4. Molecules

We have talked about atoms, but chemistry is "all about molecules" (with apologies to the polymer chemists and materials' scientists). To introduce the "key approach" to molecules, let's remember how we learned about atoms. We started with a "simple" system that we could discuss in great detail and with great accuracy—the one-electron atom. Once we had solved the Schrödinger equation for the hydrogen-like atom, then we moved on to other, more complicated atoms using the aufbau principle: we just "filled up" the orbitals from the one-electron atom, arguing that the 2s orbital in say, Argon, will look "qualitatively like a 2s orbital in the hydrogen atom, but with an effective nuclear charge." Then we could say a lot more about various states of the system, degeneracies, etc..

Throughout this chapter we will work in the Born-Oppenheimer approximation and, in addition, we shall never have reason to consider the Schrödinger equation for nuclear motion. For this reason, we will consider the electronic Hamiltonian as omitting the nuclear-nuclear repulsion term (V_{nn}), though we will add this term back in when we plot potential energy surfaces.

I. The One-Electron Diatomic Molecule—Exact Solution

Much of our understanding of molecular systems is inferred from results for the one-electron molecule, which has the Hamiltonian

$$\hat{H}_{\substack{1\,el. \\ molecule}} \equiv \left(-\frac{\nabla^2}{2} - \frac{Z_l}{|\boldsymbol{r}-\boldsymbol{R}_l|} - \frac{Z_r}{|\boldsymbol{r}-\boldsymbol{R}_r|} \right) \tag{4.1}$$

In Eq. (4.1), Z_l is the nuclear charge on the "left" nucleus and Z_r is the nuclear charge on the "right" nucleus. We can solve the Schrödinger equation for the one-electron diatomic molecule exactly for many different choices for Z_l and Z_r. The most important case, by far, is the case one-electron homonuclear diatomic ($Z_l = Z_r = Z$), which can be solved for any atomic number, Z. Of the one-electron diatomic molecules, the most important is easily the hydrogen molecule ion, H_2^+, wherein the atomic number is (obviously) one.

I am going to sketch how we solve the Schrödinger equation for the one-electron diatomic molecule, but, because the solution is *much* harder than the solution to the hydrogen atom, I'm not going to solve it. We start by writing the Schrödinger equation

for a molecule where the z direction is chosen as the internuclear axis, the bond midpoint is fixed at the origin, and the bond length is R. So the "left" nucleus is located at $x = y = 0$ and $z = -\frac{R}{2}$ and the "right" nucleus is located at $x = y = 0$ and $z = \frac{R}{2}$

$$\left[-\frac{\nabla^2}{2} - \frac{Z_l}{\sqrt{x^2 + y^2 + \left(z + \frac{R}{2}\right)^2}} - \frac{Z_r}{\sqrt{x^2 + y^2 + \left(z - \frac{R}{2}\right)^2}} \right] \Psi_k(x,y,z) = E_k \Psi_k(x,y,z) \qquad (4.2)$$

Recall how we solved the hydrogen atom. We found a "natural coordinate system" (spherical coordinates, because the potential had spherical symmetry) and then we solved the equation by using separation of variables in this system. Examining the figure, we see that the molecular Hamiltonian is invariant to rotation about the z-axis—we label the angle about this axis as ϕ. Next, we note that given an electron at the point $\boldsymbol{r}$, and given its value of ϕ, we can determine its position by specifying its distance from the left atom and the right atom, which are given by

$$\begin{aligned} r_l &\equiv \sqrt{x^2 + y^2 + \left(z + \frac{R}{2}\right)^2} \\ r_r &\equiv \sqrt{x^2 + y^2 + \left(z - \frac{R}{2}\right)^2} \end{aligned} \qquad (4.3)$$
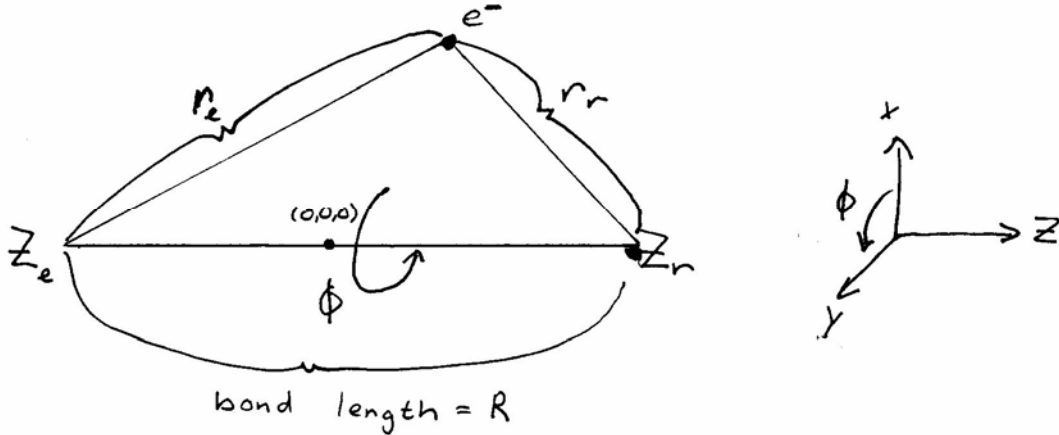
respectively.

Figure 4.1: Geometry of the 1-electron diatomic molecule.

The coordinates (r_l, r_r, ϕ) are less than optimal for describing the diatomic molecule because, unlike the usual coordinate systems $((x,y,z),(r,\theta,\phi),...)$, the "directions" r_l and r_r are not orthogonal: the angle between curves of constant r_l and those with constant r_r is not 90 degrees. We opt for the more symmetrical coordinates

$$\begin{aligned} \xi &\equiv \frac{r_l + r_r}{R} \\ \eta &\equiv \frac{r_l - r_r}{R} \end{aligned} \qquad (4.4)$$

This coordinate system, (ξ, η, ϕ), is called prolate spheroidal coordinates;[1] spheroidal coordinates capture the ellipsoidal symmetry of the one-electron homonuclear diatomic molecule.
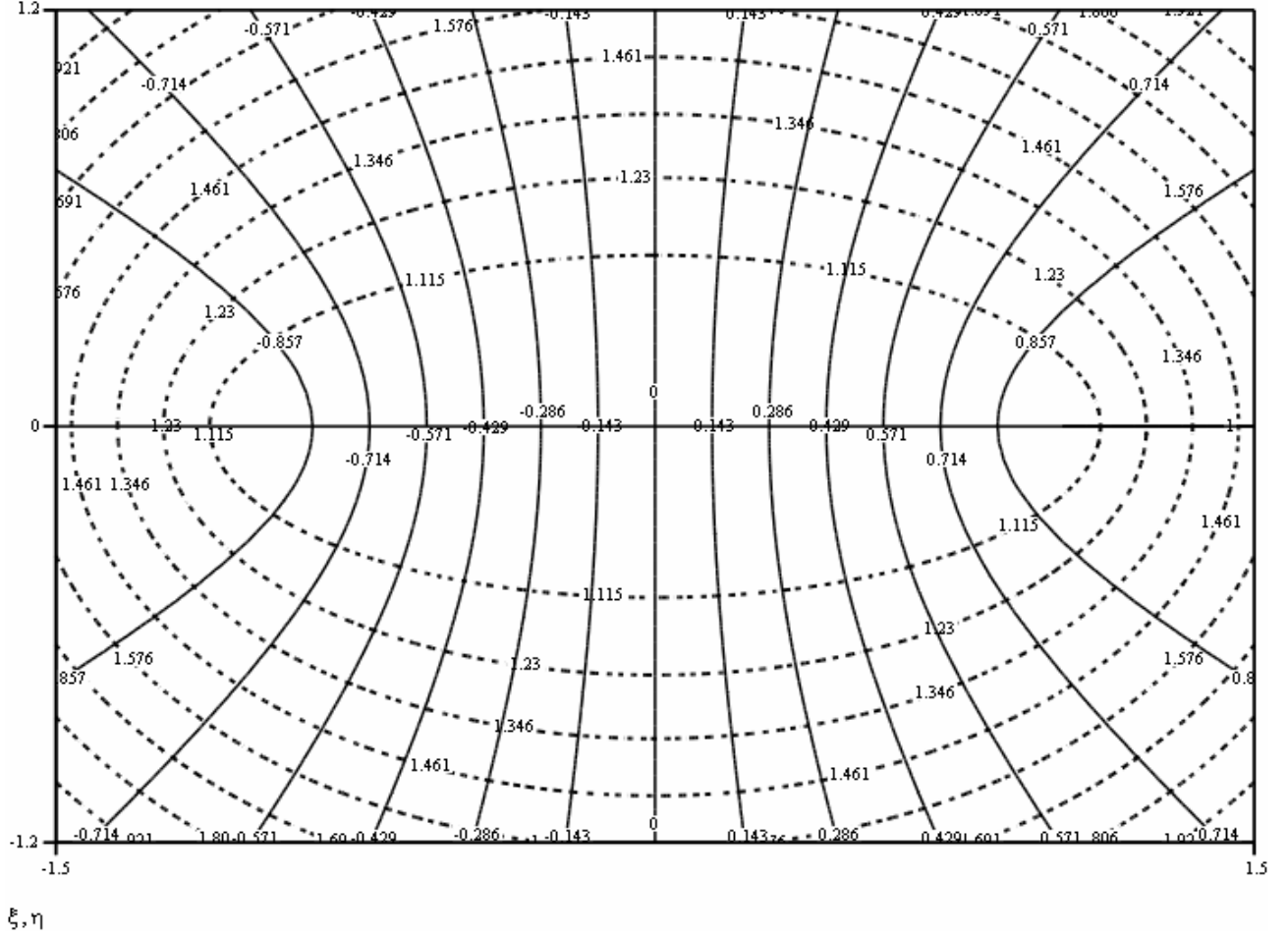

Figure 4.2: The prolate spheroidal coordinate system. The dotted lines are the ξ level curves, the sold lines are the η level curves.

Note the interpretation of these coordinates.

- ξ measures the "distance" of the electron from the nuclei, and is sometimes referred to, self-contradictorily, as the "elliptic radius." Clearly for an electron that is very far from the nuclei, $\xi \to \infty$. However, when the electron is at, say, the left nuclei, then $\xi = \frac{0+R}{R} = 1$. In general, $\xi = 1$ as long as the electron is on

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[1] It is frequently useful to know that the volume element in prolate spheroidal coordinates is $\frac{R^3(\xi^2-\eta^2)}{8}$, and so $\int f(\mathbf{r})\, d\mathbf{r} = \int_1^{\xi} \int_{-1}^{1} \int_0^{2\pi} f(\xi, \eta, \phi) \frac{R^3(\xi^2-\eta^2)}{8}\, d\phi\, d\eta\, d\xi$

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z axis and between the two nuclei. (One can think of the line segment $\xi = 1$ as characterizing the "chemical bond.") In general, curves $\xi = \text{constant}$ are ellipses whose foci are the atomic nuclei, which is why this coordinate system is sometimes called prolate spheroidal coordinates. We note that

$$1 \leq \xi < \infty \tag{4.5}$$

- η measures how much further the electron is from the "left" nucleus than it is from the "right" nucleus. Note that for any given value of η, the "total distance" of the electron from the nuclei is the same—and so, if $Z_l = Z_r$, the potential has a very simple dependence on ξ and η:

$$
\begin{aligned}
V(x,y,z) &= -\frac{Z_l}{\sqrt{x^2 + y^2 + \left(z + \frac{R}{2}\right)^2}} - \frac{Z_r}{\sqrt{x^2 + y^2 + \left(z - \frac{R}{2}\right)^2}} \\
&= -\frac{Z_l}{r_l} - \frac{Z_r}{r_r} \\
&= -\left(\frac{Z_l}{R(\xi + \eta)} + \frac{Z_r}{R(\xi - \eta)}\right) \\
&= -\frac{1}{R}\left[\frac{Z_l(\xi - \eta)}{(\xi + \eta)(\xi - \eta)} + \frac{Z_r(\xi + \eta)}{(\xi + \eta)(\xi - \eta)}\right] \\
&= -\frac{1}{R}\left[\frac{Z_l(\xi - \eta)}{(\xi + \eta)(\xi - \eta)} + \frac{Z_r(\xi + \eta)}{(\xi + \eta)(\xi - \eta)}\right] \\
&= -\frac{1}{R(\xi^2 - \eta^2)}\left(\xi(Z_r + Z_l) + \eta(Z_r - Z_l)\right) \\
&\stackrel{Z_l = Z_r}{=} -\frac{\xi(Z_r + Z_l)}{R(\xi^2 - \eta^2)}
\end{aligned} \tag{4.6}
$$

When an electron is at the "right" nucleus, $\eta = 1$, and when it is at the "left" nucleus, $\eta = -1$. It follows that

$$-1 \leq \eta \leq 1. \tag{4.7}$$

Examining figure 4.2, it is clear that curves with constant ξ (which are ellipses) are orthogonal to the curves of constant η (which are hyperbolae), where they intersect. That is, (ξ, η, ϕ) are a set of mutually orthogonal coordinates.

Writing the Schrödinger equation in terms of the (ξ, η, ϕ) (the hard part is computing the Laplacian), Equation (4.2) becomes

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$$\left[\left(-\frac{\hbar^2}{2}\right)\left(\frac{4}{R^2\left(\xi^2-\eta^2\right)}\right)\left(\begin{array}{c}\dfrac{\partial}{\partial\xi}\left(\xi^2-1\right)\dfrac{\partial}{\partial\xi}\\[2mm]+\dfrac{\partial}{\partial\eta}\left(1-\eta^2\right)\dfrac{\partial}{\partial\eta}\\[2mm]+\left(\dfrac{1}{\xi^2-1}+\dfrac{1}{1-\eta^2}\right)\dfrac{\partial}{\partial\phi^2}\end{array}\right)\right.$$
$$\left.-\frac{1}{R\left(\xi^2-\eta^2\right)}\left(\xi\left(Z_r+Z_l\right)+\eta\left(Z_r-Z_l\right)\right)\right]\Psi_k\left(\xi,\eta,\phi\right)=E\Psi_k\left(\xi,\eta,\phi\right) \qquad (4.8)$$

where the first line contains the kinetic energy term. We can multiply Equation (4.8) by $R^2\left(\xi^2-\eta^2\right)$, and then we will never have any term in which both ξ and η occurs. This lets us separate variables. Defining

$$\Psi_{n,\lambda,m}\left(\xi,\eta,\phi\right)\equiv X_n\left(\xi\right)H_\lambda\left(\eta\right)F_m\left(\phi\right) \qquad (4.9)$$

we then have the three equations,

$$\frac{d^2F}{d\phi^2}=-m^2F\left(\phi\right)\rightarrow F\left(\phi\right)\propto e^{-im\phi} \qquad (m=0,\pm1,\pm2,...) \qquad (4.10)$$

$$\left(\frac{-2}{R^2\xi^2}\right)\left(\frac{d}{d\xi}\left(\xi^2-1\right)\frac{d}{d\xi}+A_{n,\lambda,m}+R\left(Z_r+Z_l\right)\xi-\frac{m^2}{\xi^2-1}\right)X_n\left(\xi\right)=E_{n,\lambda,m}X_n\left(\xi\right) \qquad (4.11)$$

$$\left(\frac{-2}{R^2\eta^2}\right)\left(\frac{d}{d\eta}\left(\eta^2-1\right)\frac{d}{d\eta}+A_{n,\lambda,m}+R\left(Z_r-Z_l\right)\eta-\frac{m^2}{\eta^2-1}\right)H_\lambda\left(\eta\right)=E_{n,\lambda,m}H_\lambda\left(\eta\right) \qquad (4.12)$$

Note that, because both Eq. (4.11) and Eq. (4.12) depend on $A_{n,\lambda,m}$, they must be solved simultaneously—there will only be very special values of $A_{n,\lambda,m}$ for which both eigenvalue problems can be solved at the same time. This is the main reason why solving the Schrödinger equation for a one-electron diatomic molecule is so much more difficult than solving the Schrödinger equation for a one-electron atom.

II. Approximate Wave functions for the One-Electron diatomic molecule and "correlation diagrams."

Even if we are too lazy to solve Eqs. (4.10)-(4.12) for the hydrogen molecule ion in the general case, there are two "special cases" where we can easily solve the system. Most simple, of course, is when $R=0$. In that case, the two nuclei in Eq. (4.2) are at the same location, and we have

$$\left[-\frac{\nabla^2}{2} - \frac{2\left(Z_l + Z_r\right)}{r}\right]\Psi_k\left(r, \theta, \phi\right) = E_k\Psi_k\left(r, \theta, \phi\right) \tag{4.13}$$

which is just a one-electron atom with atomic number $Z_l + Z_r$.

It is less obvious, perhaps, but we can also solve Eq. (4.2) in the limit where the separation between the nuclei is large, $R \to \infty$. Here we have

$$\left[-\frac{\nabla^2}{2} - \frac{Z_l}{r_l} - \frac{Z_r}{r_r}\right]\Psi_k\left(r_l, r_r, \phi\right) = E_k\Psi_k\left(r_l, r_r, \phi\right). \tag{4.14}$$

It seems reasonable that the wave function for an electron on the "left" atom will not be much affected by the presence of another atom a very large distance away, and so we may suppose that we could write the wave function as a sum of two wave functions: one that describes an electron on the "left hand" nucleus and one that describes an electron on the "right hand" nucleus. This leads us to examine the wave function,

$$\Psi\left(\boldsymbol{r}\right) \equiv c\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right) + \sqrt{1 - |c|^2}\,\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right). \tag{4.15}$$

Here, $\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right)$ denotes a one-electron eigenfunction of the left-hand atom: a hydrogenic orbital with the specified quantum numbers, centered at the "left" nucleus. Similarly, $\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right)$ is an eigenstate of the "right-hand" atom.

