h}_B | \psi_B \rangle. \quad (1.21)$$

Denoting the overlap as $S_{AB} = \langle \psi_A^{(r)} | \psi_B^{(l)} \rangle$ we approximate the overlap matrix in terms of the overlaps of the homonuclear species:

$$S_{AB} \approx \sqrt{S_{AA} S_{BB}}. \quad (1.22)$$

Along with Eq. (1.16), this gives,

$$|\beta_{AB}| \approx \sqrt{\beta_{AA} \beta_{BB}} \quad (1.23)$$

which might be simply “assumed.” Again, Eq. (1.23) is not perfect, but it captures the essence of the Wolfsberg-Helmoltz approximation.

We now have three different Hamiltonian matrices,

$$\begin{aligned} \mathbf{h}_{AB} &\equiv \begin{bmatrix} \alpha_A & \sqrt{\beta_{AA} \beta_{BB}} \\ \sqrt{\beta_{AA} \beta_{BB}} & \alpha_B \end{bmatrix} \\ \mathbf{h}_{A_2} &\equiv \begin{bmatrix} \alpha_A & \beta_{AA} \\ \beta_{AA} & \alpha_A \end{bmatrix} \\ \mathbf{h}_{B_2} &\equiv \begin{bmatrix} \alpha_B & \beta_{BB} \\ \beta_{BB} & \alpha_B \end{bmatrix} \end{aligned} \quad (1.24)$$

F. Show that the eigenvalues of \mathbf{h}_{AB} are given by

$$\varepsilon_{AB}^{\pm} \equiv \frac{\alpha_A + \alpha_B \pm \sqrt{(\alpha_A - \alpha_B)^2 + 4|\beta_{AA} \beta_{BB}|}}{2} \quad (1.25)$$

From the same analysis, we find that the eigenvalues \mathbf{h}_{A_2} and \mathbf{h}_{B_2} are given by

$$\begin{aligned} \varepsilon_{A_2}^{\pm} &= \alpha_A \pm |\beta_{AA}| \\ \varepsilon_{B_2}^{\pm} &= \alpha_B \pm |\beta_{BB}| \end{aligned} \quad (1.26)$$

When we dissociate a molecule, we lengthen the bond and so the overlap between the atomic orbitals goes to zero. As a consequence of Eq. (I.16), then, $\beta \rightarrow 0$ and so the orbital energies of the bonding and antibonding orbitals are the same, both being $\frac{\alpha_A + \alpha_B}{2}$.

We approximate the energy of the molecule as the sum of the occupied orbital energies. Thus

$$E_{AB} \equiv (2 \text{ electrons}) \left(\frac{\alpha_A + \alpha_B - \sqrt{(\alpha_A - \alpha_B)^2 + 4|\beta_{AA}\beta_{BB}|}}{2} \right) \quad (\text{I.27})$$

is the energy of AB , and as the molecule dissociates, $R \rightarrow \infty$, and

$$E_{AB}^{R \rightarrow \infty} \equiv 2 \left(\frac{\alpha_A + \alpha_B}{2} \right) \quad (\text{I.28})$$

G. Derive the expression

$$\begin{aligned} \chi_A^{(P)} - \chi_B^{(P)} &\propto \sqrt{D_{AB}} - \sqrt{D_{AA}D_{BB}} \\ &\propto \sqrt{\sqrt{(\alpha_A - \alpha_B)^2 + 4|\beta_{AA}\beta_{BB}|} - 2\sqrt{|\beta_{AA}||\beta_{BB}|}} \end{aligned} \quad (\text{I.29})$$

In general, making a detailed argument for the equivalence of Pauling and Mulliken's electronegativities requires rather sophisticated arguments (preferably considering the valence bond model + ionic terms). However, we can establish the “reasonableness” of the model from Eq. (I.29) by treating the special case where the electronegativities of the atoms are *very* similar. In this case,

$$4|\beta_{AA}\beta_{BB}| \gg (\alpha_A - \alpha_B)^2 \quad (\text{I.30})$$

and so we can use the binomial expansion to derive

$$\begin{aligned} \chi_A^{(P)} - \chi_B^{(P)} &\propto \sqrt{4|\beta_{AA}\beta_{BB}| + (\alpha_A - \alpha_B)^2} - 2\sqrt{|\beta_{AA}||\beta_{BB}|} \\ &\propto \sqrt{2\sqrt{|\beta_{AA}\beta_{BB}|} \sqrt{1 + \frac{(\alpha_A - \alpha_B)^2}{4|\beta_{AA}\beta_{BB}|}}} - 2\sqrt{|\beta_{AA}||\beta_{BB}|} \\ &\propto \sqrt{2} \sqrt{\sqrt{|\beta_{AA}\beta_{BB}|} \left(1 + \frac{1}{2} \frac{(\alpha_A - \alpha_B)^2}{4|\beta_{AA}\beta_{BB}|} \right)} - \sqrt{|\beta_{AA}||\beta_{BB}|} \\ &\propto \sqrt{\frac{(\alpha_A - \alpha_B)^2}{4|\beta_{AA}\beta_{BB}|}} \\ &\propto \frac{|\alpha_A - \alpha_B|}{2\sqrt{|\beta_{AA}\beta_{BB}|}} \end{aligned} \quad (\text{I.31})$$

H. Based on this model, what is the interpretation of α_A and α_B in Eq. (I.24).

I. Referring back to Eq. (I.24), what are the coefficients of $\psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$ for the bonding molecular orbital.

Given the bonding molecular orbital,

$$\psi_{bond}(\mathbf{r}) \equiv c_A \psi_A^{(r)}(\mathbf{r}) + c_B \psi_B^{(l)}(\mathbf{r}) \quad (\text{I.32})$$

we could approximate the “probability of observing an electron at atom A as

$$|c_A|^2 \cdot (\# \text{ of electrons in the orbital}) \quad (\text{I.33})$$

If we carried out this procedure, we could compute molecular charges of A and B , and recover results similar to those in Eq. (I.13). This sort of procedure is referred to as population analysis.

II. Orbital Hybridization and Resonance (.7)

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,

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

which suggests the valence-bond wave function

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

where \mathcal{A} denotes the antisymmetrizer, which permutes all the electrons in the right-hand side of Eq. (II.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:

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

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

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

which we usually abbreviate to simply

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

Returning to Eq. (II.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 μ_s and μ_p are mixing coefficients. In particular, if we “mix” in a fraction, \mathcal{F} , of s character, we have the hybrid orbitals,

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

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. (II.6) are orthonormal.

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

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

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

In Eq. (II.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

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

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

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

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

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

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

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

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

$$HF \leftrightarrow H^+F^- \quad (\text{II.12})$$

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

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

and then the resonance-hybrid wave function will be

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

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

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

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?