- The wave function in Eq. (4.15) is normalized. In particular, we have

$$\left\langle c\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right) + \sqrt{1 - |c|^2}\,\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right)\middle| c\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right) + \sqrt{1 - |c|^2}\,\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right)\right\rangle$$
$$= |c|^2 \left\langle \psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right)\middle|\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right)\right\rangle$$
$$+ \left(\left\langle c\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right)\middle|\sqrt{1 - |c|^2}\,\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right)\right\rangle + \left\langle \sqrt{1 - |c|^2}\,\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right)\middle|\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right)\right\rangle\right)$$
$$\left(\sqrt{1 - |c|^2}\right)^2 \left\langle \psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right)\middle|\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right)\right\rangle$$
$$= \left|c^{(l)}\right|^2 + 0 + 0 + \left(1 - \left|c^{(l)}\right|^2\right)$$
$$= 1 \tag{4.16}$$

where we have used the fact that (a) the one-electron atomic orbitals are normalized and (b) because $\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right)$ is infinitesimal near the "right" atom (owing to the infinite distance between the atoms),

$$\psi_{n,l,m}^{(l)}\left(\boldsymbol{r}\right)\psi_{n',l',m'}^{(r)}\left(\boldsymbol{r}\right) = 0. \tag{4.17}$$

That is, because the atoms are very far apart, everywhere an orbital centered on the "left" atom has significant magnitude, the orbital centered on the "right" atom will be negligible, and vice versa. Equation (4.17) and the consequent vanishing of the two "cross terms" in Eq. (4.16) immediately follow.

- From the same argument as that used in Eq. (4.16), two different states,

$$\Psi_i\left(\boldsymbol{r}\right) \equiv c_i \psi^{(l)}_{n_i,l_i,m_i}\left(\boldsymbol{r}\right) + \sqrt{1 - \left(c_i\right)^2}\, \psi^{(r)}_{n'_i,l'_i,m'_i}\left(\boldsymbol{r}\right) \tag{4.18}$$

and

$$\Psi_j\left(\boldsymbol{r}\right) \equiv c_j \psi^{(l)}_{n_j,l_j,m_j}\left(\boldsymbol{r}\right) + \sqrt{1 - \left(c_j\right)^2}\, \psi^{(r)}_{n'_j,l'_j,m'_j}\left(\boldsymbol{r}\right) \tag{4.19}$$

will be orthogonal as long as the orbitals on each center are orthogonal. That is,

$$
\begin{aligned}
\left\langle \Psi_i \,\middle|\, \Psi_j \right\rangle &= c_i^* c_j \left\langle \psi^{(l)}_{n_i,l_i,m_i} \,\middle|\, \psi^{(l)}_{n_j,l_j,m_j} \right\rangle + c_i^* c_j \sqrt{1 - \left|c_i\right|^2}\,\sqrt{1 - \left|c_j\right|^2}\, \left\langle \psi^{(r)}_{n'_i,l'_i,m'_i} \,\middle|\, \psi^{(r)}_{n'_j,l'_j,m'_j} \right\rangle \\
&= c_i^* c_j \delta_{n_i n_j} \delta_{l_i l_j} \delta_{m_i m_j} + c_i^* c_j \delta_{n'_i n'_j} \delta_{l'_i l'_j} \delta_{m'_i m'_j} \sqrt{1 - \left|c_i\right|^2}\,\sqrt{1 - \left|c_j\right|^2}.
\end{aligned}
\tag{4.20}
$$

- If and only if the "left" and "right" states have the same energy, then the wave function is an eigenfunction of the Hamiltonian for large R for any choice of the number, c. Otherwise, the magnitude of c must be zero or one. We start by substituting Eq. (4.15) into the Hamiltonian, Eq. (4.14),

$$
\begin{aligned}
\left[-\frac{\nabla^2}{2} - \frac{Z_l}{r_l} - \frac{Z_r}{r_r} \right] &\left(c\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right) + \sqrt{1 - |c|^2}\, \psi^{(r)}_{n',l',m'}\left(\boldsymbol{r}\right) \right) \\
&= \left(-\frac{\nabla^2}{2} - \frac{Z_l}{r_l} \right) \left(c\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right) \right) - \left(\frac{Z_r}{r_r} \right) \left(c\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right) \right) \\
&\quad + \left(-\frac{\nabla^2}{2} - \frac{Z_r}{r_r} \right) \left(\sqrt{1 - |c|^2}\, \psi^{(r)}_{n',l',m'}\left(\boldsymbol{r}\right) \right) - \left(\frac{Z_l}{r_l} \right) \left(\sqrt{1 - |c|^2}\, \psi^{(r)}_{n',l',m'}\left(\boldsymbol{r}\right) \right)
\end{aligned}
\tag{4.21}
$$

The second term on both lines is zero: the electron-nuclear attraction between an electron on the "left" atom and the nucleus of the "right" atom will be zero if the atoms are infinitely far apart because $\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right)$ will be infinitesimal everywhere the distance from the right atom is small (which is required so that $\frac{Z_r}{r_r}$ is big). Similarly, $\frac{Z_r}{r_r}$ is vanishingly small near the "left" atom, where $\left|\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right)\right|$, is large, owing to the infinite distance between the atoms. Using the Schrödinger Equation for the one-electron atom, we can simplify the first terms on the second and third lines of Eq. (4.21) to

$$
\begin{aligned}
\left[-\frac{\nabla^2}{2} - \frac{Z_l}{r_l} - \frac{Z_r}{r_r} \right] &\left(c\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right) + \sqrt{1 - |c|^2}\, \psi^{(r)}_{n',l',m'}\left(\boldsymbol{r}\right) \right) \\
&= \left(-\frac{\nabla^2}{2} - \frac{Z_l}{r_l} \right) \left(c\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right) \right) + \left(-\frac{\nabla^2}{2} - \frac{Z_r}{r_r} \right) \left(\sqrt{1 - |c|^2}\, \psi^{(r)}_{n',l',m'}\left(\boldsymbol{r}\right) \right) \\
&= E^{(l)}_n \left(c\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right) \right) + E^{(r)}_{n'} \sqrt{1 - |c|^2}\, \psi^{(r)}_{n',l',m'}\left(\boldsymbol{r}\right) \\
&= -\frac{Z_l^2}{2n^2} \left(c\psi^{(l)}_{n,l,m}\left(\boldsymbol{r}\right) \right) - \frac{Z_r^2}{2\left(n'\right)^2} \left(\sqrt{1 - |c|^2}\, \psi^{(r)}_{n',l',m'}\left(\boldsymbol{r}\right) \right)
\end{aligned}
\tag{4.22}
$$

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If the energies of the "left hand" and "right hand" atoms are the same, this can be rewritten as

$$
\left[-\frac{\nabla^2}{2} - \frac{Z_l}{r_l} - \frac{Z_r}{r_r} \right] \left(c\psi_{n,l,m}^{(l)}(\boldsymbol{r}) + \sqrt{1-|c|^2}\,\psi_{n',l',m'}^{(r)}(\boldsymbol{r}) \right)
$$
$$
= -\frac{Z_l^2}{2n^2} \left(c\psi_{n,l,m}^{(l)}(\boldsymbol{r}) + \sqrt{1-|c|^2}\,\psi_{n',l',m'}^{(r)}(\boldsymbol{r}) \right) \tag{4.23}
$$

which establishes that Eq. (4.15) as an eigenfunction of the Hamiltonian for any value of c. If the two energies are not the same, as is typically the case for a heteronuclear diatomic molecule, then Eq. (4.22) indicates that the electron must be exclusively located on one atom or the other, and so $|c| = 0,1$.

- More generally, consider any diatomic molecule, AB. The Hamiltonian for this molecule can be written as

$$
\hat{H} = \sum_{i=1}^{N} \left(\frac{-\nabla_i^2}{2} - \frac{Z_l}{|\boldsymbol{r}_i - \boldsymbol{R}_l|} - \frac{Z_r}{|\boldsymbol{r}_i - \boldsymbol{R}_r|} \right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{4.24}
$$

which can clearly be written as the sum of the Hamiltonians for the "left" and "right" atoms, $\hat{H}^{(l)}$ and $\hat{H}^{(r)}$ plus the repulsive potentials between the electrons in the "left" atom and those in the "right" atom:

$$
\hat{H} \equiv \hat{H}^{(l)}\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_l} \right) + \hat{H}\left(\boldsymbol{r}_{N_l+1}, \boldsymbol{r}_{N_l+2}, \ldots, \boldsymbol{r}_{N_l+N_r} \right)
$$
$$
+ \sum_{i=1}^{N_l} \sum_{j=N_l+1}^{N_l+N_r} \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{4.25}
$$

When the atoms are infinitely far apart, the electrons on the "left" and "right" atoms move independently and are not correlated. Thus, we can us separation of variables to write the eigenfunctions of the molecule as simple products[2] of the eigenfunctions of the isolated atoms.[3]

$$
\Psi \equiv \Psi_m^{(l)}\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{N_l} \right) \Psi_n^{(r)}\left(\boldsymbol{r}_{N_l+1}, \boldsymbol{r}_{N_l+2}, \ldots, \boldsymbol{r}_{N_l+N_r} \right) \tag{4.26}
$$

Similarly, when the bond length is zero, we have a single atom with nuclear charge $Z_l + Z_r$. For obvious reasons, we call the $R \to \infty$ limit the *separated atom limit* and the $R \to 0$ limit the *united atom limit*.

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[2] In theory, we should use antisymmetric products. However, when the two atoms are infinitely far apart, we can consider the electrons on the atoms to be distinguishable (because the atoms are so far apart that we can unambiguously assign some electrons to the left atom and the remaining electrons to the right atom).

[3] In particular, the electron-electron repulsion terms are zero because the distance between the atoms is infinite, and thus the distance between the "left" and "right" atoms electrons is also infinite.

III. The Non-Crossing Rule

It is difficult, even for the one-electron diatomic molecule, to compute the wave functions and energies for reasonable bond lengths. However, we have just seen that we can compute the wave functions and energies of H_2^+ when the bond length, R, is zero or infinity. It seems reasonable, then, to try to "guess" what happens for intermediate values of R, $0 < R < \infty$ based on known results in the united-atom and separated-atom limits. But how do we determine which "united atom state" corresponds to a given "separated atom" state? Naïvely, we might expect that we should just connect the lowest-energy states of the united atom and the separated atom, the second-lowest energy states of the united and separated atoms, etc.. However, looking ahead to figures 4.4 and 4.5, it is obvious that this is not as simple as just connecting the lowest-energy states of the united atom to those of the separated atom. The reason for this complexity is that certain states can never have the same energy[4] and thus, certain states can never cross. The rule for determining when curves can (and when they can't) cross is called the non-crossing rule.

A. Variational Argument

The origin of the non-crossing rule is easily understood. Suppose we are given two *approximate* eigenstates of the Hamiltonian, each of which depends on the nuclear coordinates, $\{\boldsymbol{R}_\alpha\}_{\alpha=1}^P$. Since these are "approximate" states, we can improve the approximation by taking the "new" states to be a linear combination of the old states. (Of course, if the "old" states are exact then no correction is made.) So[5]

$$\Psi_m^{better}\left(\{\boldsymbol{R}_\alpha\}\right) = a\Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) + \sqrt{1-|a|^2}\,\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)$$
$$\Psi_n^{better}\left(\{\boldsymbol{R}_\alpha\}\right) = \sqrt{1-|a|^2}\,\Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) - a\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)$$

(4.27)

To find a we solve the eigenvalue problem[6]

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[4] More precisely, such states have the same energy with probability zero.

[5] The value of the coefficient of $\Psi_n^{approx}\left(\{\boldsymbol{R}_\alpha\}\right)$ is determined by normalization in the first equation and by the requirement that the two states be orthogonal in the second equation. The initial states are assumed to be orthonormal.

[6] Here, for compactness, we have defined $b_k = \sqrt{1-a_k^2}$.

$$\begin{bmatrix} \left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle & \left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle \\ \left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle^* & \left\langle \Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle \end{bmatrix}\begin{bmatrix} a_k \\ b_k \end{bmatrix} = E_k \begin{bmatrix} a_k \\ b_k \end{bmatrix} \tag{4.28}$$

We can identify the approximate potential energy surfaces, for the mth and n^{th} excited states as

$$U_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) = V_{nn}\left(\{\boldsymbol{R}_\alpha\}\right) + \left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle$$
$$U_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) = V_{nn}\left(\{\boldsymbol{R}_\alpha\}\right) + \left\langle \Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle \tag{4.29}$$

where $V_{nn}\left(\{\boldsymbol{R}_\alpha\}\right)$ denotes the nuclear-nuclear repulsion energy. Choosing, in addition, real wave functions,[7] then Eq. (4.28) becomes

$$\begin{bmatrix} U_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) & \left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle \\ \left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle^* & U_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) \end{bmatrix}\begin{bmatrix} a_k \\ b_k \end{bmatrix} = E_k \begin{bmatrix} a_k \\ b_k \end{bmatrix}. \tag{4.30}$$

The solution to this eigenvalue problem is easily found, and the eigenvalues are

$$U_{m,n}^{better}\left(\{\boldsymbol{R}_\alpha\}\right) = \frac{U_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) + U_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)}{2}$$
$$\pm \frac{\sqrt{\left(U_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) - U_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right)^2 + 4\left|\left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle\right|^2}}{2} \tag{4.31}$$

If the two potential energy surfaces did cross then the discriminant (the term in the square root) must be zero. This implies that both

$$U_m^{better}\left(\{\boldsymbol{R}_\alpha\}\right) = U_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right) \tag{4.32}$$

and

$$\left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\middle|\hat{H}\middle|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle = 0. \tag{4.33}$$

This gives two nonlinear equations depending on $3N - 6$ (*3N-5* for a linear molecule) unknowns.

Equation (4.33) is always true if there is some molecular symmetry element for which these two states differ. To see this, suppose that $\hat{\Sigma}$ is a molecular symmetry operators (molecular rotation, reflection, inversion, etc.), and Ψ_m and Ψ_n differ in the way they behave when $\hat{\Sigma}$ acts on them. (For example, $\hat{\Sigma}$ could be reflection in some plane, and if Ψ_m is symmetric with respect to this plane, but Ψ_n is antisymmetric, then $\hat{\Sigma}\Psi_m = \Psi_m$ and $\hat{\Sigma}\Psi_n = -\Psi_n$. The Hamiltonian is always fully symmetric, and operating on the wave functions with the symmetry operator will always produce another

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[7]   In time-independent quantum mechanics, we can always choose our wave functions to be real-valued.

appropriate wave function describing the state in question. Consequently, operating with the symmetry operator *must not change the value of the integral in Eq.* (4.33)[8] and so

$$\left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\Big|\hat{H}\Big|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle = \left\langle \hat{\Sigma}\Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\Big|\hat{\Sigma}\hat{H}\Big|\hat{\Sigma}\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle$$
$$= -1\left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\Big|\hat{H}\Big|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle \tag{4.34}$$

which implies that unless $\Psi_m^{approx.}$ and $\Psi_n^{approx.}$ have the same symmetry, then

$$\left\langle \Psi_m^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\Big|\hat{H}\Big|\Psi_n^{approx.}\left(\{\boldsymbol{R}_\alpha\}\right)\right\rangle = 0 \tag{4.35}$$

So we have two cases:

- For states with different symmetry, Eq. (4.33) is true automatically. We then have one equation, Eq. (4.33), in *3N-6* unknowns (one unknown for a diatomic molecule). The solutions to this equation will then be sets of *3N-7* (or fewer[9]) dimensions. When this occurs, we say the potential energy surfaces cross. (Recall that if two *3N-6*-dimensional surfaces cross, then where they cross defines a curve in *3N-7* dimensions).

  For the important case of a diatomic molecule, the curves can cross at points, which are a set of zero dimension.

- For states with the same symmetry, Eq. (4.33) is only true for special nuclear positions. We then have two equations (Eqs. (4.32) and (4.33)) and *3N-6* unknowns. As a result, the solutions are generally on surfaces with dimension *3N-8* (or fewer) dimensions. When curves intersect in this way, we speak of a *conical intersection*. (Conical intersections are important for describing the non-radiative decay of some excited states. The Jahn-Teller distortion is another

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8   For example, for the hydrogen atom there is a mirror plane in the xy plane, and reflection in that plane is associated with an operator $\hat{\Sigma}_{xy}$, where $\hat{\Sigma}_{xy}\Psi(x,y,z) = \Psi(x,y,-z)$. Clearly this changes the phase of states with $m_l = 0$ and $l = 1, 3, \ldots$, but does not affect other states. However, it doesn't convert $2p_0$ orbitals into $2p_{\pm 1}$ orbitals—it just changes $\psi_{2p_0}(x,y,z)$ to $-\psi_{2p_0}(x,y,z)$. For a homonuclear diatomic, the important symmetry elements are (a) angular momentum about the internuclear axis and (b) inversion about the bond midpoint. We do not have the second symmetry in heteronuclear diatomics.

9   Owing to the nonlinearity of these equations, there may be no solutions or, as is frequently the case, the solutions may have lower dimension than would be expected. The most important case is associated with curves that never cross (for example, the curves associated with a high energy state and a low energy state of the same symmetry).

example, wherein the "symmetric" (e.g., octahedral) state is the "conical intersection point"), but the different electronic states do not cross when one moves away from this point (which typically has high symmetry).) Potential energy surfaces of this sort look like "hourglasses" with the "upper globe" being one surface and the "lower globe" being the other, with the two repositories connected by an infinitely small hole. If you slice the surface in a vertical direction, you see what looks like an "avoided crossing" unless you slice it just right—through the infinitely small "hole" in the hourglass. It is through this infinitesimal "hole" (which is "broadened" by nonadiabatic (= non-Born-Oppenheimer) effects that excited states can decay without fluorescing.

For a diatomic, we have only one unknown (bond length) but two equations (Eqs. (4.32) and (4.33)), which means that except in very exceptional cases (where the two equations have the same solution), curves with the same symmetry do not cross. The only case I know of where two curves with the same symmetry are degenerate are in the "united atom" limit and the "separated atom" limits.[10]

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[10] It is true, albeit infinitely improbable, that the curves could cross. Matehmatically, the situation is similar to the odds that at randomly selected line, $y = mx + b$ will pass through the origin. Unless you make the very special choice $b = 0$, it does not occur. This doesn't say that it never happens, but merely that, in general, lines do not pass through the origin.
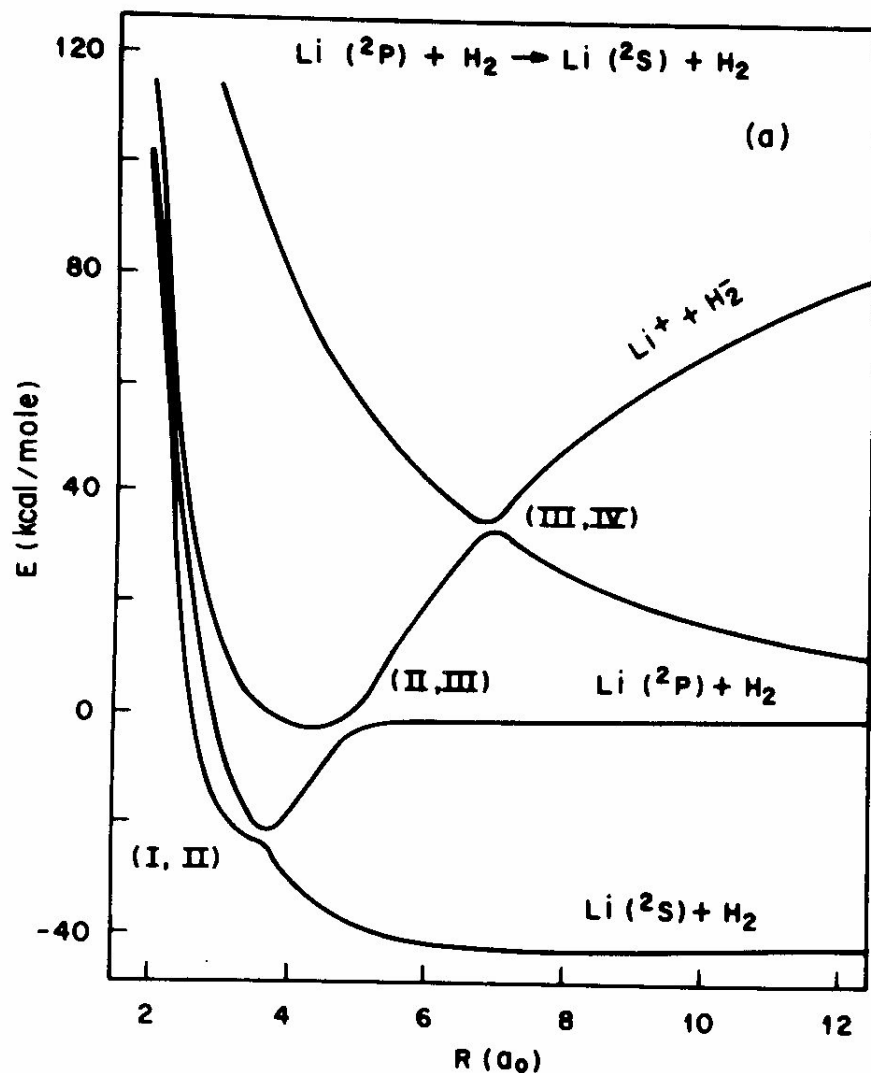
Figure 4.3: Demonstration of the non-crossing rule's effects on potential energy curves. From Chemical Kinetics and Dynamics by J. I. Steinfeld, J. S. Francisco, and W. L. Hase (Prentice, New Jersey, 1989).

B.   Argument from Perturbation Theory

For another perspective on the non-crossing rule, we use perturbation theory. Suppose we are given the exact wave functions, $\Psi_m^{(0)}$ and $\Psi_n^{(0)}$ for a system at some molecular geometry, $\left\{ R_\alpha^{(0)} \right\}$ and we wish to consider what the energy is at some other,

nearby, geometry $\left\{\boldsymbol{R}_\alpha^{cross}\right\}$. When the nuclear geometry changes, only the external potential[11] changes, giving the change in the Hamiltonian

$$\Delta\hat{V}\left(\left\{\boldsymbol{R}_\alpha\right\}\right) \equiv \sum_{i=1}^{N}\left(\sum_{\alpha=1}^{P}\frac{-Z_\alpha}{\left|\boldsymbol{r}_i - \boldsymbol{R}_\alpha^{cross}\right|} - \sum_{\alpha=1}^{P}\frac{-Z_\alpha}{\left|\boldsymbol{r}_i - \boldsymbol{R}_\alpha^{(0)}\right|}\right). \tag{4.36}$$

We can use perturbation theory to approximate the change in energy of the two states, which we assume have different energies at $\left\{\boldsymbol{R}_\alpha^{(0)}\right\}$. We obtain, to second order,

$$\Delta U_m\left(\left\{\boldsymbol{R}_\alpha\right\}\right) = \left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle + \sum_{\substack{k=0\\k\neq m}}^{\infty}\frac{\left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_k^{(0)}\right\rangle\left\langle\Psi_k^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle}{U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_k\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)} \tag{4.37}$$

$$\Delta U_n\left(\left\{\boldsymbol{R}_\alpha\right\}\right) = \left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle + \sum_{\substack{k=0\\k\neq n}}^{\infty}\frac{\left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_k^{(0)}\right\rangle\left\langle\Psi_k^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle}{U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_k\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)} \tag{4.38}$$

where $U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)$ and $U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)$ are the exact potential energy surfaces at the initial geometry. If the states cross, then, when the nuclear positions, $\left\{\boldsymbol{R}_\alpha^{(0)}\right\}$, are close enough to the "crossing point," we have that

$$\begin{aligned}
U_m&\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) + \left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle + \sum_{\substack{k=0\\k\neq m}}^{\infty}\frac{\left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_k^{(0)}\right\rangle\left\langle\Psi_k^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle}{U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_k\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)}\\
&\approx U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) + \left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle + \sum_{\substack{k=0\\k\neq n}}^{\infty}\frac{\left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_k^{(0)}\right\rangle\left\langle\Psi_k^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle}{U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_k\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)}
\end{aligned} \tag{4.39}$$

Let's assume that

$$U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) + \left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle \approx U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) + \left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle \tag{4.40}$$

which is just one equation in *3N-6* unknowns. If Eq. (4.40) is true, then $U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)$ and $U_n^{(0)}\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)$ are very close together in energy, and so there will be one large term in the denominator of Eq. (4.39). If the other terms are small, we obtain a second equation namely,

$$\begin{aligned}
\frac{\left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle\left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle}{U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)} &\approx \frac{\left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle\left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle}{U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)}\\
&\approx -\frac{\left\langle\Psi_n^{(0)}\left|\Delta V\right|\Psi_m^{(0)}\right\rangle\left\langle\Psi_m^{(0)}\left|\Delta V\right|\Psi_n^{(0)}\right\rangle}{U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)}
\end{aligned} \tag{4.41}$$

which implies that

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[11]   For an isolated molecule, the external potential is just the nuclear-electron attraction potential.

$$\left| \left\langle \Psi_m^{(0)} \middle| \Delta V \middle| \Psi_n^{(0)} \right\rangle \right|^2 \approx 0$$
$$\left\langle \Psi_m^{(0)} \middle| \Delta V \middle| \Psi_n^{(0)} \right\rangle \approx 0 \tag{4.42}$$

Suppose the perturbation preserves some symmetries in the molecule, with symmetry operators $\hat{\Sigma}_1, \hat{\Sigma}_2, \ldots$. If the two states in question have different symmetry with respect to one of these operations, then Eq. (4.42) is true automatically. However, if both states are symmetric under these operations, then Eq. (4.42) will not be true. In consequence, the upper surface is "pushed up" from the lower surface by an amount

$$\frac{\left\langle \Psi_n^{(0)} \middle| \Delta V \middle| \Psi_m^{(0)} \right\rangle \left\langle \Psi_m^{(0)} \middle| \Delta V \middle| \Psi_n^{(0)} \right\rangle}{U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) - U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)} \tag{4.43}$$

while the lower surface is "pushed down" from the upper surface by an equal amount. The closer the two surfaces come together, the greater this "repulsion" between the states is and the more acute the "avoided crossing" becomes.

Conical intersections often occur at points of high symmetry. For example, the octahedral structure of transition metal complexes with partially occupied orbitals has several degenerate ground states, which can be chosen to have different symmetries (owing to the different symmetries of the d-orbitals). For this "high-symmetry" state, Eq. (4.35) is automatically satisfied. However, when one performs the Jahn-Teller distortion, the symmetry of the system is reduced. Now there are no longer quite so many symmetry operators, and (if we choose the appropriate degenerate states for the perturbation in question using degenerate perturbation theory), the symmetry operators available to us in Eq. (4.42) will, in general, be unable to distinguish between the symmetries of some (or all) of the formerly degenerate states.

Said mathematically, consider two wave functions which have the same symmetry with respect to the subset of the system's symmetry operators under which ΔV is invariant, $\Sigma_1^V, \Sigma_2^V, \ldots$ but differ with respect to some symmetry operator in the initial state, $\Sigma_1^{(0)}, \Sigma_2^{(0)}, \ldots$. At the initial state, the two states can have the same energy—the non-crossing rule does not apply since the states have different symmetry; in particular Eq. (4.41) is automatically satisfied. Suppose the two states do in fact have the same energy at $\left\{\boldsymbol{R}_\alpha^{(0)}\right\}$. Equation (4.40) will also be satisfied since $U_m\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right) = U_n\left(\left\{\boldsymbol{R}_\alpha^{(0)}\right\}\right)$ and the perturbation does not break the symmetry:

$$\left\langle \Psi_m^{(0)} \left| \Delta V \right| \Psi_m^{(0)} \right\rangle = \left\langle \hat{\Sigma}_i^V \Psi_m^{(0)} \left| \hat{\Sigma}_i^V \Delta V \right| \hat{\Sigma}_i^V \Psi_m^{(0)} \right\rangle$$

$$\left\langle \Psi_n^{(0)} \left| \Delta V \right| \Psi_n^{(0)} \right\rangle = \left\langle \hat{\Sigma}_i^V \Psi_n^{(0)} \left| \hat{\Sigma}_i^V \Delta V \right| \hat{\Sigma}_i^V \Psi_n^{(0)} \right\rangle.$$

$$(4.44)$$

However, as soon as we "move away" from the initial geometry, $\left\{ \boldsymbol{R}_\alpha^{(0)} \right\}$, we find that there is a "repulsion" between the states owing to the fact that Eq. (4.42) is not valid for the symmetry operators in question. That is, the states have the same symmetry when viewed with regard to the lower-symmetry system, $\hat{H} \equiv \hat{H}\left(\left\{ \boldsymbol{R}_\alpha^{(0)} \right\} \right) + \Delta V$, and are subject to the non-crossing rule.

Thus, in an octahedral transition metal complex, there is a degenerate ground state that is preserved for some motions (e.g., uniform dilation of the bond lenths, $\left\{ \boldsymbol{R}_\alpha^0 \right\} \rightarrow \left\{ \gamma \boldsymbol{R}_\alpha^{(0)} \right\}$ but the degeneracy is "broken" (partially or totally) with respect to certain other molecular motions, at which point the states "repel each other strongly" according to Eq. (4.43). (A similar phenomenon happens for triatomic molecules, where there tend to be a large number of "conical" intersections in the linear conformation.)

Clearly "accidental" degeneracies can still occur, but it takes an extremely fortuitous cancellation of terms in Eq. (4.39).

For a diatomic molecule, the only relevant change in nuclear coordinates is dilation and/or contraction of the bond length; this change does not alter the symmetry of the molecule. Consequently, ΔV is always fully symmetric. Equation (4.42) is only zero, then, if the two wave functions have different symmetry. If the two wave functions have the same symmetry, then—except for possible exceptional circumstances— $\left| \left\langle \Psi_m^{(0)} \left| \Delta V \right| \Psi_n^{(0)} \right\rangle \right|^2 > 0$ and as the two states approach each other the potential energy curves strongly repel each other, giving the picture we observe in Figure 4.3.

IV. The Correlation Diagram for Diatomics

From the non-crossing rule we recognize that we should match the states of the "united atom" with those of the "separated atoms" based on the fact that the potential energy curves for states with the same symmetry never cross. What are the key symmetry elements for labeling states of diatomic molecules?

Looking at Eq. (4.9), we see that the wave function for a one-electron diatomic can be written as $\Psi_{n,\lambda,m}\left(\xi, \eta, \phi \right) \equiv X_n\left(\xi \right) H_\lambda\left(\eta \right) F_m\left(\phi \right)$. The n quantum number is the analogue of the principle quantum number in atoms, and orders "energy levels". λ is quite a bit

more difficult to interpret, but it is usually related to the number of nodes that cross the internuclear axis but do not contain it. (n and λ are coupled in a complicated way.)

The m quantum number is easy to interpret since it is fundamentally similar to the magnetic quantum number in atoms—notice that both atomic and molecular orbitals have an $e^{im\phi}$ factor. For a state with $m = 0$, there are no "angular" nodes containing the internuclear axis (the line that connects the two nuclei), as we denote such states as σ-orbitals. (Compare s orbitals, where $l = 0$, in atoms.) When $m = 1$, there is a first-order node containing the internuclear axis, and we denote such states as π-orbitals. π orbitals always come in pairs, corresponding to an angular factor of $e^{i\phi}$ and $e^{-i\phi}$. Choosing the internuclear axis to be the z axis, these two states can be distinguished because the action of the $\hat{L}_z$ operator, which measures angular momentum about the z axis. When $\frac{\hat{L}_z\psi(\xi,\eta,\phi)}{\psi(\xi,\eta,\phi)}$ is greater than zero, we say we have a "$+$" state; when $\frac{\hat{L}_z\psi(\xi,\eta,\phi)}{\psi(\xi,\eta,\phi)}$ is less than zero, we say we have a "$-$" state, and when $\frac{\hat{L}_z\psi(\xi,\eta,\phi)}{\psi(\xi,\eta,\phi)}$ equals zero, we conventionally either (a) omit the distinction or (b) label the state "$+$".[12]

$$m \equiv \frac{\hat{L}_z\psi(\xi,\eta,\phi)}{\psi(\xi,\eta,\phi)}$$

$$\begin{aligned} m < 0 &\to\ "-\," \\ m > 0 &\to\ "+\," \\ m = 0 &\to\ "+\," \text{ or no designation.} \end{aligned} \tag{4.45}$$

Just as we often chose to use "Cartesian" p-orbitals, we often choose to use "Cartesian" π orbitals. Then

$$\begin{aligned} \pi_x &= \frac{\pi_1 + \pi_{-1}}{\sqrt{2}} \sim \frac{e^{i\phi} + e^{-i\phi}}{\sqrt{2}} \propto \cos(\phi) \\ \pi_y &= \frac{\pi_1 - \pi_{-1}}{\sqrt{2}i} \sim \frac{e^{i\phi} - e^{-i\phi}}{\sqrt{2}i} \propto \sin(\phi) \end{aligned} \tag{4.46}$$

The "x" and "y" designations denote the direction in which the orbitals point: using spherical coordinates and denoting the distance from the z axis as r, then $r\cos(\phi) = x$ and $r\sin(\phi) = y$. There are several designations for the "$+$"/"$-$" convention in Cartesian orbitals. My preferred convention is that if the orbital is symmetric with respect to reflection in the xz-plane, then it is a "$+$" orbital, and it is a "$-$" orbital otherwise. Thus

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[12]   Whether the m quantum number is positive or negative has to do with whether the electron is moving clockwise or counterclockwise about the z axis.

$$\left. \begin{array}{l} \text{symmetric with respect} \\ \text{to reflection in the } xz\text{-plane} \end{array} \right) \to \text{"}+\text{"} \qquad \left(\text{e.g. } \pi_x, \delta_{x^2-y^2} \right)$$

$$\left. \begin{array}{l} \text{antisymmetric with respect} \\ \text{to reflection in the } xz\text{-plane} \end{array} \right) \to \text{"}-\text{"} \qquad \left(\text{e.g. } \pi_y, \delta_{xy} \right)$$

(4.47)

I usually choose the xz-plane to be the plane of the paper (or the blackboard).

When an orbital has two nodes intersecting the internuclear axis, we call it a δ-orbital. (The d orbitals in atoms are comparable.) In this case the angular part of the wave functions are $e^{2i\phi}$ and $e^{-2i\phi}$, and again we define $+,-$ states using Eq. (4.45). We can again form "Cartesian" δ orbitals, and we obtain

$$\delta_{x^2-y^2} = \frac{\delta_{+2}+\delta_{-2}}{\sqrt{2}} \sim \frac{e^{2i\phi}+e^{-2i\phi}}{\sqrt{2}} \propto \cos(2\phi)$$

$$\delta_{xy} = \frac{\delta_{+2}-\delta_{-2}}{\sqrt{2}i} \sim \frac{e^{2i\phi}-e^{-2i\phi}}{\sqrt{2}i} \propto \sin(2\phi).$$

(4.48)

and if we multiply the angular portion by the square of the distance from the internuclear axis, we obtain

$$r^2 \cos(2\phi) = r^2 \left(\cos^2(\phi) - \sin^2(\phi) \right) = x^2 - y^2$$

$$r^2 \sin(2\phi) = 2r^2 \cos(\phi)\sin(\phi) = 2xy.$$

(4.49)

For the Cartesian δ-orbitals, we again employ a $\pm$ designation using the xz-plane, cf. Eq. (4.47).

Finally, for a homonuclear diatomic molecule there is a center of symmetry, and if the orbital is symmetric with respect to this center, so that $\psi(x,y,z) = +\psi(-x,-y,-z)$ we say it is "gerade" (designated "g") but if $\psi(x,y,z) = -\psi(-x,-y,-z)$, then the orbital is "ungerade", (designated "u"). Clearly, for a heteronuclear diatomic molecule $\psi(x,y,z) \neq \pm\psi(-x,-y,-z)$, so the gerade/ungerade designation is irrelevant.

Putting all this together we find a prescription for constructing the symmetry labels for the molecular orbitals in homonuclear diatomic:

- Count the number of "angular" nodes, m. Then

$$m = \begin{cases} 0 \to \sigma \\ 1 \to \pi \\ 2 \to \delta \\ 3 \to \phi \\ 4 \to \gamma \\ \vdots \end{cases}$$

(4.50)

- Denote the symmetry of the node according to Eq. (4.45) or (4.47), depending on whether the "spherical" or the "Cartesian" molecular orbitals are being used.