III. The Electrostatic Theorem (.8)

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

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

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

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

Recall that the force on nucleus A is defined as

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

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

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

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

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

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

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

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

We use the Hellmann-Feynman theorem,

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

to write,

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

and so

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

B. Show that Eq. (III.9) gives that

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

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

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

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

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. (III.10) and (III.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. (III.10), argue the force on nucleus A due to the electron density at \mathbf{r} , $\rho(\mathbf{r}) d\mathbf{r}$, is just

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

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

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

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

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

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

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

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

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

In order to understand Eq. (III.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. (III.15) becomes

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

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

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

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

F. Explain why this gives the condition

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

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

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

$$\frac{\sqrt{\frac{Z_A}{Z_B}} + 1}{\sqrt{\frac{Z_A}{Z_B}} - 1} > z \quad (\text{III.19})$$

is favorable for binding.

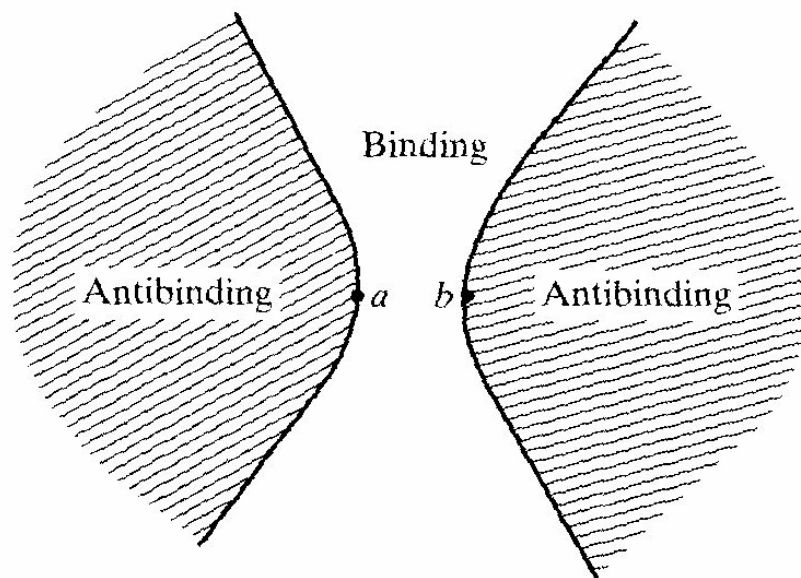


FIGURE 14.5 Cross section of binding and antibinding regions in a homonuclear diatomic molecule. To obtain the three-dimensional regions, rotate the figure about the internuclear axis.

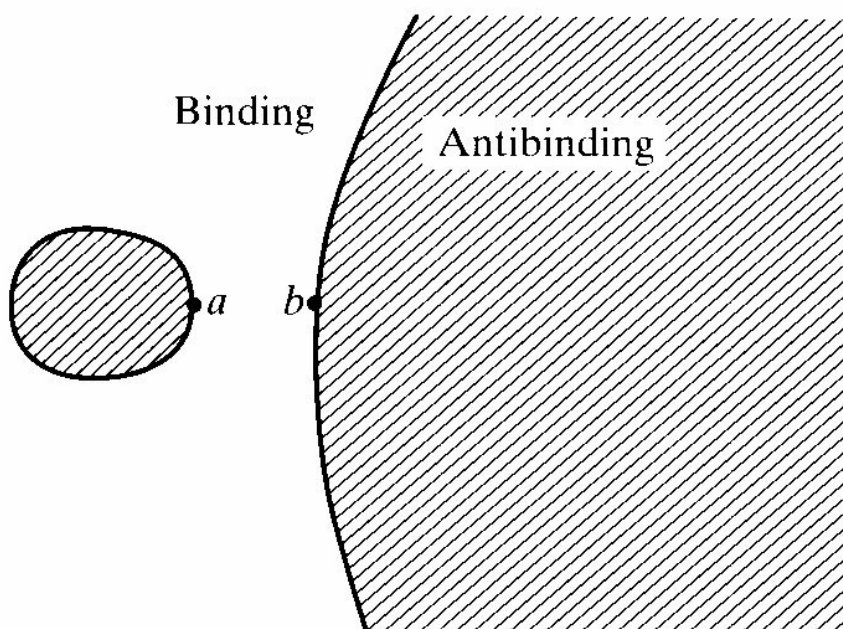


FIGURE 14.6 Binding and antibinding regions for a heteronuclear diatomic molecule with $Z_b > Z_a$.

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

IV. The Extended Koopmans' Theorem (.8)

Given the exact wave function, how can you determine its first ionization potential? One possibility, proposed independently by Morrell, Parr, and Levy and Day, Smith, and Garrod is given by the so-called "Extended Koopmans' Theorem."

The idea is rather simple. Remember how ionization potentials were derived in Hartree Fock? One took a Slater determinant and "eliminated" or "annihilated" a single orbital. Why can't we do the same thing to the exact wave function. That is, take the exact N -electron wave function, $\Psi^{(N)}(z_1, z_2, \dots, z_N)$, and remove an electron from it by taking¹

$$\Psi_k^{EKT}(z_1, \dots, z_{N-1}) \equiv \sqrt{N} \int \phi_k^{EKT}(z_N) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N \quad (IV.1)$$

A. Argue that when $\psi_i(z)$ is i^{th} an occupied orbital in the Slater determinant, $|\psi_1 \dots \psi_N|$, that operating with Eq. (IV.1) gives

$$(-1)^{i+1} \sqrt{N} |\psi_1 \dots \psi_{i-1} \psi_{i+1} \dots \psi_N|. \quad (IV.2)$$

You may wish to start by considering the special case where there are only three occupied orbitals.

Substituting Equation (IV.1) into the Schrödinger equation for the $(N-1)$ -electron system, we have

$$\begin{aligned} \hat{H}^{(N-1)}(r_1, \dots, r_{N-1}) \left[\int \phi_k^{EKT}(z_N) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N \right] \\ = E_k^{(N-1)} \int \phi_k^{EKT}(z_N) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N \end{aligned} \quad (IV.3)$$

Equation (IV.3) will be satisfied if and only if the form of the wave function in Eq. (IV.1) is exactly correct for a given excited state.

Noting that the Hamiltonian for the $(N-1)$ -electron system, $\hat{H}^{(N-1)}$ operates only on the electrons first $N-1$ electronic coordinates, we can bring the Hamiltonian inside the integral, obtaining

$$\begin{aligned} \int \phi_k^{EKT}(z_N) \hat{H}^{(N-1)}(r_1, \dots, r_{N-1}) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N \\ = E_k^{(N-1)} \int \phi_k^{EKT}(z_N) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N \end{aligned} \quad (IV.4)$$

Using the Schrödinger equation for the N -electron system.

$$(E^{(N)} - \hat{H}^{(N)}(r_1, r_2, \dots, r_N)) \Psi_N(z_1, \dots, z_N) = 0, \quad (IV.5)$$

we can write

$$\begin{aligned} \int \phi_k^{EKT}(z_N) (\hat{H}^{(N-1)}(r_1, \dots, r_{N-1}) + E^{(N)} - \hat{H}^{(N)}(r_1, r_2, \dots, r_N)) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N \\ = E_k^{(N-1)} \int \phi_k^{EKT}(z_N) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N. \end{aligned} \quad (IV.6)$$

Using Eq. (IV.6) in problem set 2, we have that

$$\begin{aligned} \int \phi_k^{EKT}(z_N) \left(-\frac{\nabla_N^2}{2} + v(r_N) + \sum_{i=1}^{N-1} \frac{1}{|r_i - r_N|} \right) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N \\ = (E^{(N)} - E_k^{(N-1)}) \int \phi_k^{EKT}(z_N) \Psi^{(N)}(z_1, z_2, \dots, z_N) dz_N. \end{aligned} \quad (IV.7)$$

¹ The factor of \sqrt{N} comes from the fact we should not really assume that it is the N^{th} -electron that is removed.

Equation (IV.7) is the “extended Koopmans’ theorem equation”, and can be used to find exact ionization potentials for the system.

B. The foregoing argument assures us that to every $\phi_k(z_N)$ that solves Eq. (IV.7), there corresponds a state of the cation such that the exact wave function for this state of the cation is given by Eq. (IV.1). It has been proved that there is always such an orbital for the ground state of the cation, and numerical evidence suggests solutions exist for many other states of the cation also. However, for systems with more than two electrons, there will always be some states of the cation that cannot be accessed using the extended Koopmans’ theorem. Why?

C. What is the advantage of using the Extended Koopmans’ theorem as opposed to solving the Schrödinger equation for a molecule and its cation?

Note: some people think that the Feynman-Dyson (or generalized-overlap) amplitudes,

$$f_k(z_N) \equiv \langle \Psi_k^{(N-1)} | \Psi^{(N)} \rangle_{1\dots N-1} \quad (\text{IV.8})$$

and the extended Koopmans’ theorem orbitals, $\{\phi_k^{EKT}(z_N)\}$ are identical. This, however, has yet to be established. Some (maybe most) researchers believe it to be true, but it is a difficult, and open, theoretical question.

V. Integrals between Slater determinants (1.0)

Brillouin’s theorem states that if Φ_0 is a Hartree-Fock determinant (so every orbital in Φ_0 is obtained from solving the Hartree-Fock equations to self consistency), then

$$\langle \Phi_i^a | \hat{H} | \Phi_0 \rangle = 0 \quad (\text{V.1})$$

where Φ_i^a is the Slater determinant obtained by replacing the occupied orbital, $\psi_i(\mathbf{r})$ by the unoccupied orbital, $\psi_a(\mathbf{r})$, in the Slater determinant. This indicates that there is no correction in molecular orbital theory due to “configuration interaction” with single excitations (unless, of course, the Slater determinant is not from the Hartree-Fock solution).

A. Derive Brillouin’s Theorem

Another useful result is that the electron density of a Slater determinant is

$$\begin{aligned} \rho(\mathbf{x}) &\equiv \left\langle |\psi_1 \dots \psi_N| \left| \sum_{i=1}^N \delta(\mathbf{r}_i - \mathbf{x}) \right| |\psi_1 \dots \psi_N| \right\rangle \\ &= \sum_{i=1}^N |\psi_i(\mathbf{x})|^2. \end{aligned} \quad (\text{V.2})$$

B. Derive Eq. (V.2). Use the result to rewrite the Hartree-Fock Energy and Hartree-Fock Equations in a more “intuitive” form.

VI. Basis Sets, Secular Determinants, and the Mathematics of Computational Chemistry (1.2)

We usually solve the Hartree-Fock equations,

$$\hat{f}(\mathbf{r}) \psi_\alpha(\mathbf{r}) = \varepsilon_\alpha \psi_\alpha(\mathbf{r}), \quad (\text{VI.1})$$

by introducing what is called a basis set—a set of functions in terms of which we can expand the molecular orbitals. In terms of this basis set, we have

$$\psi_\alpha(\mathbf{r}) = \sum_{i=1}^M c_{i\alpha} \chi_i(\mathbf{r}) \quad (\text{VI.2})$$

and we then have

$$\hat{f}(\mathbf{r}) \left(\sum_{i=1}^M c_{i\alpha} \chi_i(\mathbf{r}) \right) = \varepsilon_\alpha \left(\sum_{i=1}^M c_{i\alpha} \chi_i(\mathbf{r}) \right) \quad (\text{VI.3})$$

Multiplying both sides by $\chi_j(\mathbf{r})$ and integrating, we obtain

$$\sum_{i=1}^M \langle \chi_j | \hat{f} | \chi_i \rangle c_{i\alpha} = \varepsilon_\alpha \sum_{i=1}^M \langle \chi_j | \chi_i \rangle c_{i\alpha}. \quad (\text{VI.4})$$

If we define the Fock matrix,

$$f_{ij} \equiv \langle \chi_j | \hat{f} | \chi_i \rangle, \quad (\text{VI.5})$$

and the overlap matrix,

$$S_{ij} \equiv \langle \chi_j | \chi_i \rangle, \quad (\text{VI.6})$$

then Eq. (VI.4) becomes what is called a generalized eigenvalue problem, namely

$$\mathbf{f} \mathbf{c}_\alpha = \varepsilon_\alpha \mathbf{S} \mathbf{c}_\alpha \quad (\text{VI.7})$$

where

$$\mathbf{c}_\alpha \equiv \begin{bmatrix} c_{1\alpha} \\ c_{2\alpha} \\ \vdots \\ c_{M\alpha} \end{bmatrix} \quad (\text{VI.8})$$

To solve the generalized eigenvalue problem, we write Eq. (VI.7) as a homogeneous linear equation,

$$(\mathbf{f} - \varepsilon_\alpha \mathbf{S}) \mathbf{c}_\alpha = \mathbf{0} \quad (\text{VI.9})$$

and note that this equation only has nontrivial solutions when the orbital eigenvalue, ε_α , is chosen so that

$$|\mathbf{f} - \varepsilon_\alpha \mathbf{S}| = 0. \quad (\text{VI.10})$$

This is very similar to the “tricks” we used for diagonalizing a Hamiltonian matrix, except in this case the orbitals are not generally orthogonal, and so we cannot assume that \mathbf{S} is the identity matrix.

Often however, we have ignored the presence of \mathbf{S} , and our decision to do so merits some justification. Consider a two-electron diatomic molecule, with orbital l being the 1s orbital for the “left-hand” atom and orbital r being the 1s orbital for the “right-hand” atom. In general, we have

$$\Psi(z_1, z_2) \equiv \frac{(\psi^{(l)}(\mathbf{r}_1) + \psi^{(r)}(\mathbf{r}_1))(\psi^{(l)}(\mathbf{r}_2) + \psi^{(r)}(\mathbf{r}_2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))}{2(1 + S)} \quad (\text{VI.11})$$

where the overlap integral is $S = \langle \psi^{(l)} | \psi^{(r)} \rangle$.