- For homonuclear diatomics, denote whether the orbital is symmetric or antisymmetric with respect to inversion through the bond midpoint.
- The final symbol takes the form

$$(\sigma, \pi, \delta, \ldots)_{u/g}^{\pm} \tag{4.51}$$

Using these symmetry designations and the non-crossing rule, we can construct "correlation diagrams" for homonuclear and heteronuclear diatomics. Notice that the lower symmetry in the heteronuclear diatomics does, in fact, change the correlation diagram and, in particular, the level of the σ-bonding and anti-bonding orbitals.
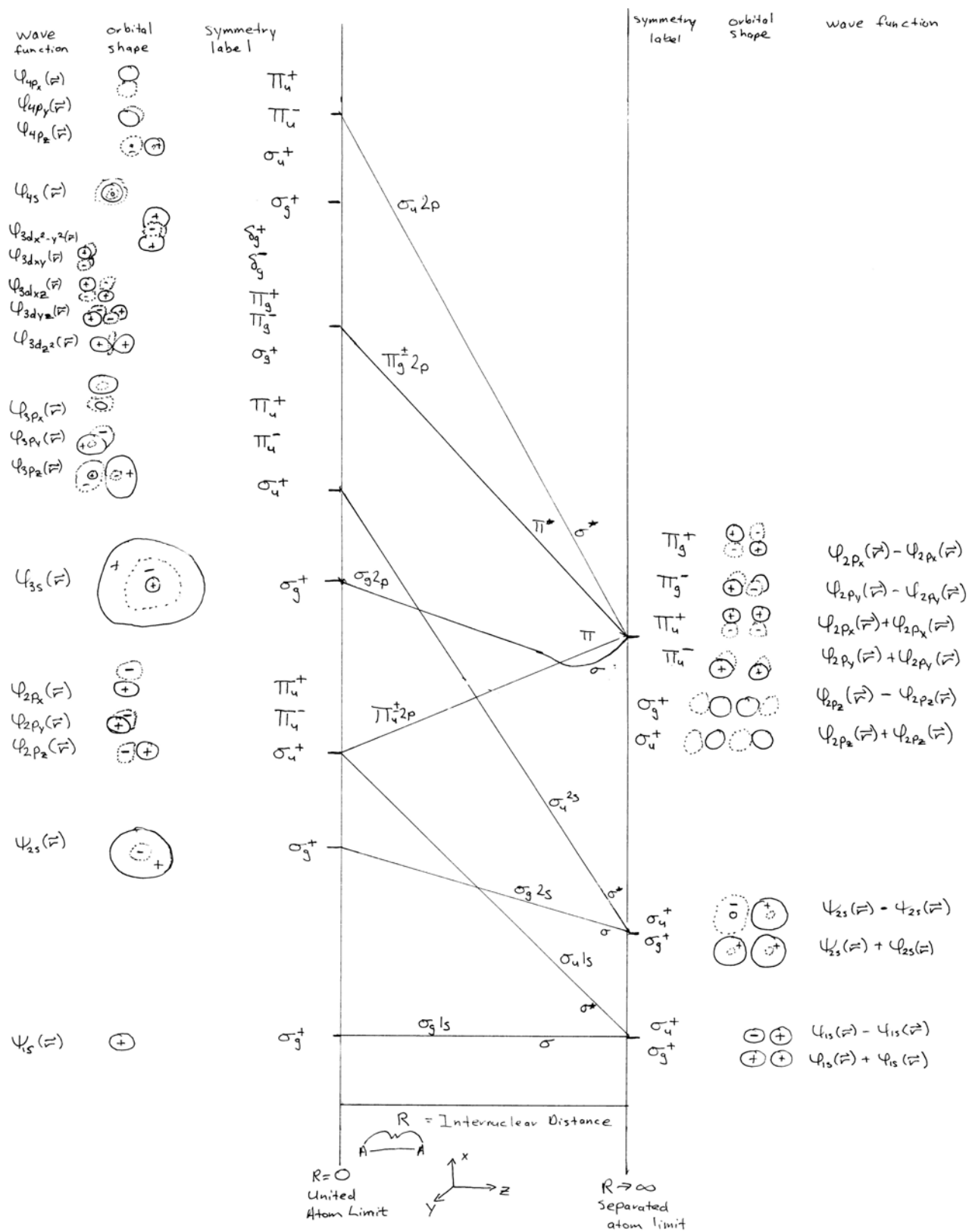
Figure 4.4. Correlation Diagram for a homonuclear diatomic molecule. The orbitals are ordered appropriately for a second-row atom.

wave function | orbital shape | symmetry label

$\psi_{4p_x}(\vec{r})$ π^+
$\psi_{4p_y}(\vec{r})$ π^-
$\psi_{4p_z}(\vec{r})$ σ^+

$\psi_{4s}(\vec{r})$ σ^+

$\psi_{3d_{x^2-y^2}(\vec{r})}$ δ^+
$\psi_{3d_{xy}}(\vec{r})$ δ^-
$\psi_{3d_{xz}}(\vec{r})$ π^+
$\psi_{3d_{yz}}(\vec{r})$ π^-
$\psi_{3d_{z^2}}(\vec{r})$ σ^+

$\psi_{3p_x}(\vec{r})$ π^+
$\psi_{3p_y}(\vec{r})$ π^-
$\psi_{3p_z}(\vec{r})$ σ^+

$\psi_{3s}(\vec{r})$ σ^+

$\psi_{2p_x}(\vec{r})$ π^+
$\psi_{2p_y}(\vec{r})$ π^-
$\psi_{2p_z}(\vec{r})$ σ^+

$\psi_{2s}(\vec{r})$ σ^+

$\psi_{1s}(\vec{r})$ σ^+

$(\sigma_{2p})^*$
$(\pi_{2p})^*$
σ_{2p}
π_{2p}
$(\sigma_{2s})^*$
σ_{2s}
$(\sigma_{1s})^*$
σ_{1s}

symmetry label | orbital shape | wave function

π^+ $\psi_{2p_x}(\vec{r}) - \psi_{2p_x}(\vec{r})$
π^- $\psi_{2p_y}(\vec{r}) - \psi_{2p_y}(\vec{r})$
π^+ $\psi_{2p_x}(\vec{r}) + \psi_{2p_x}(\vec{r})$
π^- $\psi_{2p_y}(\vec{r}) + \psi_{2p_y}(\vec{r})$
σ^+ $\psi_{2p_z}(\vec{r}) - \psi_{2p_z}(\vec{r})$
σ^+ $\psi_{2p_z}(\vec{r}) + \psi_{2p_z}(\vec{r})$

σ^+ $\psi_{2s}(\vec{r}) - \psi_{2s}(\vec{r})$
σ^+ $\psi_{2s}(\vec{r}) + \psi_{2s}(\vec{r})$

σ^+ $\psi_{1s}(\vec{r}) - \psi_{1s}(\vec{r})$
σ^+ $\psi_{1s}(\vec{r}) + \psi_{1s}(\vec{r})$

R = Internuclear Distance

A———A

$R = 0$
United Atom Limit

$R \to \infty$
Separated atom limit
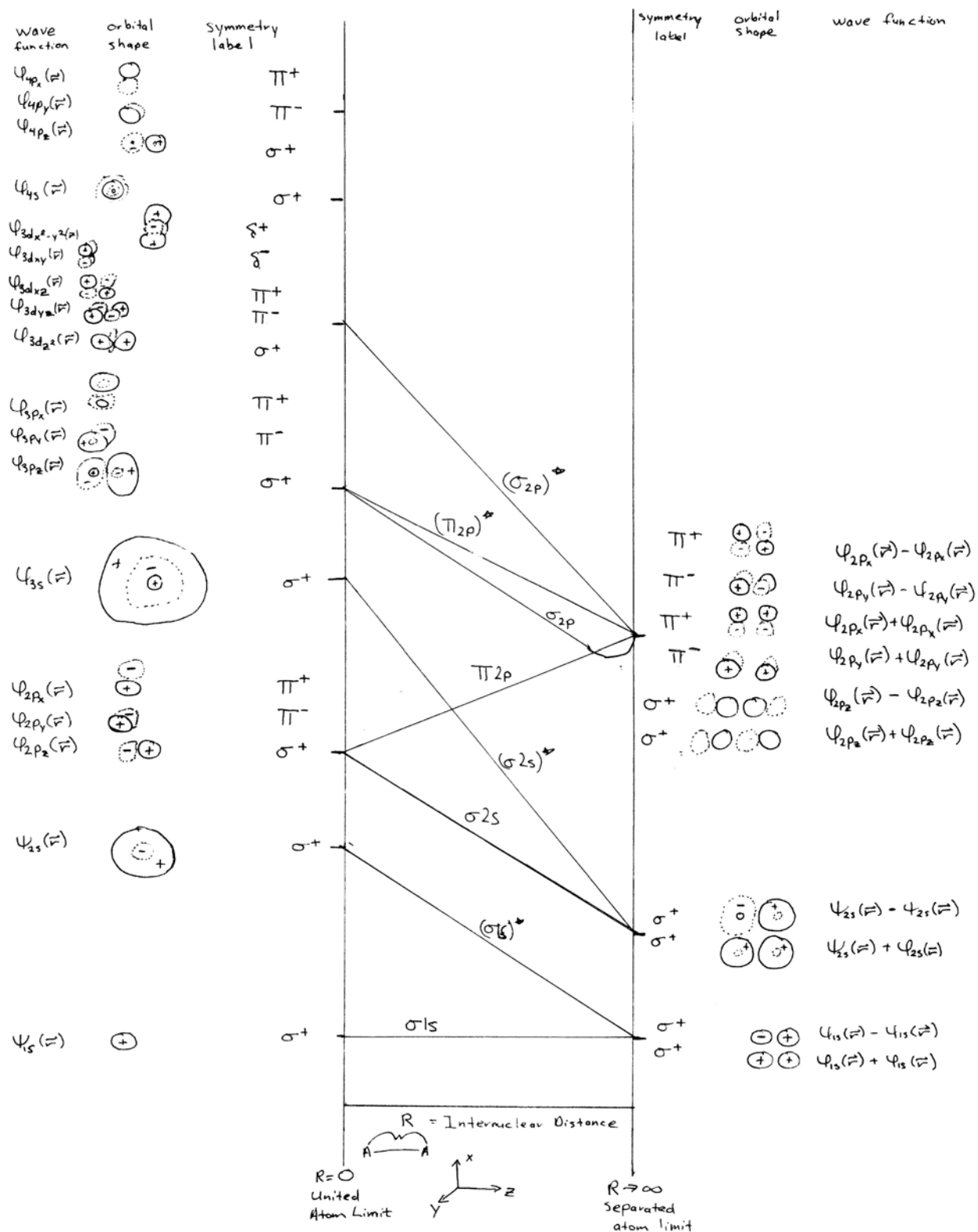
Figure 4.5: Correlation Diagram for a heteronuclear diatomic molecule. The orbitals are ordered appropriately for a second-row atom.

V. Details: The Hydrogen Molecule Ion

Let us now reconsider the one-electron diatomic molecule, this time in greater detail. We may reasonably approximate the ground state wave function with a sum of hydrogenic orbitals. We need to evaluate the energy,

$$E \equiv \frac{\left\langle \psi^{(l)}(\boldsymbol{r}) + \psi^{(r)}(\boldsymbol{r}) \left| \frac{-\nabla^2}{2} - \frac{Z_l}{|r - R_l|} - \frac{Z_r}{|r - R_r|} \right| \psi^{(l)}(\boldsymbol{r}) + \psi^{(r)}(\boldsymbol{r}) \right\rangle}{\left\langle \psi^{(l)}(\boldsymbol{r}) + \psi^{(r)}(\boldsymbol{r}) \middle| \psi^{(l)}(\boldsymbol{r}) + \psi^{(r)}(\boldsymbol{r}) \right\rangle} \tag{4.52}$$

All the integrals can be done analytically. First we break define the "Coulomb" integrals

$$\begin{aligned} H_{ll} &= \left\langle \psi^{(l)} \middle| \hat{H} \middle| \psi^{(l)} \right\rangle \\ H_{rr} &= \left\langle \psi^{(r)} \middle| \hat{H} \middle| \psi^{(r)} \right\rangle. \end{aligned} \tag{4.53}$$

the bond (or resonance, or hopping) integral

$$H_{lr} \equiv \left\langle \psi^{(l)} \middle| \hat{H} \middle| \psi^{(r)} \right\rangle \tag{4.54}$$

and the overlap integral,

$$S_{lr} \equiv \left\langle \psi^{(l)} \middle| \psi^{(r)} \right\rangle. \tag{4.55}$$

With this notation, we have

$$E \equiv \frac{H_{ll} + H_{rr} + H_{lr} + H_{lr}^*}{2 + S_{lr} + S_{lr}^*} \tag{4.56}$$

We can evaluate these integrals by using prolate spheroidal coordinates, Eq. (4.4). As an example, the overlap integral (S_{lr}) can be evaluated as

$$\int \psi^{(l)}(\boldsymbol{r})\,\psi^{(r)}(\boldsymbol{r})\,d\boldsymbol{r} = \int \sqrt{\frac{Z_l^3}{\pi}}e^{-Z_l|\boldsymbol{r}-\boldsymbol{R}_l|}\sqrt{\frac{Z_r^3}{\pi}}e^{-Z_r|\boldsymbol{r}-\boldsymbol{R}_r|}d\boldsymbol{r}$$

$$= \frac{\sqrt{Z_l^3 Z_r^3}}{\pi}\int e^{-\frac{Z_l R}{2}(\xi+\eta)}e^{-\frac{Z_r R}{2}(\xi-\eta)}d\boldsymbol{r}$$

$$= \frac{\sqrt{Z_l^3 Z_r^3}}{\pi}\int_1^\infty\int_{-1}^1\int_0^{2\pi} e^{-\frac{R}{2}(Z_l+Z_r)\xi}e^{-\frac{R}{2}(Z_l-Z_r)\eta}\left(\frac{R^3(\xi^2-\eta^2)}{8}\right)d\phi\,d\eta\,d\xi$$

$$= \frac{\sqrt{Z_l^3 Z_r^3}}{\pi}\left(\frac{2\pi R^3}{8}\right)\int_1^\infty e^{-\frac{R}{2}(Z_l+Z_r)\xi}\int_{-1}^1 e^{-\frac{R}{2}(Z_l-Z_r)\eta}\left(\xi^2-\eta^2\right)d\eta\,d\xi$$

$$= \frac{R^3\sqrt{Z_l^3 Z_r^3}}{4}\int_1^\infty e^{-\frac{R}{2}(Z_l+Z_r)\xi}\left(\begin{array}{l}\left[\dfrac{-2}{R(Z_l-Z_r)}e^{-\frac{R}{2}(Z_l-Z_r)\eta}\right]_{-1}^1\xi^2 \\[2mm] -\left[e^{-\frac{R}{2}(Z_l-Z_r)\eta}\left(\dfrac{x^2}{\frac{-R}{2}(Z_l-Z_r)}-\dfrac{2x}{\left(\frac{-R}{2}(Z_l-Z_r)\right)^2}+\dfrac{2}{\left(\frac{-R}{2}(Z_l-Z_r)\right)^3}\right)\right]_{-1}^1\end{array}\right)d\xi$$

$$= \frac{R^3\sqrt{Z_l^3 Z_r^3}}{4}\frac{-2}{R(Z_l-Z_r)}\int_1^\infty e^{-\frac{R}{2}(Z_l+Z_r)\xi}\left(\begin{array}{l}\left[e^{-\frac{R}{2}(Z_l-Z_r)\eta}\right]_{-1}^1\xi^2 \\[2mm] -\left[e^{-\frac{R}{2}(Z_l-Z_r)\eta}\left(x^2+\dfrac{2x}{\left(\frac{R}{2}(Z_l-Z_r)\right)}+\dfrac{2}{\left(\frac{R}{2}(Z_l-Z_r)\right)^2}\right)\right]_{-1}^1\end{array}\right)d\xi$$

$$= \frac{-R^2\sqrt{Z_l^3 Z_r^3}}{2(Z_l-Z_r)}\int_1^\infty e^{-\frac{R}{2}(Z_l+Z_r)\xi}\left(\begin{array}{l}\left(e^{-\frac{R}{2}(Z_l-Z_r)}-e^{+\frac{R}{2}(Z_l-Z_r)}\right)\xi^2 \\[2mm] -\left[e^{-\frac{R}{2}(Z_l-Z_r)}\left(1+\frac{4}{R(Z_l-Z_r)}+\frac{8}{R^2(Z_l-Z_r)^2}\right)\right. \\[2mm] \left.-e^{\frac{R}{2}(Z_l-Z_r)}\left(1-\frac{4}{R(Z_l-Z_r)}+\frac{8}{R^2(Z_l-Z_r)^2}\right)\right]\end{array}\right)d\xi$$

$$= \frac{R^2\sqrt{Z_l^3 Z_r^3}}{(Z_l-Z_r)}\int_1^\infty e^{-\frac{R}{2}(Z_l+Z_r)\xi}\left(\begin{array}{l}\sinh\left(\frac{R}{2}(Z_l-Z_r)\right)\xi^2+\cosh\left(\frac{R}{2}(Z_l-Z_r)\right)\frac{4}{R(Z_l-Z_R)} \\[2mm] +\sinh\left(\frac{R}{2}(Z_l-Z_r)\right)\left(1+\frac{8}{R^2(Z_l-Z_r)^2}\right)\end{array}\right)d\xi \qquad (4.57)$$

$$= \frac{-R^2\sqrt{Z_l^3 Z_r^3}}{2(Z_l-Z_r)}\left(\begin{array}{l}e^{-\frac{R}{2}(Z_l+Z_r)}\left(\dfrac{2}{\left(\frac{R}{2}(Z_l+Z_r)\right)^3}+\dfrac{2}{\left(\frac{R}{2}(Z_l+Z_r)\right)^2}+\dfrac{1}{\frac{R}{2}(Z_l+Z_r)}\right)\left(\sinh\left(\frac{R}{2}(Z_l-Z_r)\right)\right) \\[4mm] +e^{-\frac{R}{2}(Z_l+Z_r)}\left(\dfrac{1}{\frac{R}{2}(Z_l+Z_r)}\right)\left(\begin{array}{l}\cosh\left(\frac{R}{2}(Z_l-Z_r)\right)\frac{4}{R(Z_l-Z_R)} \\ +\sinh\left(\frac{R}{2}(Z_l-Z_r)\right)\left(1+\frac{8}{R^2(Z_l-Z_r)^2}\right)\end{array}\right)\end{array}\right)$$

If we had done this for the case $Z_l = Z_r$, then we would have obtained

$$S_{lr} \equiv e^{-ZR}\left(1+ZR+\tfrac{1}{3}(ZR)^2\right). \qquad (4.58)$$

Once we evaluate all the integrals, we obtain an approximate potential energy curve, which is the highest-energy curve in Figure 4.6. How can we improve this curve? Note, for instance, that for very small R, the united atom limit is more appropriate, and so

the wave functions contributing to our orbital should have atomic charges very close to two. From this we infer that just as in atoms, allowing the charges on the molecular orbitals to be determined by the variational principle (as opposed to rigorously identical to the atomic charges on the atoms in question) will lower the energy. Finkelstein and Horowitz performed just this procedure, and the energy curve they obtained is shown in the next figure. Note that the Finkelstein-Horowitz treatment produces a very accurate bond length.
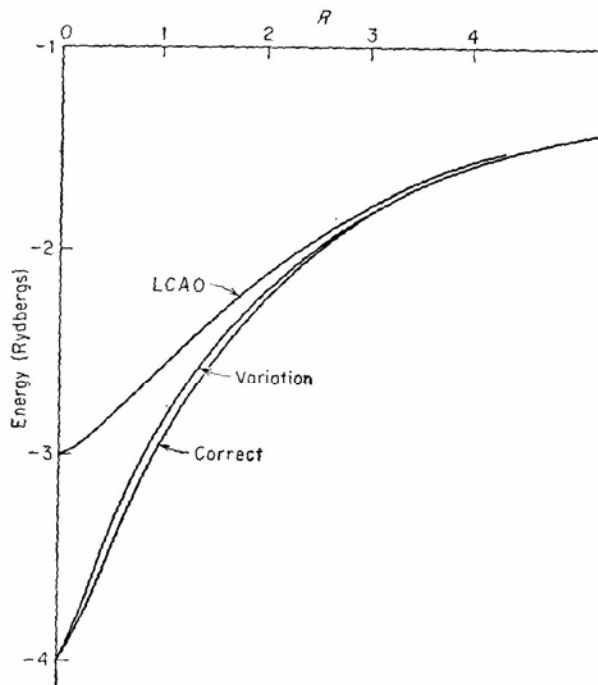
FIG. 2-2. Comparison of LCAO, variation, and correct energies for $1\sigma_g$ state of H_2^+.

Figure 4.6: Energy curves for H_2^+ (nuclear-nuclear repulsion is not included). The LCAO curve comes from Eq. (4.56), varying the effective nuclear charge gives the next curve, and the "correct" curve is obtained with subsequent corrections (e.g., polarization functions), suitably applied. Taken fron J. C. Slater's <u>Quantum Theory of Molecules and Solids vol. 1</u> (McGraw-Hill, New York, 1963).

Finally, recalling our treatment of the non-crossing rule, it is clear that "higher" σ_g states will interact with the ground state of our system, and the "repulsion" between these states will tend to lower the energy of the ground state. A simple and important correction is called due to so-called "polarization" functions, whereby we take the wave function to have the form

$$\psi\left(\boldsymbol{r}\right) = c_{1s}\left(\psi_{1s}^{(l)}\left(\boldsymbol{r}\right) + \psi_{1s}^{(r)}\left(\boldsymbol{r}\right)\right) + c_{2p}\left(\psi_{2p_z}^{(l)}\left(\boldsymbol{r}\right) - \psi_{2p_z}^{(r)}\left(\boldsymbol{r}\right)\right). \tag{4.59}$$

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Such a function was considered by Dickenson, who obtained the energy of H_2^+ (near equilibrium) to within .006 Hartree. We can approximate the amount of "2p" character in H_2^+ as

$$\frac{|c_{2p}|^2}{|c_{1s}|^2 + |c_{2p}|^2} = \frac{|c_{2p}|^2}{|c_{1s}|^2 \left(1 + \frac{|c_{2p}|^2}{|c_{1s}|^2}\right)} = \frac{|c_{2p}|^2}{|c_{1s}|^2} \left(1 - \frac{|c_{2p}|^2}{|c_{1s}|^2} + \left(\frac{|c_{2p}|^2}{|c_{1s}|^2}\right)^2 - \cdots\right) \tag{4.60}$$

where the second equality follows from the binomial theorem. Using the results from Table 4.1, we find that lowest-energy σ-bonding orbital in H_2^+ has about 1.8% 2p character (and 98.2 % 1s character). This is consistent with the fact that the 2p orbital is very high in energy and mixing too much of a high-energy orbital with the low-energy 1s orbital is not likely to be favorable.

Also, note that the optimum effective nuclear charge for the $2p$ orbitals is larger than the optimum nuclear charge for the 1s orbital. Because the 2p orbital is significantly larger than the 1s orbital, for a given bond length, R, the atoms, when viewed from the characteristic length scale of the 2p orbital, are "relatively close together." Thus, for the 2p orbital, the molecule more strongly resembles the united atom limit. The 1s orbital is quite small, and viewed at the characteristic length scale of these compact orbitals, the molecule more strongly resembles the separated atom limit. Thus, the effective nuclear charge for the 2p orbitals is larger (it is almost halfway to the united-atom value) than the effective nuclear charge of the 1s orbitals (which is closer to the separated-atom value). More generally, the optimum effective nuclear charge resembles the united-atom limit more and more strongly as the principle quantum number of the orbital increases.

Why is including the 2p orbital so important for describing the bond strength (dissociation energy) of H_2^+? In inspecting Figure 4.7, we observe that as we increase the amount of the 2p orbital that we mix with the 1s orbital, the orbital becomes more and more "polarized" towards the other atom. That is, the orbitals[13]

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[13]   In general, we need to mix in more than just the $2p_z$ atomic orbital. We also need to mix in *all* the orbitals with the appropriate symmetry for a σ-molecular orbital. (Thus, we must mix in *all* the orbitals which have no angular momentum about the z-axis.) The general form is then

$$\psi^{(l)}(\boldsymbol{r}) = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} c_{n,l} \psi_{n,l,m=0}^{(l)}(\boldsymbol{r})$$

$$\psi^{(r)}(\boldsymbol{r}) = \sum_{n=1}^{\infty} \sum_{l=0}^{n-1} c_{n,l} (-1)^l \psi_{n,l,m=0}^{(r)}(\boldsymbol{r})$$

$$\psi^{(l)}(\boldsymbol{r}) = \sqrt{1 - p^2}\,\psi_{1s}^{(l)}(\boldsymbol{r}) + \sqrt{p^2}\,\psi_{2p_z}^{(l)}(\boldsymbol{r})$$
$$\psi^{(r)}(\boldsymbol{r}) = \sqrt{1 - p^2}\,\psi_{1s}^{(r)}(\boldsymbol{r}) - \sqrt{p^2}\,\psi_{2p_z}^{(r)}(\boldsymbol{r}),$$

(4.61)

which have a fractional contribution from the 2p orbital of p, point at each other more strongly than the unpolarized orbitals (with $p = 0$).[14] Since polarized orbitals overlap more strongly, this increases the strength of the bond. (On the other hand, the 2p orbital is rather high in energy, so mixing too much 2p character into the wave function is not favorable. The Dickenson wave function makes this delicate trade-off between high overlap (good) and mixing in high-energy orbitals (bad).

Several other points about the H_2^+ system bear mention. First of all, we should note what will we will find to be general principles, applicable to many molecules (not just the hydrogen molecule ion):

- simple linear combinations of two atomic orbitals rarely gives satisfactory answers.

- the molecular geometry is usually obtained very accurately as soon as we use the variational principle to optimize the effective nuclear charges of the

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where $\psi_{n,l,m=0}^{(l)}(\boldsymbol{r})$ is the atomic orbital, centered on the left atom, with principle quantum number n, orbital angular momentum quantum number l, and magnetic quantum number $m = 0$ (so there is no orbital angular momentum about the z-axis. Thus, making an accurate description requires us to include not only the $2p_z$ orbital, but also the $2s$ orbital; the $3s$, $3p_z$, and $3d_{z^2}$ orbitals; the $4s$, $4p_z$, $4d_{z^2}$, and $4f_{z^3}$ orbitals; . . . .. Even if we do this, we will not get *exactly* the right energy, because we have to include the continuum orbitals corresponding the unbound (positive-energy) states of the atoms. However, we will get a very accurate energy from an expansion like the one listed in this footnote. If we use an expansion like this one, we do not really need to consider effective nuclear charges for all the orbitals, because mixing many orbitals with the same l but different n gives a good model for the position-dependence of the effective nuclear charge. (Consider that the 2s orbital ($\sim e^{-Zr/2}$) falls off more slowly than the 1s orbital ($\sim e^{-Zr}$), and the 3s orbital ($\sim e^{-Zr/3}$) more slowly still. As one moves away from the nucleus, the relative contribution of the 1s orbital (which is largest at the nucleus) decreases, and the relative contributions of the 2s and 3s orbitals (with their reduced rate of exponential decay) begins to dominate. This effectively simulates the behavior of a position-dependent effective nuclear charge, $e^{-\zeta(r)r}$.) When one truncates the expansion in terms of atomic orbitals, using effective nuclear charges is very helpful, especially for reproducing the equilibrium bond length.

[14] These are rather like sp hybrid orbitals, then, though the amount of "p" orbital that is being mixed in is much less than it is in a system like acetylene, because there the 2s and 2p orbitals have roughly similar energies.

atomic orbitals. The optimal values for the effective nuclear charges will like between their values for the united-atom and separated atom limits. Thus, for H_2^+, we have that

$$\underset{\text{atom}}{\zeta_{\text{united}}} = 2 > \zeta_{2p} > \zeta_{1s} > 1 = \underset{\text{atoms}}{\zeta_{\text{separated}}} \tag{4.62}$$

In general the effective nuclear charge of orbitals increases as the principle quantum number of the orbital increases.

- In order to obtain an accurate approximation to the dissociation energy (i.e. bond strength), we usually need polarization functions.

The exact potential energy curves for some low-lying states of the H_2^+ molecular are plotted in Figure 4.8. Table 4.1 summarizes the results for various wave functions for H_2^+.

Table 4.1. Summary of computational methods for H_2^+.

Method	Bond Length (Bohr)	Bond Dissociation Energy (Hartree)	Parameters
Linear Combination of Atomic Orbitals, Eq. (4.52)	2.53	.0647	(none)
Finkelstein and Horowitz Effective Nuclear Charges	2.04	.0827	$\zeta \equiv 1.23$
Dickenson Polarization functions, Eq. (4.59)	2.04	.0975	$\zeta_{1s} = 1.25$, $\zeta_{2p} = 1.43$ $\frac{c_{2p}}{c_{1s}} = .134$
Bates (exact)	2.04	.103	(none)
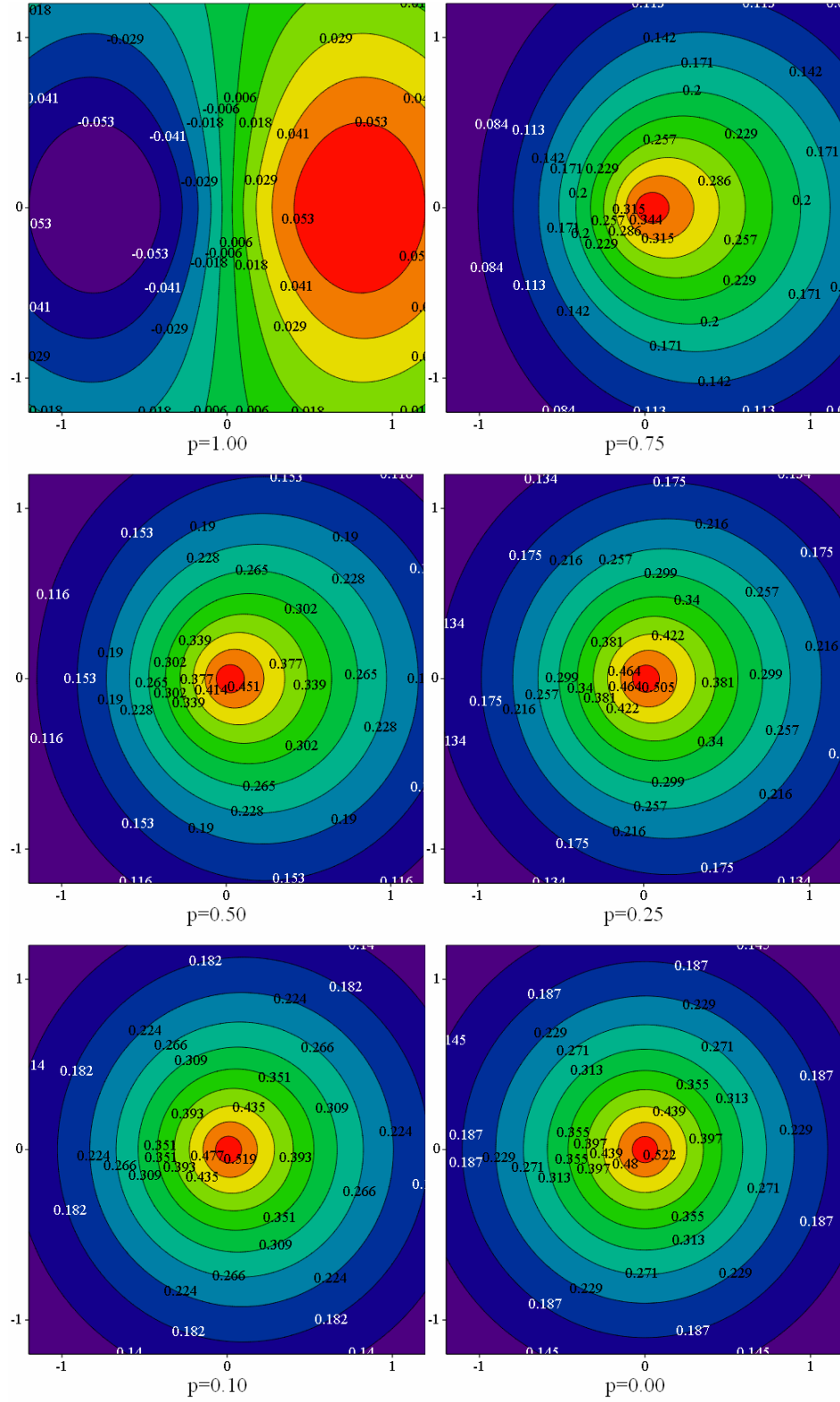
Figure 4.7. The effect of mixing the 2p orbital with the 1s orbital is plotted for different values of p in Eq. (4.61). p represents the fraction of the orbital that is "2p" in nature.
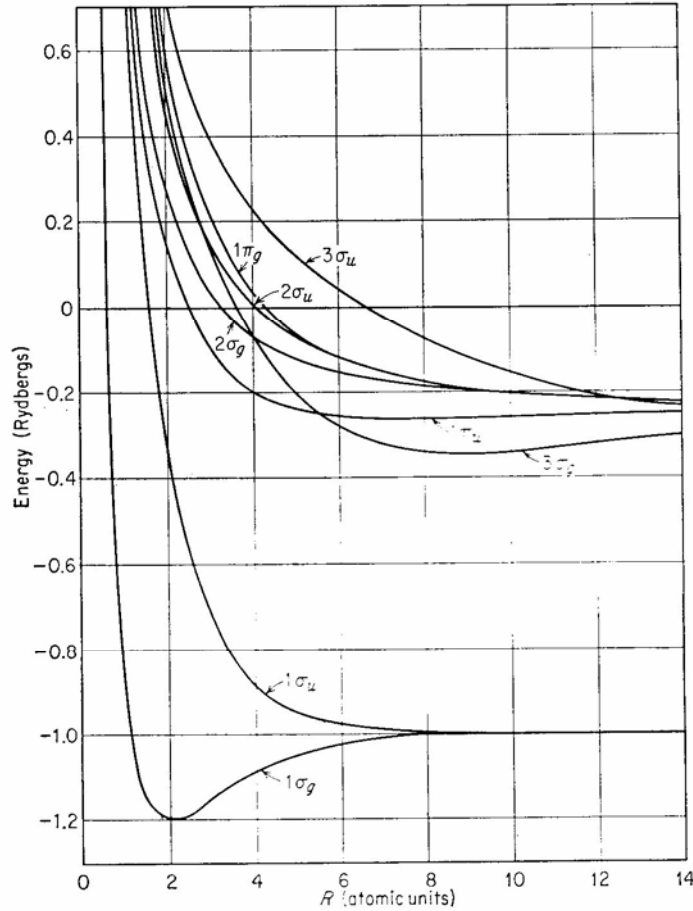
FIG. 1-5. Lowest energy levels of H_2^+ as function of internuclear distance, including internuclear repulsive energy.

Figure 4.8.   Exact potential energy curves for H_2^+. Taken from J. C. Slater's <u>Quantum Theory of Molecules and Solids vol. 1</u> (McGraw-Hill, New York, 1963).