Now, consider what happens when we consider Löwdin's localized orbitals,

$$\begin{aligned}\phi^{(l)}(\mathbf{r}) &\equiv \frac{\left((1+S)^{-1/2} + (1-S)^{-1/2}\right)\psi^{(l)}(\mathbf{r}) + \left((1+S)^{-1/2} - (1-S)^{-1/2}\right)\psi^{(r)}(\mathbf{r})}{2} \\ \phi^{(r)}(\mathbf{r}) &\equiv \frac{\left((1+S)^{-1/2} - (1-S)^{-1/2}\right)\psi^{(l)}(\mathbf{r}) + \left((1+S)^{-1/2} + (1-S)^{-1/2}\right)\psi^{(r)}(\mathbf{r})}{2}\end{aligned}\quad (\text{VI.12})$$

A. Show that $\phi^{(l)}(\mathbf{r})$ and $\phi^{(r)}(\mathbf{r})$ are orthogonal and normalized

B. Show that

$$\Psi^L(z_1, z_2) \equiv \frac{(\phi^{(l)}(\mathbf{r}_1) + \phi^{(r)}(\mathbf{r}_1))(\phi^{(l)}(\mathbf{r}_2) + \phi^{(r)}(\mathbf{r}_2))(\alpha(1)\beta(2) - \beta(1)\alpha(2))}{2} \quad (\text{VI.13})$$

is identical to Eq. (VI.11).

C. For the overlap of the 1s-orbitals between two atoms with atomic number Z , we have

$$S = \left(1 + ZR + \frac{1}{3}Z^2R^2\right)e^{-ZR} \quad (\text{VI.14})$$

For the Hydrogen molecule, $R = 1.4011$. Use Eq. (VI.14) and plot either $\phi^{(l)}(\mathbf{r})$ or $\phi^{(r)}(\mathbf{r})$. Compare to the 1s-orbitals.

$$\begin{aligned}\psi_{1s}^{(l)}(\mathbf{r}) &\equiv \sqrt{\frac{Z^3}{\pi}}e^{-Z(\mathbf{r}-\mathbf{R}_l)} \\ \psi_{1s}^{(r)}(\mathbf{r}) &\equiv \sqrt{\frac{Z^3}{\pi}}e^{-Z(\mathbf{r}-\mathbf{R}_r)}\end{aligned}\quad (\text{VI.15})$$

We conclude that by choosing to interpret the atomic orbitals as localized atomic orbitals, we can replace the “generalized” eigenvalue problem in Eq. (VI.9) with the “conventional” eigenvalue problem,

$$(\mathbf{f} - \varepsilon_\alpha \mathbf{I})\mathbf{c}_\alpha = \mathbf{0}. \quad (\text{VI.16})$$

As an example, we compare the σ -bonding structure in B_2 and the F_2 molecules and, in particular, the problem of sp -mixing. We have

$$\mathbf{f}_{B_2} \equiv \begin{bmatrix} \psi_{2s}^{(l)} & -0.56 & -0.12 & 0 & 0.15 & 0 & 0 & 0 & 0 \\ \psi_{2s}^{(r)} & -0.12 & -0.56 & -0.15 & 0 & 0 & 0 & 0 & 0 \\ \psi_{2p_z}^{(l)} & 0 & -0.15 & -0.31 & 0.1 & 0 & 0 & 0 & 0 \\ \psi_{2p_z}^{(r)} & 0.15 & 0 & 0.1 & -0.31 & 0 & 0 & 0 & 0 \\ \psi_{2p_x}^{(l)} & 0 & 0 & 0 & 0 & -0.31 & -0.05 & 0 & 0 \\ \psi_{2p_x}^{(r)} & 0 & 0 & 0 & 0 & -0.05 & -0.31 & 0 & 0 \\ \psi_{2p_y}^{(l)} & 0 & 0 & 0 & 0 & 0 & 0 & -0.31 & -0.05 \\ \psi_{2p_y}^{(r)} & 0 & 0 & 0 & 0 & 0 & 0 & -0.05 & -0.31 \end{bmatrix} \quad (\text{VI.17})$$

and

$$\mathbf{f}_{F_2} \equiv \begin{matrix} \psi_{2s}^{(l)} \\ \psi_{2s}^{(r)} \\ \psi_{2p_z}^{(l)} \\ \psi_{2p_z}^{(r)} \\ \psi_{2p_x}^{(l)} \\ \psi_{2p_x}^{(r)} \\ \psi_{2p_y}^{(l)} \\ \psi_{2p_y}^{(r)} \end{matrix} \begin{vmatrix} -1.47 & -.28 & 0 & .26 & 0 & 0 & 0 & 0 \\ -.28 & -1.47 & -.26 & 0 & 0 & 0 & 0 & 0 \\ 0 & -.26 & -.66 & .2 & 0 & 0 & 0 & 0 \\ .26 & 0 & .2 & -.66 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -.66 & -.05 & 0 & 0 \\ 0 & 0 & 0 & 0 & -.05 & -.66 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -.66 & -.05 \\ 0 & 0 & 0 & 0 & 0 & 0 & -.05 & -.66 \end{vmatrix} \quad (\text{VI.18})$$

A general principle is that when you can write a matrix in block diagonal form, then the eigenvalues and eigenvectors for each “block” can be found separately. For example, because there are no non-zero matrix elements between the σ -bonding orbitals $\psi_{2s}(\mathbf{r})$ and $\psi_{2p_z}(\mathbf{r})$ and the π -bonding orbitals, $\psi_{2p_x}(\mathbf{r})$ and $\psi_{2p_y}(\mathbf{r})$, these orbitals do not mix. (This is clearly a consequence of orbital symmetry.) Similarly, the π_x and π_y orbitals do not mix, and since the 2×2 matrices for these two problems are the same, the π_x and π_y orbitals are degenerate. Consequently, we can find the orbital energies for B_2 by diagonalizing each of the following matrices:

- for the σ, σ^* orbitals

$$\mathbf{f}_{B_2}^{\sigma} \equiv \begin{matrix} \psi_{2s}^{(l)} \\ \psi_{2s}^{(r)} \\ \psi_{2p_z}^{(l)} \\ \psi_{2p_z}^{(r)} \end{matrix} \begin{vmatrix} -.56 & -.12 & 0 & .15 \\ -.12 & -.56 & -.15 & 0 \\ 0 & -.15 & -.31 & .1 \\ .15 & 0 & .1 & -.31 \end{vmatrix} \quad (\text{VI.19})$$

- for the π -orbitals,

$$\mathbf{f}_{B_2}^{\pi} \equiv \begin{pmatrix} \psi_{2p_x}^{(l)}, \psi_{2p_y}^{(l)} \\ \psi_{2p_x}^{(r)}, \psi_{2p_y}^{(r)} \end{pmatrix} \begin{vmatrix} -.31 & -.05 \\ -.05 & -.31 \end{vmatrix} \quad (\text{VI.20})$$

D. Compute the orbital energies for the π and σ orbitals from Eq. (VI.19) and (VI.20). You will find it helpful to use a computer program to compute the eigenvalues in Eq. (VI.19). (Mathcad, Mathematica, or Maple would suffice.)