VI. The Covalent Bond

From Fig. 4.8, we observe that in addition to the "bonding" molecular orbital for the Hydrogen molecule ion, there is the antibonding orbital, namely,

$$\Psi(\boldsymbol{r}) \equiv \psi_{1s}^{(l)}(\boldsymbol{r}) - \psi_{1s}^{(r)}(\boldsymbol{r}). \tag{4.63}$$

This state is repulsive at all values of the bond length—it has no stable geometry. To understand the difference between these two states, we consider the difference between their density and the density of "overlapping" hydrogen atoms,

$$\rho_{H_2^+}^{overlapping\ H's}(\boldsymbol{r}) \equiv \frac{\left|\psi_{1s}^{(l)}(\boldsymbol{r})\right|^2 + \left|\psi_{1s}^{(r)}(\boldsymbol{r})\right|^2}{2}$$
$$= \frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}. \tag{4.64}$$

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We have:[15]

$$\rho_{H_2^+}^{\substack{\text{bonding}\\ \text{antibonding}}} - \rho_{H_2^+}^{\text{overlapping } H's}(\boldsymbol{r}) \equiv \frac{\left(\psi_{1s}^{(l)}(\boldsymbol{r}) \pm \psi_{1s}^{(r)}(\boldsymbol{r})\right)^2}{2 \pm 2S_{lr}} - \frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}$$

$$= \frac{\left|\psi_{1s}^{(l)}(\boldsymbol{r})\right|^2 + \left|\psi_{1s}^{(r)}(\boldsymbol{r})\right|^2}{2(1 \pm S_{lr})} \pm \frac{\psi_{1s}^{(l)}(\boldsymbol{r})\psi_{1s}^{(r)}(\boldsymbol{r})}{1 \pm S_{lr}} - \frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}$$

$$= \frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}\left(\frac{1}{1 \pm S_{lr}} - 1\right) \pm \frac{\frac{Z^3}{\pi}e^{-Zr_l}e^{-Zr_r}}{1 \pm S}$$

$$\approx \frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}\left(\left(1 \mp S_{lr} + S_{lr}^2 \mp \cdots\right) - 1\right) \tag{4.65}$$

$$\pm \frac{Z^3}{\pi}e^{-ZR\left(\frac{r_l + r_r}{R}\right)}\left(1 \mp S_{lr} + S_{lr}^2 \mp \cdots\right)$$

$$\approx \frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}\left(\left(1 \mp S_{lr} + S_{lr}^2 \mp \cdots\right) - 1\right)$$

$$\pm \frac{Z^3}{\pi}e^{-ZR\xi}\left(1 \mp S_{lr} + S_{lr}^2 \mp \cdots\right)$$

and so, to first order, we have

$$\rho_{H_2^+}^{\text{bonding}} - \rho_{H_2^+}^{\text{overlapping } H's}(\boldsymbol{r}) \approx \frac{Z^3}{\pi}e^{-ZR\xi} - S\left(\frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}\right)$$

$$\rho_{H_2^+}^{\text{antibonding}} - \rho_{H_2^+}^{\text{overlapping } H's}(\boldsymbol{r}) \approx -\frac{Z^3}{\pi}e^{-ZR\xi} + S\left(\frac{\rho_{1s}^{(l)}(\boldsymbol{r}) + \rho_{1s}^{(r)}(\boldsymbol{r})}{2}\right). \tag{4.66}$$

Refer back to the figure on page 5. $e^{-ZR\xi}$ is clearly a curve that falls off exponentially as one moves away from the "bond". We recognize from Eq. (4.66), then, that

- The bonding molecular orbital takes electric charge from the vicinity of the atoms and places it between the atoms near the internuclear axis. Since the nuclei are "attracted" to this negative charge between the atoms, a chemical bond is formed.

- The antibonding orbital takes electric charge away from the vicinity of bonding axis and places it near the atoms. Because there are fewer electrons between the nuclei than in the "non-bonding" form, the internuclear repulsion energy takes over, and the molecule tends to dissociate.

From this insight, we say that a molecular orbital with a nodal plane that crosses, but does not contain, the internuclear axis is a "antibonding" orbital. A molecular orbital which has no such nodes is said to be a "bonding" orbital. In homonuclear diatomic molecules, $\sigma_g, \pi_u^{\pm}, \delta_g^{\pm}, \phi_u^{\pm}, \gamma_g^{\pm}, \ldots$ are the bonding orbitals and $\sigma_u, \pi_g^{\pm}, \delta_u^{\pm}, \phi_g^{\pm}, \gamma_u^{\pm}, \ldots$ are the antibonding orbitals. Note that if the m quantum number measuring angular momentum about the internuclear axis is even, then the symmetric gerade orbitals are bonding; if m is

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[15]   Here, we have included the normalization factor for the bonding $\left(\frac{1}{\sqrt{2(1+S_{lr})}}\right)$ and antibonding $\left(\frac{1}{\sqrt{2(1-S_{lr})}}\right)$ orbitals. As before S_{lr} is the orbital overlap, cf. Eq. (4.55).)

odd, then the ungerade orbitals are bonding. Why this is so is clear from the correlation diagrams on pages 19 and 20. For heteronuclear diatomics it is more difficult to discern the bonding orbitals, with one useful criterion being that *an orbital is antibonding if there is a nodal surface, crossing but not containing the internuclear axis, that persists to infinity* (as opposed to wrapping back around the atom like the innermost nodal surface(s) in a $2s$, $3s$, $3p$,… orbital).

VII. The Molecular Orbital Theory Idea

When we discussed many-electron atoms, we built our intuition on the one-electron atom. Simply stated, we took the wave functions from the one-electron atom and filled these orbitals in order of increasing energy. Ergo, Neon is assigned the electron configuration $1s^2 2s^2 2p^6$, with the orbitals of the Neon atom assumed to resemble the corresponding hydrogenic orbitals. For diatomic molecules the situation is similar. The Hamiltonian can be written as

$$\hat{H}_{\text{diatomic mol.}} = \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} - \frac{Z_l}{\left|r_i - R_l\right|} - \frac{Z_r}{\left|r_i - R_r\right|} + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|r_i - r_j\right|} \tag{4.67}$$

Substituting in the Hamiltonian of the one-electron molecule (cf. Eq. (4.1)), we have that

$$\hat{H}_{\text{diatomic mol.}} = \sum_{i=1}^{N} \hat{H}_{\substack{1\,el. \\ molecule}}\left(r_i\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|r_i - r_j\right|} \tag{4.68}$$

The one-electron Hamiltonian for a P-atom molecule is more often written as

$$\hat{h}\left(r_i\right) \equiv -\frac{\nabla_i^2}{2} - \sum_{\alpha=1}^{P}\frac{Z_\alpha}{\left|r_i - R_\alpha\right|}, \tag{4.69}$$

giving the common expression

$$\hat{H}_{molecule} = \sum_{i=1}^{N} \hat{h}\left(r_i\right) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\left|r_i - r_j\right|}. \tag{4.70}$$

Since $\hat{h}(r)$ is a one-electron Hamiltonian, we can find the associated orbitals and energy levels with relative ease. If we assume that the electron-electron repulsion does not change these orbitals in a qualitative way, we can build up a description of a many-electron molecule using the wave functions of the one-electron system. The occupied orbitals are then placed in a Slater determinant, forming an approximate wave function for the molecule. Such a method is the direct analogue of the method we used for atoms. This general approach to constructing wave functions for molecules is called the *molecular-orbital method* or sometimes just *molecular orbital (MO) theory.*

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Unfortunately, while we can find the solutions of a one-electron Hamiltonian computationally, this approach is less useful conceptually, because the wave functions do not have a simple form. For conceptual utility, we usually consider a specific form of the molecular-orbital (MO) method, using linear combinations of atomic orbitals (LCAO). Simply put, we observe that (usually, but not always[16]) molecules are closer to the separated atom limit than the united atom limit. So, for simplicity's sake, we write the molecular orbitals as a linear combination of the atomic orbitals. Thus, for a P-atom molecule, each molecular orbital has the form

$$\psi_i = \sum_{\alpha=1}^{P}\sum_{k=1}^{\infty} c_{\alpha k,i}\phi_{\alpha k}(\boldsymbol{r}) \tag{4.71}$$

where $\{\phi_{\alpha k}(\boldsymbol{r})\}$ are the atomic orbitals of atom α that are involved in chemical bonding.

VIII. Simple Molecular Orbital Theory for Homonuclear Diatomics

The discussion in the preceding section is abstract, and matters become clearer when we consider a simple case as an example. Let's consider homonuclear diatomic molecules in detail. In each case, we follow the molecular orbital method. Namely

i.   *decide which orbitals are occupied.*

ii.   *form linear combinations of atomic orbitals associated with those orbitals*

iii.   *form a Slater determinant wave function from those orbitals*

iv.   *analyze the properties of the system.*

A. H$_2$ (2 electrons)

i.   The correlation diagram in figure 4.4 is appropriate for a homonuclear diatomic molecule. The lowest-energy orbital is the σ_g orbital. Thus, the first two electrons go into this orbital.

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[16]   Historically there was some interest in forming molecular wave functions using only orbitals centered on a few of the atoms in the system. This approach has fallen into disuse. One may argue, however, that hydrides of heavy atoms are better described by the united-atom limit, with the hydrogen atom "buried" in the electron cloud of the larger atom.

ii. Looking at the separated atom limit of the first σ_g orbital, we surmise that this orbital can be approximately described as a linear combination between the 1s orbitals. Thus, we have that

$$\psi_{\sigma_g(1s)}(\boldsymbol{r}) \propto \phi_{1s}^{(l)}(\boldsymbol{r}) + \phi_{1s}^{(r)}(\boldsymbol{r}) \tag{4.72}$$

We use a proportionality sign in Eq. (4.72) because this linear combination of atomic orbitals is not normalized.

iii. The system can be described with a Slater determinant with the form

$$\Psi_{H_2} = \left| \psi_{\sigma_g(1s)}\alpha \quad \psi_{\sigma_g(1s)}\beta \right| \tag{4.73}$$

iv. Among the important properties of this system, we note that the molecule has no unpaired electrons. The ground state of H_2 is a singlet. In addition, we notice that there are two bonding electrons. We define the bond order as

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2} \tag{4.74}$$

The bond order of H_2 is one; H_2 has a single bond.

Homonuclear diatomic molecules that are isoelectronic to H_2 (i.e., two-electron homonuclear diatomic molecules) are similarly described.

B. He_2 (4 electrons)

i. Referring to figure 4.4, we see that we have a dilemma. When the bond length is small, the σ_g orbital constructed from the *2s* orbitals is lower in energy than the σ_u orbital constructed from the *1s* orbitals. Which orbital fills first? The *2s* orbital for He^+ has an energy that is $\frac{4}{2(1)} - \frac{4}{2(2)} = 1$ Hartree higher in energy than the *1s* orbital. (The actual splitting in orbital energy will be substantially larger, because the *2s* orbital is well-screened, and has a small effective nuclear charge.) 1 Hartree is 2625 kJ/mol, which is about ten times the strength of a typical chemical bond. We surmise that, for the energy scales accessible in chemical bonding, the σ_u orbital lies lower in energy.[17] Thus, for He_2. the electron configuration is $\sigma_g^2\sigma_u^2$.

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[17] This is not to say that one cannot conceive of *any* case where the $\sigma_g(2s)$ orbital would lie lower in energy than the $\sigma_u(1s)$ orbital. If one squeezes two Helium atoms very hard (providing the requisite thousands of kJ/mol with extraordinary pressure), then we will find that the $\sigma_g(2s)$ does dip below the

ii. Looking at the separated atom limit of the first σ_u orbital, we surmise that this orbital can be approximately described as a linear combination between the *1s* orbitals. Thus, we have that

$$\psi_{\sigma_u(1s)}(\boldsymbol{r}) \propto \phi_{1s}^{(l)}(\boldsymbol{r}) - \phi_{1s}^{(r)}(\boldsymbol{r}) \tag{4.75}$$

We use a proportionality sign in Eq. (4.72) because this linear combination of atomic orbitals is not normalized.

iii. The system can be described with a Slater determinant with the form

$$\Psi_{He_2} = \left| \psi_{\sigma_g(1s)}\alpha \quad \psi_{\sigma_g(1s)}\beta \quad \psi_{\sigma_u(1s)}\alpha \quad \psi_{\sigma_u(1s)}\beta \right| \tag{4.76}$$

iv. Among the important properties of this system, we note that the molecule has no unpaired electrons. The ground state of He_2 is a singlet. The bond order is

$$\text{bond order} = \frac{2-2}{2} = 0 \tag{4.77}$$

There is no covalent bond in He_2, which is reflected in the fact that He_2 forms only a very weakly bound "van der Waal's dimer."

C. Li$_2$ (6 electrons)

i. Referring to figure 4.4, the electron configuration is $\sigma_g^2 \sigma_u^2 \sigma_g^2$.

ii. Looking at the separated atom limit of the second σ_g orbital, we surmise that this orbital can be approximately described as a linear combination between the *2s* orbitals. Thus, we have that

$$\psi_{\sigma_g(2s)}(\boldsymbol{r}) \propto \phi_{2s}^{(l)}(\boldsymbol{r}) + \phi_{2s}^{(r)}(\boldsymbol{r}) \tag{4.78}$$

iii. The system can be described with a Slater determinant with the form

$$\Psi_{Li_2} = \left| \psi_{\sigma_g(1s)}\alpha \quad \psi_{\sigma_g(1s)}\beta \quad \psi_{\sigma_u(1s)}\alpha \quad \psi_{\sigma_u(1s)}\beta \quad \psi_{\sigma_g(2s)}\alpha \quad \psi_{\sigma_g(2s)}\beta \right| \tag{4.79}$$

iv. The ground state of Li_2 is a singlet. The bond order is

$$\text{bond order} = \frac{4-2}{2} = 1 \tag{4.80}$$

Li_2 has a single bond.

$\sigma_u(1s)$ in energy. (Such things could be observed, for example, in nuclear fusion, where atoms are "smashed together" with extraordinary force.)

D. Be$_2$ (8 electrons)

i.   Referring to figure 5.4, we have another dilemma. Is the $\pi_u^{\pm}$ orbital formed from the 2p orbitals lower in energy, or is the σ_u orbital formed from the *2s* orbitals lower in energy. The *2p* orbital of Be is about 350 kJ/mol higher in energy than the *2s* orbital. It would cost ca. 750 kJ/mol to promote a pair of electrons into this orbital, which far supercedes the energetic benefit accrued by forming a relatively weak (compared to a σ-bond) π-bond. The electron configuration is then $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2$.

ii.   Looking at the separated atom limit of the second σ_u orbital, we surmise that this orbital can be approximately described as a linear combination between the *2s* orbitals. Thus, we have that

$$\psi_{\sigma_u(2s)}(\boldsymbol{r}) \propto \phi_{2s}^{(l)}(\boldsymbol{r}) - \phi_{2s}^{(r)}(\boldsymbol{r}) \tag{4.81}$$

iii.   The system can be described with a Slater determinant with the form

$$\Psi_{Be_2} = \left| \psi_{\sigma_g(1s)}\alpha \quad \psi_{\sigma_g(1s)}\beta \quad \psi_{\sigma_u(1s)}\alpha \quad \psi_{\sigma_u(1s)}\beta \quad \psi_{\sigma_g(2s)}\alpha \quad \psi_{\sigma_g(2s)}\beta \quad \psi_{\sigma_u(2s)}\alpha \quad \psi_{\sigma_u(2s)}\beta \right| \tag{4.82}$$

iv.   The ground state of Be_2 is a singlet. The bond order is

$$\text{bond order} = \frac{4-4}{2} = 0 \tag{4.83}$$

As with He_2, Be_2 forms only a weakly bound van der Waals complex.

E. B$_2$ (10 electrons)

i.   Yet again we have a dilemma. Is the $\pi_u^{\pm}$ orbital formed from the *2p* orbitals lower in energy, or is the σ_g orbital formed from the *2p* orbitals lower in energy. Experimental studies indicate that the π-bonding orbitals are actually *more strongly bound*, which leads to the somewhat counterintuitive molecular orbital diagram shown in Figure 4.9.

The electron configuration is then $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \pi_u^+ \pi_u^-$.

The orbital shapes sketched in Figure 4.9 give some insight into why the $1\pi_u^{\pm}$ bonds are stronger than the $3\sigma_g$. Recall that, in H_2^+, p-orbitals oriented along the bond axis could mix with s-orbitals, thereby strengthening the bonds. Because the 2s orbitals and 2p orbitals have similar energy, here this effect is much more dramatic. Thus, in B_2, the $2\sigma_g$ and $3\sigma_g$ orbitals (that is, the second and third molecular orbital with σ_g symmetry) are formed with "sp

hybrid" orbitals. In the lower-lying $(2\sigma_g)$ orbital, the p function is mixed in such a way as to enhance overlap, and so the $2\sigma_g$ orbital is more strongly binding that one might otherwise expect. Having "used up" the favorable portions of the p-orbitals, however, the $3\sigma_g$ orbitals has *less overlap* (and is thus associated with a weaker bond) than would otherwise be expected. This is clear from the figure. This effect—which is usually called *sp* mixing—is so strong that the $3\sigma_g$ orbital actually becomes less binding that the $1\pi_u^\pm$ orbitals, in accord with the correlation diagram in Figure 4.4.
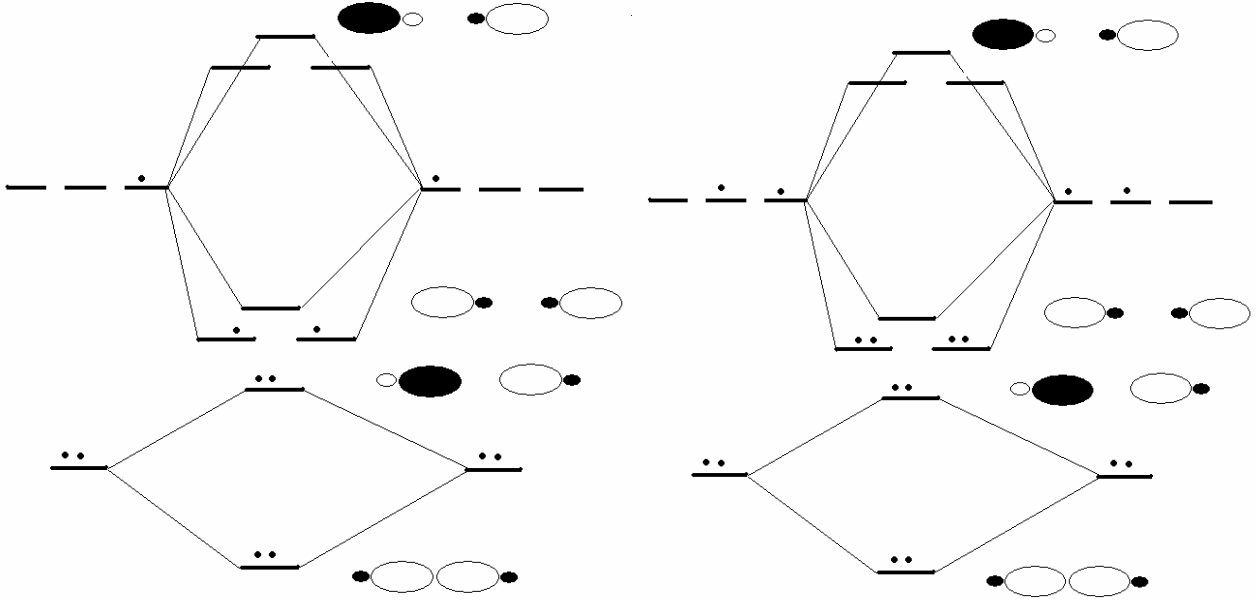
Figure 4.9. MO diagrams for B_2 and C_2.

   ii.   Looking at the separated atom limit of the second $\pi_u^\pm$ orbital, we surmise that this orbital can be approximately described as a linear combination between the *2p* orbitals. Thus, we have that

$$\psi_{\pi_u^\pm(2p)}(\boldsymbol{r}) \propto \phi_{2p_{\pm1}}^{(l)}(\boldsymbol{r}) + \phi_{2p_{\pm1}}^{(r)}(\boldsymbol{r}) \tag{4.84}$$

   iii.   The system can be described with a Slater determinant with the form

$$\Psi_{B_2} = \left| \psi_{\sigma_g(1s)}\alpha \quad \psi_{\sigma_g(1s)}\beta \quad \psi_{\sigma_u(1s)}\alpha \quad \psi_{\sigma_u(1s)}\beta \quad \psi_{\sigma_g(2s)}\alpha \quad \psi_{\sigma_g(2s)}\beta \quad \psi_{\sigma_u(2s)}\alpha \quad \psi_{\sigma_u(2s)}\beta \quad \psi_{\pi_u^+(2p)}\alpha \quad \psi_{\pi_u^-(2p)}\alpha \right| \tag{4.85}$$

   iv.   The ground state of B_2 is a triplet. The bond order is

$$\text{bond order} = \frac{6-4}{2} = 1 \tag{4.86}$$

F. C₂ (12 electrons)

i. Referring to Figure 4.9, it is clear that the electron configuration for C_2 is

The electron configuration is then $\sigma_g^2\sigma_u^2\sigma_g^2\sigma_u^2\left(\pi_u^+\right)^2\left(\pi_u^-\right)^2$. From this one can write the Slater determinant.

iv. The ground state of C_2 is a singlet. The bond order is

$$\text{bond order} = \frac{8-4}{2} = 2 \tag{4.87}$$

C_2 has a double bond.

It should be stated that, because the $\sigma_g\,(2p)\ (3\sigma_g)$ orbital is close in energy to the $\pi_u^\pm$ orbitals, one might worry that the benefit of forming a triplet state (recall that triplet states are usually lower in energy than singlet states, mostly because the Pauli exclusion principle intimates that same-spin electrons tend to avoid each other more readily and so repel each other less) would outweigh the slightly higher energy of the $3\sigma_g$ orbital, so that the electron configuration might be, for example,

$$\sigma_g^2\sigma_u^2\sigma_g^2\sigma_u^2\left(\pi_u^+\right)^2\pi_u^-\sigma_g \tag{4.88}$$

This is not observed: the electron configuration in Eq. (4.88) is a little higher than the ground state (albeit by only .00331 Hartree!).

G. N₂ (14 electrons)

i. The ordering of molecular orbital energy levels in N_2 is similar to that in C_2, with the third σ_g orbital being only a little bit higher in energy than the $\pi_u^\pm$ orbitals.

The electron configuration is then $\sigma_g^2\sigma_u^2\sigma_g^2\sigma_u^2\left(\pi_u^+\right)^2\left(\pi_u^-\right)^2\sigma_g^2$.

iv. The ground state of N_2 is a singlet. The bond order is

$$\text{bond order} = \frac{10-4}{2} = 3 \tag{4.89}$$

N_2 has a triple bond.

H. O₂ (16 electrons)

i. The orbitals that are occupied in O_2 is easily inferred from Figure 4.4, leading to the configuration

$$\sigma_g^2\sigma_u^2\sigma_g^2\sigma_u^2\sigma_g^2\left(\pi_u^+\right)^2\left(\pi_u^-\right)^2\pi_g^+\pi_g^- \tag{4.90}$$

However, note that I have written this electron configuration as if the $3\sigma_g$ orbital has a lower orbital energy that the $\pi_u^{\pm}$ orbitals. This is, in part, because as the atomic number increases, one moves towards the separated atom limit. From the correlation diagram from homonuclear diatomic molecules (Fig. 4.4), we see that as one moves towards the separated atom limit, *sp* mixing becomes less pronounced and the "intuitive" ordering of orbitals ($3\sigma_g$ before $1\pi_u^{\pm}$) is recovered.[18] The "cross-over" is right between Nitrogen and Oxygen.[19]

The electron configuration is then $\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \left(\pi_u^+\right)^2 \left(\pi_u^-\right)^2 \sigma_g^2$.

iv. The ground state of O_2 is a triplet. The bond order is

$$\text{bond order} = \frac{10-6}{2} = 2 \tag{4.91}$$

O_2 has a double bond.

The oxygen molecule does, in fact, have a triplet ground state. The simple description of this result using the molecular orbital picture was one of the first great success of molecular-orbital theory, and was important, historically, insofar as it led to the widespread acceptance of the molecular orbital theory over other competing pictures of molecular structure (e.g., the theory of resonance).

I.   F$_2$ (18 electrons)

i.   The orbitals that are occupied in F_2 is easily inferred from the correlation diagram, leading to the configuration

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[18]   Recall that the whole reason that *sp* mixing is favorable is because it enhances the overlap between the orbitals. As atoms move apart, the overlap becomes weaker, so the "benefit" gained from the enhanced overlap decreases. As the energetic payoff from the enhanced overlap decreases, it becomes less and less favorable to mix the higher-energy 2p orbitals with the 2s orbitals, and so the extent of *sp* mixing decreases. Thus, in Figure 4.4, the "intuitive" ordering of orbitals is recovered for large bond lengths.

[19]   You would expect that, in the third row of the periodic table, the large atomic size makes it so that the separated atom limit is an even better approximation than it is in the second row. This, in fact, is observed, and the σ_g orbital that is nominally formed from the 3p orbitals ($5\sigma_g$) is lower in energy than the $2\pi_u^{\pm}$ orbitals (also formed from the atomic 3p orbitals). For Al_2 the splitting is very small (about .00073 Hartree), so that for Al_2 (with six valence electrons) the preference for the triplet state over a singlet state gives a ground-state electronic configuration of $\left[Ne_2\right]\sigma_g^2 \sigma_u^2 \sigma_g \pi_u^{\pm}$, which is a triplet.

$$\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \sigma_g^2 \left(\pi_u^+\right)^2 \left(\pi_u^-\right)^2 \left(\pi_g^+\right)^2 \left(\pi_g^-\right)^2 \tag{4.92}$$

The ordering of molecular orbital energy levels in F_2 is similar to those in O_2.

iv. The ground state of F_2 is a singlet. The bond order is

$$\text{bond order} = \frac{10-8}{2} = 2 \tag{4.93}$$

F_2 has a single bond.

J.   Ne$_2$ (20 electrons)

i.   The orbitals that are occupied in Ne_2 is easily inferred from the correlation diagram, leading to the configuration

$$\sigma_g^2 \sigma_u^2 \sigma_g^2 \sigma_u^2 \sigma_g^2 \left(\pi_u^+\right)^2 \left(\pi_u^-\right)^2 \left(\pi_g^+\right)^2 \left(\pi_g^-\right)^2 \sigma_u^2 \tag{4.94}$$

iv.   The ground state of Ne_2 is a singlet. The bond order is

$$\text{bond order} = \frac{10-10}{2} = 0 \tag{4.95}$$

Ne_2 does not form a conventional covalently bound molecule, but only a van der Waals complex.

Ne_2 and He_2 are prototypical van der Waals complexes. However, though Be_2 is very weakly bound compared to usual covalent compounds (the bond is about 50 times weaker than the bond in H_2 and 10 times weaker than the bond in Li_2), the bond is much stronger (about 1000 times stronger than the bond in He_2 and 300 times stronger than the bond in Ne_2) than typical van der Waals molecules. This can be understood based on the orbital diagram in Figure 4.9. The effect of sp mixing is to make the $2\sigma_g$ bond much stronger (and the $3\sigma_g$ bond much weaker) than one would otherwise expect. Similarly, the $2\sigma_u$ is more antibonding than it would be without sp-mixing. However, the enhanced bonding of the $2\sigma_g$ is not totally cancelled out by increased antibonding in the $2\sigma_u$ orbital, and so the doubly occupied antibonding orbital doesn't "totally cancel out" the effects of the doubly occupied bonding orbital in Be_2.[20] The net effect is a stronger bond than normal van der Waals bonds.

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[20]   This can be partially explained by the very high energy of the $3\sigma_u$ orbital, which is required by the correlation diagram. (Recall that the $3\sigma_u$ orbital is associated with a 4p orbital in the united-atom limit.) In order for the $3\sigma_u$ orbital to be so strongly antibonding, the extent of sp-mixing in the antibonding orbitals must be such that the $2\sigma_u$ is not to strongly antibonding. This means that the

IX. What makes a Chemical Bond?

In the preceding section, we have established, and then used, all of the essential tools for understanding bonds in homonuclear diatomics and thus, more generally, homonuclear bonds. One key insight was obtained from Eq. (4.66) and the surrounding discussion: strong chemical bonds are associated with substantial overlap between the densities of the constituent atoms, along with the concomitant accumulation of binding density along the bond between the atoms. This key idea transfers to the case of heteronuclear molecules.

To explore the heteronuclear case in more detail, we consider the general case of a bond between an acid, denoted A, and a base, denoted B. The orbital that will be used by the acid to form the chemical bond will be denoted $\phi_A(\boldsymbol{r})$, while the orbital that will be used by the base will be denoted $\phi_B(\boldsymbol{r})$. We let ε_A and ε_B denote the orbital energies of $\phi_A(\boldsymbol{r})$ and $\phi_B(\boldsymbol{r})$, respectively. The orbital energy of an orbital is just the amount of energy that it takes to remove an electron from that orbital. Ergo, the orbital energy is minus the ionization potential of that orbital. If, as is usually the case, the orbitals involved in bonding are the highest occupied orbitals, then the orbital energy is just minus the ionization potential of the atom. Our notation is depicted pictorially in Figure 4.10.

Using the linear combination of atomic orbitals concept, the binding molecular orbital between A and B can be written

$$\psi(\boldsymbol{r}) = c_A \phi_A(\boldsymbol{r}) + c_B \phi_B(\boldsymbol{r}). \tag{4.96}$$

First, let us consider the case where $c_A = 1$. This corresponds to electron transfer from the base to the acid, leading (eventually) to the formation of an ionic bond

$$A + B \rightarrow A^- + B^+ \tag{4.97}$$

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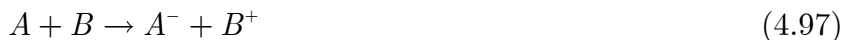
atomic orbitals contributing to the $3\sigma_u$ have to be "more directional" than they are shown as being in Fig. 4.9, so that the "overlap deficit" in formulae like Eq. (4.66) is stronger. As a consequence, the atomic orbitals composing the $2\sigma_u$ are less directional than those shown in Figure 4.9. Thus, the "increased overlap" of the bonding orbitals is not totally cancelled out by the "decreased bonding" of the antibonding orbitals. (Viewed differently, the energies of the σ_g-σ_u pairs in Fig. 4.9 are not symmetric about the energies of composing atomic orbitals. Since the $3\sigma_g$ is only weakly binding but the $3\sigma_u$ is very antibinding, the symmetry of the situation requires that the $2\sigma_g$ orbital be strongly binding while the $2\sigma_u$ orbital is comparatively weakly antibinding, yielding to the observed anomalous bond strength in Be_2.

The energy associated with this reaction—consequently, a primitive measure of the strength of the ionic bond—is

$$D_e^{ionic} = \varepsilon_B - \varepsilon_A. \tag{4.98}$$

What about the more general case of the covalent bond? To describe this, we need to write the Hamiltonian for the molecular orbital. The Hamiltonian for the molecular orbital will have a kinetic energy term, $-\frac{\nabla^2}{2}$, an attractive potential toward the nucleus of atom A, $v_A(\boldsymbol{r})$, and an attractive potential toward the nucleus of atom B, $v_B(\boldsymbol{r})$.[21] The molecular-orbital Hamiltonian can thus be approximated in terms of the atomic-orbital Hamiltonians, i.e.

$$\hat{h}(\boldsymbol{r}) = -\frac{\nabla^2}{2} + v_A(\boldsymbol{r}) + v_B(\boldsymbol{r}). \tag{4.99}$$

Since

$$\hat{h}_A \equiv -\frac{\nabla^2}{2} + v_A(\boldsymbol{r}) \tag{4.100}$$

is just the Hamiltonian for atom A, we have that

$$\left(-\frac{\nabla^2}{2} + v_A(\boldsymbol{r})\right)\psi_A(\boldsymbol{r}) = \varepsilon_A \psi_A(\boldsymbol{r}). \tag{4.101}$$

Similarly,

$$\left(-\frac{\nabla^2}{2} + v_B(\boldsymbol{r})\right)\psi_B(\boldsymbol{r}) = \varepsilon_B \psi_B(\boldsymbol{r}). \tag{4.102}$$

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[21] In general, $v_A(\boldsymbol{r})$ will not equal $\frac{-Z_A}{|\boldsymbol{r}-\boldsymbol{R}_A|}$, which would be the "bare" nuclear attraction towards the nucleus of atom A. Rather, from our discussion of atoms, we know that the valence electron in an atom will generally feel a position-dependent effective nuclear charge centered on the nucleus of atom A, $Z_{eff,A}(\boldsymbol{r}-\boldsymbol{R}_A)$. This effective nuclear charge could be determined, for example, from the Hartree-Fock procedure. Most generally, then, $v_A(\boldsymbol{r}) = \dfrac{-Z_{eff,A}(\boldsymbol{r}-\boldsymbol{R}_A)}{|\boldsymbol{r}-\boldsymbol{R}_A|}$, where $\boldsymbol{R}_A$ is understood to be the position of atom A.
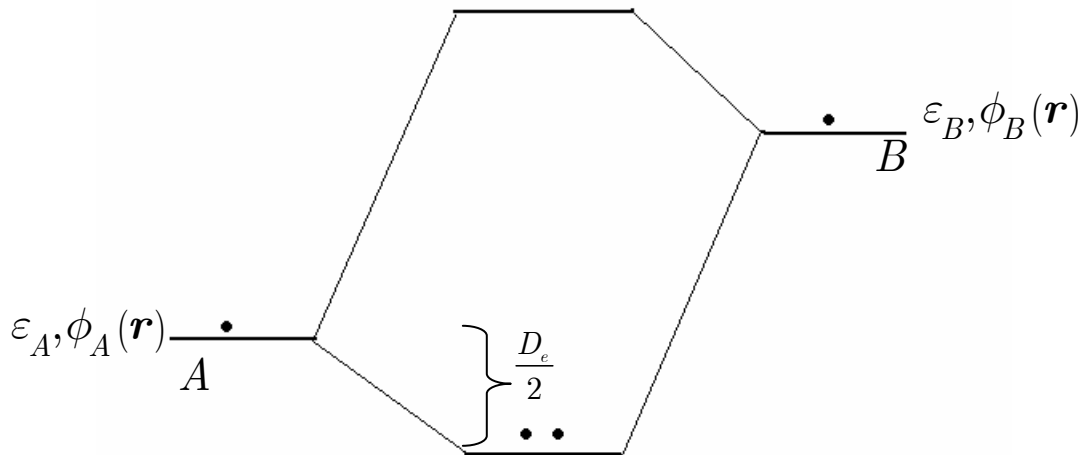
Figure 4.10. Binding in a heteronuclear diatomic molecule.