E. Compute the orbital energies for F_2 using Eq. (VI.18). Notice the change in orbital ordering.

It is often helpful to have a simple way to evaluate the eigenvalues of a 4×4 (or larger) matrix. Perturbation theory is particularly effective for this purpose. To do this, we can write

$$\begin{aligned}
\mathbf{f}_{B_2}^\sigma &\equiv \mathbf{f}_{B_2}^{(0)} + \mathbf{f}'_{B_2} \\
&= \begin{bmatrix} -.56 & -.12 & 0 & 0 \\ -.12 & -.56 & 0 & 0 \\ 0 & 0 & -.31 & .1 \\ 0 & 0 & .1 & -.31 \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 & .15 \\ 0 & 0 & -.15 & 0 \\ 0 & -.15 & 0 & 0 \\ .15 & 0 & 0 & 0 \end{bmatrix}
\end{aligned} \tag{VI.21}$$

F. Find the eigenvalues and eigenvectors of $\mathbf{f}_{B_2}^{(0)}$.

Denoting the eigenvectors of $\mathbf{f}_{B_2}^{(0)}$ as $\{\mathbf{c}_\alpha\}_{\alpha=1}^4$ and the eigenvalues as $\{\varepsilon_\alpha\}_{\alpha=1}^4$, we find that the improved eigenvalues are

$$\mathbf{c}_\alpha^{pert.} \approx \mathbf{c}_\alpha + \sum_{\substack{i=1 \\ i \neq \alpha}}^4 \frac{(\mathbf{c}_i \cdot \mathbf{f}'_{B_2} \cdot \mathbf{c}_\alpha)}{\varepsilon_\alpha - \varepsilon_i} \mathbf{c}_i \tag{VI.22}$$

The corrected eigenvalues are then

$$\varepsilon_\alpha^{pert.} \approx \varepsilon_\alpha + \sum_{\substack{i=1 \\ i \neq \alpha}}^4 \frac{(\mathbf{c}_\alpha \cdot \mathbf{f}'_{B_2} \cdot \mathbf{c}_i)(\mathbf{c}_i \cdot \mathbf{f}'_{B_2} \cdot \mathbf{c}_\alpha)}{\varepsilon_\alpha - \varepsilon_i} \tag{VI.23}$$

G. Calculate the correction to the σ_{2p_z} orbital energy using Eq. (VI.23). Why is the only “non-vanishing” correction due to the σ_{2s} orbital? How does one interpret this shift in orbital energies?

VII. Exchange Integrals are Positive (.9)

We have often stated that the “exchange integral” is positive. (For example, we said that the difference in energy between the singlet and triplet states of an atom or molecule would be equal to $2K$,

$$2K = E(^1\Lambda) - E(^3\Lambda), \tag{VII.1}$$

where

$$\begin{aligned}
K &\equiv \iint \frac{(\psi_1^*(\mathbf{r}_1)\psi_2(\mathbf{r}_1))(\psi_1^*(\mathbf{r}_2)\psi_2(\mathbf{r}_2))^*}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\
&> 0
\end{aligned} \tag{VII.2}$$

Since $K > 0$, the energy of the singlet state was greater than that of the triplet state. This is a special case of the theorem that

For any well-behaved function, $f(\mathbf{r}_1)$,

$$\iint \frac{f(\mathbf{r}_1)f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \geq 0. \tag{VII.3}$$

If $f(\mathbf{r})$ is continuous and has continuous first derivatives then this is sufficient (but not necessary) for the theorem. Thus, most functions we’ll be interested in will be “well-behaved.”

Because we can always choose the wave functions in time-independent quantum mechanics to be real, we have opted to consider only the “real” case of the theorem. (The complex case—where $f(\mathbf{r}_2)$ is replaced by $f^*(\mathbf{r}_2)$ —is similar though.)

To prove Eq. (VII.3), we first rewrite the equation as

$$\iint \frac{f(\mathbf{r}_1)f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \int f(\mathbf{r}_1) \left[\int \frac{f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \right] d\mathbf{r}_1 \quad (\text{VII.4})$$

Now, we recognize that the innermost integral is just the electrostatic potential, $\Phi(\mathbf{r}_1)$, due to a charge distribution, $f(\mathbf{r}_2)$,

$$\Phi(\mathbf{r}_1) = \int \frac{f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 \quad (\text{VII.5})$$

Now, recall Poisson’s equation; Poisson’s equation says that the electrostatic potential due to a charge distribution satisfies the equation

$$\nabla^2 \Phi(\mathbf{r}_1) = -4\pi f(\mathbf{r}_1) \quad (\text{VII.6})$$

This lets us write Eq. (VII.4) as

$$\iint \frac{f(\mathbf{r}_1)f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{-1}{4\pi} \int (\nabla^2 \Phi(\mathbf{r}_1)) \Phi(\mathbf{r}_1) d\mathbf{r}_1 \quad (\text{VII.7})$$

We simplify this result using Green’s first identity:

$$\iiint \phi(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) + \nabla \phi(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}) d\mathbf{r} \equiv \oint \phi(\mathbf{r}) \nabla \psi(\mathbf{r}) \cdot \mathbf{n} da \quad (\text{VII.8})$$

A. Show that

$$\iint \frac{f(\mathbf{r}_1)f(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{4\pi} \iiint \nabla \Phi(\mathbf{r}) \cdot \nabla \Phi(\mathbf{r}) d\mathbf{r} - \frac{1}{4\pi} \left(\oint \Phi(\mathbf{r}) \nabla \Phi(\mathbf{r}) \cdot \mathbf{n} da \right) \quad (\text{VII.9})$$

The integral on the right-hand-side is over the “surface” of the volume of integration. If the volume of integration is all of space, then the surface integral can be evaluated on a sphere of infinite radius, which we can evaluate using

$$\begin{aligned} \oint_{R \rightarrow \infty} \phi(\mathbf{r}) \nabla \psi(\mathbf{r}) \cdot \mathbf{n} da &= \int_0^\pi \int_0^{2\pi} \lim_{r \rightarrow \infty} [(\phi(\mathbf{r}) \nabla \psi(\mathbf{r}) \cdot \hat{\mathbf{r}}) r^2] \sin \theta d\theta d\phi \\ &= \int_0^\pi \int_0^{2\pi} \lim_{r \rightarrow \infty} \left[\phi(\mathbf{r}) \frac{\partial \psi(\mathbf{r})}{\partial r} r^2 \right] \sin \theta d\theta d\phi \end{aligned} \quad (\text{VII.10})$$

We can always write the electrostatic potential in terms of what is termed a multipole expansion. That is, the electrostatic potential can be expressed as a sum of the electrostatic potential due to the charge of a distribution, plus that from the dipole moment of the distribution, plus that of the quadrupole moment of the distribution. . . . Since we are integrating over a sphere, it is most convenient to express the multipole moments using the spherical harmonics.

B. Show that

$$\begin{aligned} \Phi(\mathbf{r}) &\equiv \int \frac{f(\mathbf{x})}{|\mathbf{r} - \mathbf{x}|} d\mathbf{x} \\ &= \sum_{l=0}^{\infty} \sum_{m=-l}^{m=l} \frac{4\pi}{2l+1} \frac{Y_l^m(\theta, \phi)}{r^{l+1}} \int f(\mathbf{x}) Y_l^m(\theta_x, \phi_x) d\mathbf{x} \end{aligned} \quad (\text{VII.11})$$

The numbers

$$\int f(\mathbf{x}) Y_l^m(\theta_x, \phi_x) d\mathbf{x} \quad (\text{VII.12})$$

are called the multipole moments. In the convention used here,

$$Y_0^0(\theta, \phi) = \frac{1}{\sqrt{4\pi}}. \quad (\text{VII.13})$$

C. Show that the first multipole moment is just $\frac{1}{\sqrt{4\pi}}$ times the total charge in the distribution,

$$q = \int f(\mathbf{x}) d\mathbf{x}. \quad (\text{VII.14})$$

For exchange integrals, the total charge is zero. For Coulomb integrals, the total charge is negative.

D. Use Eq. (VII.11) to evaluate Eq. (VII.9).

The equation you derive in part D completes the proof of the theorem. Specifically, we have that

$$\frac{1}{4\pi} \iiint \nabla \Phi(\mathbf{r}) \cdot \nabla \Phi(\mathbf{r}) d\mathbf{r} = \frac{1}{4\pi} \iiint |\nabla \Phi(\mathbf{r})|^2 d\mathbf{r}, \quad (\text{VII.15})$$

which is positive (unless $\nabla \Phi(\mathbf{r}) = 0$ over all space) since the integral of a positive function is always positive.

VIII. Electronegativity, Hardness, and Electronegativity Equalization (1.6)

The energy of an atom or molecule can be written in the form

$$E_0(N_0) \equiv \left\langle \Psi_0(N_0) \left| \sum_{i=1}^{N_0} \left[-\frac{\nabla_i^2}{2} + v_0(\mathbf{r}_i) \right] + \sum_{j=i+1}^{N_0} \sum_{i=1}^{N_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \Psi_0(N_0) \right\rangle$$

Here, we have opted to explicitly denote the dependence of the energy, wave function, and Hamiltonian on the number of electrons, N_0 . We can define

$$h(N_0) \equiv \left\langle \Psi_0(N_0) \left| -\frac{\nabla_1^2}{2} + v_0(\mathbf{r}_1) \right| \Psi_0(N_0) \right\rangle$$

$$v_{ee}(N_0) \equiv \left\langle \Psi_0(N_0) \left| \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \right| \Psi_0(N_0) \right\rangle$$

A. Show that the energy can be written as

$$E_0(N_0) = h(N_0) \cdot N_0 + v_{ee}(N_0) \cdot \frac{N_0(N_0-1)}{2}.$$

B. In analogy to thermodynamics, the rate of change of the energy with respect to the number of electrons is called the electronic chemical potential, $\mu(N_0)$. Show that

$$\mu(N_0) \equiv \left. \frac{\partial E_0(N)}{\partial N} \right|_{N_0}$$

$$= h(N_0) + \frac{N_0}{2} \left(2 \cdot \left. \frac{\partial h(N)}{\partial N} \right|_{N_0} + \left(\frac{2N_0-1}{N_0} \right) v_{ee}(N_0) + (N_0-1) \left. \frac{\partial v_{ee}(N)}{\partial N} \right|_{N_0} \right) \quad (\text{VIII.1})$$

It is often an excellent approximation to assume that $h(N_0)$ and $v_{ee}(N_0)$ do not depend very strongly on the number of electrons. Thus,

$$\left. \frac{\partial h(N)}{\partial N} \right|_{N=N_0} \approx 0$$

$$\left. \frac{\partial v_{ee}(N)}{\partial N} \right|_{N=N_0} \approx 0 \quad (\text{VIII.2})$$

- C. The second derivative of the energy is related to the hardness of a molecular species, $\eta(N_0)$. Assuming that Eqs. (VIII.2) are exact, show that

$$\eta(N_0) \equiv \left. \frac{\partial^2 E_0(N)}{\partial N^2} \right|_{N_0}$$

$$= v_{ee}(N_0) \quad (\text{VIII.3})$$

- D. Based on Eqs. (VIII.2) and the definition of the electronic chemical potential and the chemical hardness, derive the following expression for the energy as a function of the number of electrons,

$$E(N) = E(N_0) + (N - N_0)\mu(N_0) + \frac{1}{2}(N - N_0)^2 \eta(N_0) \quad (\text{VIII.4})$$

- E. In analogy to thermodynamics, the rate of change of the energy with respect to the number of electrons is called the electronic chemical potential, $\mu(N_0)$. Show that

Suppose we know, from experiment or calculation, the ionization potential,

$$I = E(N_0 - 1) - E(N_0),$$

and electron affinity,

$$A = E(N_0) - E(N_0 + 1)$$

of the system. We can use this information, plus Eqs. (VIII.1), (VIII.2), (VIII.3), and (VIII.4) to derive

$$v_{ee}(N_0) = \eta(N_0) = I - A \quad (\text{VIII.5})$$

$$h(N_0) = -N_0(I - A) - A \quad (\text{VIII.6})$$

$$\mu(N_0) = -\frac{I + A}{2} \quad (\text{VIII.7})$$

- F. Derive Eq. (VIII.5). This is called Pariser's approximation; it is of great historical significance. Because evaluating electron-electron repulsion integrals is difficult, in the early days of quantum mechanics, people did not compute the electron-electron repulsion energy, but instead approximated it using experimental data.

- G. Derive Eq. (VIII.6).

- H. Derive Eq. (VIII.7). Since $\frac{I+A}{2}$ is the Mulliken electronegativity of a molecule, we infer that the electronic chemical potential is the negative of the electronegativity.

Back in the 1950's R. T. Sanderson established the "electronegativity equalization principle," which states that when one performs an acid-base reaction, the base transfers electrons to the acid until the

electronegativity of the two fragments equalize. It is not difficult to derive this result. Write the energy of the acid as

$$E_A(N_A) = E(N_A^0) + (N_A - N_A^0)\mu_A(N_A^0) + \frac{1}{2}(N_A - N_A^0)^2\eta_A(N_A^0) \quad (\text{VIII.8})$$

where $E_A(N_A)$ is the energy of the acid after charge transfer, N_A is the number of electrons on the acid after charge transfer, N_A^0 is the number of electrons in the acid before charge transfer, and $E_A(N_A^0)$, $\mu_A(N_A^0)$, and $\eta_A(N_A^0)$ are the energy, chemical potential, and chemical hardness of the acid prior to charge transfer. Similarly, we write the energy of the base as

$$E_B(N_B) = E_B(N_B^0) + (N_B - N_B^0)\mu_B(N_B^0) + \frac{1}{2}(N_B - N_B^0)^2\eta_B(N_B^0) \quad (\text{VIII.9})$$

The total number of electrons does not change during this reaction, so

$$N_A^0 + N_B^0 = N_A + N_B \quad (\text{VIII.10})$$

and so the number of electrons transferred from the acid to the base must be given by.

$$\Delta N = N_A - N_A^0 = N_B^0 - N_B \quad (\text{VIII.11})$$

Rewriting Eqs. (VIII.8) and (VIII.9) in obvious shorthand, we have that

$$\begin{aligned} E_A(N_A^0 + \Delta N) &= E_A^0 + \Delta N\mu_A + \frac{(\Delta N)^2}{2}\eta_A \\ E_B(N_B^0 - \Delta N) &= E_B^0 - \Delta N\mu_B + \frac{(\Delta N)^2}{2}\eta_B \end{aligned} \quad (\text{VIII.12})$$

The energy of the product acid-base reaction,



where ΔN electrons are transferred from the acid to the base is then (approximately)

$$E_{AB}(\Delta N) = E_A(N_A^0 + \Delta N) + E_B(N_B^0 - \Delta N) \quad (\text{VIII.14})$$

I. Explain why finding the “ground state energy” of the product necessarily implies that the chemical potential of the acid and the base are equal.

J. Show that the optimum extent of charge transfer is given by

$$\Delta N = \frac{\mu_B - \mu_A}{\eta_A + \eta_B} \quad (\text{VIII.15})$$

The energy of the acid-base reaction, Eq. (VIII.13), can be written as

$$\Delta E_{AB}^{rxn}(\Delta N) = E_A(\Delta N) + E_B(\Delta N) - E_A - E_B \quad (\text{VIII.16})$$

K. Show that the acid-base reaction is always exothermic, with (approximate) reaction energy

$$\Delta E_{AB}^{rxn} = -\frac{(\mu_A - \mu_B)^2}{2(\eta_A + \eta_B)} \quad (\text{VIII.17})$$

L. Show that the chemical potential of the acid *and* the base in the product is given by the expression:

$$\frac{\mu_A + \mu_B}{2} \quad (\text{VIII.18})$$

(Hint: Use Eqs. (VIII.15), (VIII.8), and (VIII.9), along with the definition of the chemical potential.)

M. Using the ionization potentials and electron affinities of the alkali metals and the halides, calculate the Mulliken electronegativity and hardness of these systems. (See the following table.) Estimate the charge on the halide in the associated species.

N. Repeat the analysis in part M but this time consider the alkali hydrides and the hydrogen halides.

Atom	Ionization Potential (eV)	Electron Affinity (eV)	Mulliken Electronegativity (eV)	Chemical Hardness (eV)
H	13.598	.754		
Li	5.392	.618		
Na	5.139	.548		
K	4.341	.501		
Rb	4.117	.486		
Cs	3.894	.472		
F	17.422	3.401		
Cl	12.967	3.613		
Br	11.814	3.364		
I	10.451	3.059		

IX. The Hard-Soft Acid-Base Principle (.8)

You will find it helpful to do problem VIII before attempting this problem.

You might question why, in problem VIII, we refer to

$$\eta(N_0) \equiv \left. \frac{\partial^2 E_0(N)}{\partial N^2} \right|_{N_0} = I - A \quad (\text{IX.1})$$

as the chemical hardness. The definition was first proposed because of a strong correlation between $I - A$ and the empirically observed hardnesses of atoms. This should be clear from part “M” of problem VIII. But does this definition of the hardness correspond to the Hard-Soft Acid-Base (HSAB) principle? The HSAB principle is, after all, the *raison d’être* for the concept of the hardness and indubitably the most important application of the concept.

In abstract terms, the HSAB principle says that: ***all other things being equal, hard acids prefer to bind to hard bases and soft acids prefer to bond to soft bases.*** In abstract terms, we write that the equilibrium in the “HSAB exchange reaction”



lies to the right. Here, A_h denotes the hard acid, B_h denotes the hard base, A_s denotes the soft acid, and B_s denotes the soft base. In the gas phase or in cases where the entropy and enthalpy of solvation are negligible, the fact that the equilibrium in Eq. (IX.2) lies to the right is associated with the fact that the reaction is exothermic, $\Delta U^{HSAB} < 0$.

A. Show that the internal energy change in reaction (IX.2) can be written as

$$\Delta U^{HSAB} = \frac{(\mu_{A_s} - \mu_{B_h})^2}{2(\eta_{A_s} + \eta_{B_h})} + \frac{(\mu_{A_h} - \mu_{B_s})^2}{2(\eta_{A_h} + \eta_{B_s})} - \frac{(\mu_{A_s} - \mu_{B_s})^2}{2(\eta_{A_s} + \eta_{B_s})} - \frac{(\mu_{A_h} - \mu_{B_h})^2}{2(\eta_{A_h} + \eta_{B_h})} < 0 \quad (\text{IX.3})$$

(Hint: you will need to at least read (and preferably do) problem VIII in order to show this.)

Exceptions to the HSAB rule are common when the “all other things being equal” assumption is not accurate. In particular, the HSAB rule often fails when the strength (that is, the electronegativity) of the acids or bases involved in the reactions differ. Consequently, we require that the chemical potential of the hard and soft acids are the same. In addition, we require that the chemical potentials of the hard and soft bases are the same. Finally, since electrons will move from the bases to the acids, we require that the chemical potential of the base is greater than the chemical potential of the acid. We summarize these constraints by

$$\mu_A \equiv \mu_{A_h} = \mu_{A_s} < \mu_{B_h} = \mu_{B_s} \equiv \mu_B \quad (\text{IX.4})$$

Now, let us suppose that the “hard” acid and “hard” base have hardnesses ξ times that of the “soft” acid and the “soft” base and that, moreover, the hard species both have the same hardness, while the soft species also both have the same hardness. That is, we assume that

$$\eta \equiv \eta_{A_s} = \eta_{B_s} \quad (\text{IX.5})$$

$$\eta_{A_h} = \eta_{B_h} = \xi\eta \quad (\text{IX.6})$$

B. Using the assumptions in Eqs. (IX.4)-(IX.6), show that

$$\Delta U^{HSAB} = -\frac{(\mu_A - \mu_B)^2 (\xi - 1)^2}{4\eta\xi(\xi + 1)} \quad (\text{IX.7})$$

C. Why is ΔU^{HSAB} less than zero?

X. “Delta Function” Atoms and Molecules (1.5)

Back in 1956, Arthur Frost proposed a “delta function model” for the one-electron atom and the one-electron molecule. In order to consider this molecule, we will need to understand the properties of the delta function. The key properties are as follows:

(a) The Dirac delta function is zero almost everywhere.

$$\delta(x - a) = \begin{cases} \infty & x = a \\ 0 & x \neq a \end{cases} \quad (\text{X.1})$$

(b) The Dirac delta function is normalized. So

$$\int_{-\infty}^{\infty} \delta(x - a) dx = 1 \quad (\text{X.2})$$

(c) The “sifting” property of the Dirac delta function,

$$\int_{-\infty}^{\infty} f(x) \delta(x - a) dx = f(a) \quad (\text{X.3})$$

Properties (a) and (b) can actually be derived from the sifting property.

A. Using properties (a) and (b), argue that

$$\int_l^u \delta(x - a) dx = \begin{cases} 0 & l < u < 0 \\ 1 & l < 0 < u \\ 0 & 0 < l < u \end{cases} \quad (\text{X.4})$$

It is also useful to define the so-called Heaviside function,

$$\Theta(x - a) = \begin{cases} 0 & x < a \\ 1 & x \geq a \end{cases} \quad (\text{X.5})$$

B. Show that the derivative of the Heaviside function is the Dirac delta function,

$$\frac{d\Theta(x-a)}{dx} = \delta(x-a). \quad (\text{X.6})$$

In atomic units, the “delta function atom” has the Hamiltonian

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} - g\delta(x) \quad (\text{X.7})$$

Just as we did for the Hydrogen atom, we use the asymptotic form of the wave function to make a guess for the wave function. Thus, we have that

$$\psi(x) = e^{-\sqrt{2E}|x|} \quad (\text{X.8})$$

where $|x|$ is, of course, just the distance from the origin. Using the definition of the absolute value, we can rewrite Eq. (X.8) in the useful form

$$\psi(x) = \begin{cases} e^{x\sqrt{2E}} & x < 0 \\ e^{-x\sqrt{2E}} & x > 0. \end{cases} \quad (\text{X.9})$$

C. By substituting $\psi(x)$ into the Hamiltonian, show that

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} - g\delta(x)\right) e^{-\sqrt{2E}|x|} = E e^{-\sqrt{2E}|x|} \quad (\text{X.10})$$

only if

$$E = -\frac{g^2}{2}. \quad (\text{X.11})$$

$$\psi(x) \propto e^{-g|x|}. \quad (\text{X.12})$$

Next, let's examine the “delta function” one-electron molecule. The Hamiltonian will be

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} - g\delta\left(x - \frac{R}{2}\right) - g\delta\left(x + \frac{R}{2}\right) \quad (\text{X.13})$$

where the “bond length” (the distance between the delta functions) is R . We can approximate the wave functions for the one-electron delta-function molecule as a linear combination of the wave functions for the delta function atom, so $\psi_{mol}(x) = c_1 e^{-g|x-\frac{R}{2}|} + c_2 e^{-g|x+\frac{R}{2}|}$. In order to determine the eigenvalues, one solves the secular equation

$$\begin{bmatrix} \left\langle e^{-g|x+\frac{R}{2}} \right| \hat{H} \left| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x+\frac{R}{2}} \right| \hat{H} \left| e^{-g|x-\frac{R}{2}} \right\rangle \\ \left\langle e^{-g|x-\frac{R}{2}} \right| \hat{H} \left| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x-\frac{R}{2}} \right| \hat{H} \left| e^{-g|x-\frac{R}{2}} \right\rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} \left\langle e^{-g|x+\frac{R}{2}} \right| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x+\frac{R}{2}} \right| e^{-g|x-\frac{R}{2}} \right\rangle \\ \left\langle e^{-g|x-\frac{R}{2}} \right| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x-\frac{R}{2}} \right| e^{-g|x-\frac{R}{2}} \right\rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \quad (\text{X.14})$$

$$\begin{bmatrix} \left\langle e^{-g|x+\frac{R}{2}} \right| \hat{H} \left| e^{-g|x+\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x+\frac{R}{2}} \right| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x+\frac{R}{2}} \right| \hat{H} \left| e^{-g|x-\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x+\frac{R}{2}} \right| e^{-g|x-\frac{R}{2}} \right\rangle \\ \left\langle e^{-g|x-\frac{R}{2}} \right| \hat{H} \left| e^{-g|x+\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x-\frac{R}{2}} \right| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x-\frac{R}{2}} \right| \hat{H} \left| e^{-g|x-\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x-\frac{R}{2}} \right| e^{-g|x-\frac{R}{2}} \right\rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

The eigenvalues are determined by solving the determinant

$$\begin{vmatrix} \left\langle e^{-g|x+\frac{R}{2}} \right| \hat{H} \left| e^{-g|x+\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x+\frac{R}{2}} \right| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x+\frac{R}{2}} \right| \hat{H} \left| e^{-g|x-\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x+\frac{R}{2}} \right| e^{-g|x-\frac{R}{2}} \right\rangle \\ \left\langle e^{-g|x-\frac{R}{2}} \right| \hat{H} \left| e^{-g|x+\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x-\frac{R}{2}} \right| e^{-g|x+\frac{R}{2}} \right\rangle & \left\langle e^{-g|x-\frac{R}{2}} \right| \hat{H} \left| e^{-g|x-\frac{R}{2}} \right\rangle - E \left\langle e^{-g|x-\frac{R}{2}} \right| e^{-g|x-\frac{R}{2}} \right\rangle \end{vmatrix} = 0 \quad (\text{X.15})$$

D. Show that the eigenvalues are given by

$$E = -\frac{g^2}{2} (1 \pm e^{-gR})^2 \quad (\text{X.16})$$

Recall that for the H_2^+ molecule, we dramatically improved our description by using an effective nuclear charge. With an “effective charge,” for the delta-function molecule the approximate molecular orbital wave function becomes

$$\psi_{mol}(x) = c_1 e^{-\gamma|x-\frac{R}{2}|} + c_2 e^{-\gamma|x+\frac{R}{2}|} \quad (\text{X.17})$$

E. Show that, if one uses the “effective charge,” then the energy eigenvalues are given by

$$E = -\frac{g^2}{2} (1 \pm e^{-\gamma R})^2 \quad (\text{X.18})$$

Now, let's consider the “heteronuclear” diatomic delta function, with

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} - g_a \delta(x - \frac{R}{2}) - g_b \delta(x + \frac{R}{2}) \quad (\text{X.19})$$

but we still use the “old” homonuclear molecular orbital (albeit with an effective nuclear charge)

$$\psi_{mol}(x) = c_1 e^{-\gamma|x-\frac{R}{2}|} + c_2 e^{-\gamma|x+\frac{R}{2}|} \quad (\text{X.20})$$

F. Show that the energy is given by

$$E = -\frac{1}{2} \left(\frac{(g_a + g_b)}{2} \pm \frac{1}{2} \sqrt{(g_a - g_b)^2 + 4g_a g_b e^{-2\gamma R}} \right)^2 \quad (\text{X.21})$$

G. Show that Eq. (X.21) gives the correct result in the “united-atom” ($R = 0$) and separated-atom ($R \rightarrow \infty$) limits.