We now need to determine the coefficients of the atomic orbitals that contribute to the molecular orbital. We do this in the usual way. Specifically, we

1. **Start by writing the Schrödinger equation:**

$$\hat{h}\left(c_A\psi_A\left(\boldsymbol{r}\right)+c_B\psi_B\left(\boldsymbol{r}\right)\right)=E\left(c_A\psi_A\left(\boldsymbol{r}\right)+c_B\psi_B\left(\boldsymbol{r}\right)\right) \tag{4.103}$$

2. **Multiply on both sides by the orbital** $\psi_\alpha\left(\boldsymbol{r}\right)$ $\left(\alpha=A,B\right)$**; then integrate:**

$$\sum_{\beta=A,B}\left\langle\psi_\alpha\left|\hat{h}\right|\psi_\beta\right\rangle c_\beta=E\sum_{\beta=A,B}\left\langle\psi_\alpha|\psi_\beta\right\rangle c_\beta \tag{4.104}$$

From Eq. (4.104), it is clear that we need to solve the linear equations

$$\begin{bmatrix}\left\langle\psi_A\left|\hat{h}\right|\psi_A\right\rangle-E\left\langle\psi_A|\psi_A\right\rangle & \left\langle\psi_A\left|\hat{h}\right|\psi_B\right\rangle-E\left\langle\psi_A|\psi_B\right\rangle \\ \left\langle\psi_B\left|\hat{h}\right|\psi_A\right\rangle-E\left\langle\psi_B|\psi_A\right\rangle & \left\langle\psi_B\left|\hat{h}\right|\psi_B\right\rangle-E\left\langle\psi_B|\psi_B\right\rangle\end{bmatrix}\begin{bmatrix}c_A\\c_B\end{bmatrix}=0 \tag{4.105}$$

Next, note that because the atomic orbitals are normalized,

$$\left\langle\psi_A|\psi_A\right\rangle=\left\langle\psi_B|\psi_B\right\rangle=1 \tag{4.106}$$

In addition, we note that because $\psi_A\left(\boldsymbol{r}\right)$ is centered on atom A and $\psi_B\left(\boldsymbol{r}\right)$ is centered on atom B, the overlap between these orbitals will be rather small. Thus[22]

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[22] This approximation is surprising good. Indeed, owing to some flexibility in the way we can define the atomic orbitals (we can *define* them to be orthogonal, if we want to), we can consider this approximation to be exact. Even with the "conventional" definition of the atomic orbitals, this approximation will be

$$S_{AB} = \langle \psi_B | \psi_A \rangle = \int \psi_B^* (\boldsymbol{r}) \psi_A (\boldsymbol{r}) \, d\boldsymbol{r} \approx 0 \,. \tag{4.107}$$

With these substitutions, Eq. (4.105) takes the form of a typical eigenvalue problem, with

$$\begin{bmatrix} \langle \psi_A | \hat{h} | \psi_A \rangle - E & \langle \psi_A | \hat{h} | \psi_B \rangle \\ \langle \psi_B | \hat{h} | \psi_A \rangle & \langle \psi_B | \hat{h} | \psi_B \rangle - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = 0 \tag{4.108}$$

Now we examine the remaining integrals. First, using the definition of the molecular-orbital Hamiltonian (Eq. (4.99)) along with the eigenvalue condition for atom A (Eq. (4.101)), we have

$$\begin{aligned} \langle \psi_A | \hat{h} | \psi_A \rangle &= \left\langle \psi_A \left| -\tfrac{\nabla^2}{2} + v_A (\boldsymbol{r}) + v_B (\boldsymbol{r}) \right| \psi_A \right\rangle \\ &= \left\langle \psi_A \left| -\tfrac{\nabla^2}{2} + v_A (\boldsymbol{r}) \right| \psi_A \right\rangle + \langle \psi_A | v_B (\boldsymbol{r}) | \psi_A \rangle \\ &= \langle \psi_A | \varepsilon_A | \psi_A \rangle + \langle \psi_A | v_B (\boldsymbol{r}) | \psi_A \rangle \\ &= \varepsilon_A \langle \psi_A | \psi_A \rangle + \langle \psi_A | v_B (\boldsymbol{r}) | \psi_A \rangle \\ &= \varepsilon_A + \langle \psi_A | v_B (\boldsymbol{r}) | \psi_A \rangle . \end{aligned} \tag{4.109}$$

We note that because $v_B (\boldsymbol{r})$ is the attractive potential for atom B, it will be centered on atom B, with the consequence that the magnitude of $v_B (\boldsymbol{r})$ will be small on atom A, where $|\psi_A (\boldsymbol{r})|^2$ is large. Similarly, $|\psi_A (\boldsymbol{r})|^2$ will be small near atom B, where the magnitude of $v_B (\boldsymbol{r})$ is appreciable. Thus, since one of the terms in the integrand is always almost zero and the integral of a function that is everywhere very small is also small, we have that[23]

$$\langle \psi_A | v_B (\boldsymbol{r}) | \psi_A \rangle = \int |\psi_A (\boldsymbol{r})|^2 \, v_B (\boldsymbol{r}) \, d\boldsymbol{r} \approx 0 \,. \tag{4.110}$$

Performing a similar analysis for atom B, we can rewrite the eigenvalue problem as

$$\begin{bmatrix} \varepsilon_A - E & \langle \psi_A | \hat{h} | \psi_B \rangle \\ \langle \psi_B | \hat{h} | \psi_A \rangle & \varepsilon_B - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = 0 \,. \tag{4.111}$$

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very good whenever $\left| \langle \psi_B | \hat{h} | \psi_A \rangle \right| \gg \left| \langle \psi_B | \psi_A \rangle \right|$. That is, as long as the term we are neglecting is small compared to the term we are keeping, this approximation is justified. Because the norm (this is just a precise mathematical definition of the "size" of an operator) of $\hat{h}$ is substantially greater than one, it is clear that, in general, $\left| \langle \psi_B | \hat{h} | \psi_A \rangle \right| \gg \langle \psi_B | 1 | \psi_A \rangle$. For example, the fact that $v_A (\boldsymbol{r})$ and $v_B (\boldsymbol{r})$ diverge to $-\infty$ near the atomic nuclei is enough to infer the likely validity of this approximation.

[23] Again, this approximation will be acceptable whenever the size of the term we are neglecting is much smaller than the term we are keeping, so that $|\varepsilon_A| \gg \left| \langle \psi_A | v_B (\boldsymbol{r}) | \psi_A \rangle \right|$. This seems very plausible in this case.

The remaining integral we denote, in analogy to Hückel theory, as

$$\beta = \left\langle \psi_B \left| \hat{h} \right| \psi_A \right\rangle. \tag{4.112}$$

This integral is usually called the "resonance integral," though physicists and materials' chemists usually call β the "hopping integral," since it pertains to the likelihood that the molecular-orbital Hamiltonian will stimulate an electron to "hop" from an initial state on one atom, $\psi_A(\boldsymbol{r})$, to a final state on the other atom, $\psi_B(\boldsymbol{r})$. The same concept underlies the "electron pushing" idea, beloved by organic chemists, that is the foundation for the theory of resonance.

To approximate the value of the resonance integral, we perform the following manipulation:

$$
\begin{aligned}
\beta &= \left\langle \psi_B \left| \hat{h} \right| \psi_A \right\rangle \\
&= \left\langle \psi_B \left| -\tfrac{\nabla^2}{2} + v_A(\boldsymbol{r}) + v_B(\boldsymbol{r}) \right| \psi_A \right\rangle \\
&= \left\langle \psi_B \left| \tfrac{1}{2}\left(-\tfrac{\nabla^2}{2} + v_A(\boldsymbol{r})\right) + \tfrac{1}{2}\left(-\tfrac{\nabla^2}{2} + v_B(\boldsymbol{r})\right) + \tfrac{v_A(\boldsymbol{r}) + v_B(\boldsymbol{r})}{2} \right| \psi_A \right\rangle \\
&= \left\langle \psi_B \left| \tfrac{1}{2}\left(-\tfrac{\nabla^2}{2} + v_A(\boldsymbol{r})\right) \right| \psi_A \right\rangle + \left\langle \psi_B \left| \tfrac{1}{2}\left(-\tfrac{\nabla^2}{2} + v_B(\boldsymbol{r})\right) \right| \psi_A \right\rangle + \left\langle \psi_B \left| \tfrac{v_A(\boldsymbol{r}) + v_B(\boldsymbol{r})}{2} \right| \psi_A \right\rangle \\
&= \tfrac{1}{2}\left\langle \psi_B \left| \varepsilon_A \right| \psi_A \right\rangle + \tfrac{1}{2}\left\langle \left(-\tfrac{\nabla^2}{2} + v_B(\boldsymbol{r})\right)\psi_B \middle| \psi_A \right\rangle + \tfrac{1}{2}\left\langle \psi_B \left| v_A(\boldsymbol{r}) + v_B(\boldsymbol{r}) \right| \psi_A \right\rangle \\
&= \left(\tfrac{1}{2}\varepsilon_A S_{AB} + \tfrac{1}{2}\varepsilon_B S_{AB}\right) + \tfrac{1}{2}\left(\left\langle \psi_B \left| v_A(\boldsymbol{r}) \right| \psi_A \right\rangle + \left\langle \psi_B \left| v_B(\boldsymbol{r}) \right| \psi_A \right\rangle\right).
\end{aligned}
\tag{4.113}
$$

In the next to last line, we have used the fact that the atomic Hamiltonian is a Hermitian operator. The last term in Eq. (4.113) is particularly problematic, but we can see some general trends. First of all, since $v_A(\boldsymbol{r})$ and $v_B(\boldsymbol{r})$ are the potentials that bind electrons to atoms A and B respectively, we expect that $\left\langle \psi_B \left| v_A(\boldsymbol{r}) \right| \psi_A \right\rangle$ will be roughly proportional to the electron binding energy of atom A, ε_A. Next, if the overlap between the orbitals is very small, then $\psi_B(\boldsymbol{r})$ will be very small near atom A, and so $\left\langle \psi_B \left| v_A(\boldsymbol{r}) \right| \psi_A \right\rangle$ will also be small. Thus, we expect that $\left\langle \psi_B \left| v_A(\boldsymbol{r}) \right| \psi_A \right\rangle$ will be proportional to the overlap between the atomic orbitals, S_{AB}. Thus, we have

$$\left\langle \psi_B \left| v_A(\boldsymbol{r}) \right| \psi_A \right\rangle \propto \varepsilon_A S_{AB} \tag{4.114}$$

Wolfsberg and Helmolz argued that the constant of proportionality is about $\tfrac{3}{8}$, which gives[24]

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[24] Despite the fact this is called the Wolfsberg-Helmolz approximation, it seems to have been first proposed by Mulliken.

$$\left\langle \psi_B \left| v_A \left(\boldsymbol{r} \right) \right| \psi_A \right\rangle \approx \tfrac{3}{8} \varepsilon_A S_{AB}$$
$$\left\langle \psi_B \left| v_B \left(\boldsymbol{r} \right) \right| \psi_A \right\rangle \approx \tfrac{3}{8} \varepsilon_B S_{AB} \qquad \text{(Wolfsberg-Helmolz Approximation)} \qquad (4.115)$$

Inserting Eq. (4.115) into Eq. (4.113), we find that

$$\beta \approx \tfrac{7}{4} \left(\tfrac{\varepsilon_A + \varepsilon_B}{2} \right) S_{AB} \qquad (4.116)$$

Substituting into Eq. (4.111), we finally obtain[25]

$$\begin{bmatrix} \varepsilon_A - E & \beta \\ \beta^* & \varepsilon_B - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = 0$$

$$\begin{bmatrix} \varepsilon_A - E & \tfrac{7}{4} \left(\tfrac{\varepsilon_A + \varepsilon_B}{2} \right) S_{AB} \\ \tfrac{7}{4} \left(\tfrac{\varepsilon_A + \varepsilon_B}{2} \right) S_{AB}^* & \varepsilon_B - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = 0 \qquad (4.117)$$

As usual, we can find the eigenvalues, E, by requiring that Eq. (4.117) have a nontrivial solution. Thus, we have that

$$\begin{vmatrix} \varepsilon_A - E & \beta \\ \beta^* & \varepsilon_B - E \end{vmatrix} = 0 \qquad (4.118)$$

$$E^2 - \left(\varepsilon_A + \varepsilon_B \right) E + \varepsilon_A \varepsilon_B - \left| \beta \right|^2 = 0$$

Next, we solve (and manipulate) the quadratic equation, obtaining the energies of the bonding and antibonding orbital as

---

[25] The reader will probably recognize the similarity between this equation and the equations considred in Huckel theory. Indeed, the analysis here is essential a derivation of the "extended Hückel" approach (extended because no only π-bonds are considered). Given the number of uncertain approximations made in this approach, it is perhaps not too surprising that the "extended Hückel" theory does not give quantitatively accurate results. However, extended Hückel theory (and the related families of more sophisticated semiempirical theories) do give reliable intuitive pictures of chemical binding, as might be expected from this derivation: approximations are made, to be sure, but the approximations are well-motivated and *qualitatively* reasonable, even if they are not quantitatively rigorous. Much the same can be said about the results of extended Hückel calculations.

$$E = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\sqrt{\left(\varepsilon_A + \varepsilon_B\right)^2 - 4\left(\varepsilon_A \varepsilon_B - |\beta|^2\right)}}{2}$$

$$= \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\sqrt{\varepsilon_A^2 + 2\varepsilon_A \varepsilon_B + \varepsilon_B^2 - 4\varepsilon_A \varepsilon_B + 4|\beta|^2}}{2}$$

$$= \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\sqrt{\varepsilon_A^2 - 2\varepsilon_A \varepsilon_B + \varepsilon_B^2 + 4|\beta|^2}}{2}$$

$$= \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\sqrt{\left(\varepsilon_A - \varepsilon_B\right)^2 + 4|\beta|^2}}{2}$$

$$= \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\sqrt{\left(\varepsilon_A - \varepsilon_B\right)^2 \left[1 + \frac{4|\beta|^2}{\left(\varepsilon_A - \varepsilon_B\right)^2}\right]}}{2}$$

$$= \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\sqrt{\left(\varepsilon_A - \varepsilon_B\right)^2} \sqrt{1 + \frac{4|\beta|^2}{\left(\varepsilon_A - \varepsilon_B\right)^2}}}{2}$$

$$= \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{|\varepsilon_A - \varepsilon_B|}{2} \sqrt{1 + \frac{4|\beta|^2}{\left(\varepsilon_A - \varepsilon_B\right)^2}}$$

(4.119)

Next, we use the fact that, because $\varepsilon_B > \varepsilon_A$ (cf. Fig. 4.10), $|\varepsilon_A - \varepsilon_B| = \varepsilon_B - \varepsilon_A$. Then

$$E = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\varepsilon_B - \varepsilon_A}{2} \sqrt{1 + \frac{4|\beta|^2}{\left(\varepsilon_A - \varepsilon_B\right)^2}} \tag{4.120}$$

Because β depends on the overlap integral, S_{AB}, which is rather small, for a heteronuclear diatomic molecule it is usually true that $4|\beta|^2 \ll \left(\varepsilon_A - \varepsilon_B\right)^2$.[26] Consequently, we can use the binomial series for the square root[27] to obtain

---

[26]   This is clearly *not* true for a homonuclear diatomic molecule, where $\varepsilon_A = \varepsilon_B$. In that case, however, we have exactly the energies

$$E = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\varepsilon_B - \varepsilon_A}{2} \left(\frac{2|\beta|}{\varepsilon_B - \varepsilon_A}\right) = \frac{\varepsilon_A + \varepsilon_A}{2} \pm |\beta|$$

$$= \varepsilon_A \pm |\beta|$$

and we infer that the binding energy of the molecule is about $2|\beta|$ (because we have moved two electrons from atomic orbitals with energy $\varepsilon_A = \varepsilon_B$ to a binding molecular orbital with energy $\varepsilon_A - |\beta|$). Referring to Eq. (4.116), we infer that a strong orbital overlap leads to favorable binding, in concord with our earlier conclusions about binding in homonuclear diatomic molecules.

[27]   Recall that the general binomial series is

$$(1 + x)^k = 1 + kx + \frac{k(k-1)}{2}x^2 + \frac{k(k-1)(k-2)}{3!}x^3 + \frac{k(k-1)(k-2)(k-3)}{4!}x^4 + \cdots.$$

$$E \approx \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\varepsilon_B - \varepsilon_A}{2}\left(1 + \frac{2|\beta|^2}{\left(\varepsilon_A - \varepsilon_B\right)^2}\right)$$

$$\approx \frac{\varepsilon_A + \varepsilon_B}{2} \pm \frac{\varepsilon_B - \varepsilon_A}{2} \pm \frac{\left(\varepsilon_B - \varepsilon_A\right)}{\left(\varepsilon_A - \varepsilon_B\right)^2}|\beta|^2 \qquad (4.121)$$

$$\approx \begin{cases} \varepsilon_A - \dfrac{|\beta|^2}{\varepsilon_B - \varepsilon_A} & \text{from "-" sign} \\[4mm] \varepsilon_B + \dfrac{|\beta|^2}{\varepsilon_B - \varepsilon_A} & \text{from "+" sign} \end{cases}$$

The binding energy, relative to the *ionic* configuration where both electrons are located on the acidic fragment, is then given by

$$D_e \approx 2\left(\frac{|\beta|^2}{\varepsilon_B - \varepsilon_A}\right) \approx \frac{49 S_{AB}}{32}\frac{\left(\varepsilon_A + \varepsilon_B\right)^2}{\varepsilon_B - \varepsilon_A} \qquad (4.122)$$

where we have used the Wolfsberg-Helmolz formula, Eq. (4.116), in obtaining the second approximation. We conclude that strong bonds in heteronuclear diatomics are associated with

- a larger overlap, S_{AB} between the atomic orbitals composing the bond.
- orbitals that are close together in energy as compared to the average energy of the orbitals, so that $\varepsilon_B - \varepsilon_A \ll \left(\dfrac{\varepsilon_A + \varepsilon_B}{2}\right)^2$.

Based on these insights, we can draw several conclusions about chemical binding.

- covalent bonds are formed between atomic orbitals with similar energies. When two orbitals have vastly different energies, the bond strength from Eq. (4.122) will be small. In this case, the bonding is best described as being *ionic*; electrons are transferred from the base to the acid, rather than shared between them. This explains why the bonds in a species like UO_2 do not involve the $2p$ orbitals of the Uranium atom; the $2p$ orbitals of the Uranium atom are very low in energy, so that $\varepsilon_B - \varepsilon_A$ is small. (The $2p$ orbitals in Uranium are also very compact, so the orbital overlap with the oxygen $2p$ orbitals would be small also.) This also explains why

---

Then

$$\sqrt{1+x} = (1+x)^{1/2} \approx 1 + \tfrac{1}{2}x - \tfrac{1}{8}x^2 - \cdots.$$

The binomial series converges whenever $-1 < x < 1$ and it converges rapidly whenever $0 \approx |x| \ll 1$.

the bonds between atoms in the same row of the periodic table tend to be stronger: these atoms have similar electronic structure, so they have similar orbital energies.

- chemical bonds are formed between valence orbitals. This is mostly because the orbital overlap between core orbitals is very small.[28]

- diffuse orbitals form weaker bonds than compact orbitals, because the overlap between diffuse orbitals is weak. This explains why the alkali metal dimers (the outermost s orbital in these atoms is very diffuse) form weak bonds, even though the orbital energies of all the alkali metal atoms[29] is rather similar. This also explains why the bonds between second-row atoms (B-F) are usually stronger than those between third-row atoms (Al-Cl).[30] It also explains why bonds between p-block elements (the p orbitals are highly directional, and thus conducive to large overlap) are stronger than those between s block elements.

In a homonuclear diatomic, we have that $|c_A| = |c_B|$. This is consistent with the interpretation that the electron is shared equally between the two atoms. In the heteronuclear case, we have that $|c_A| > |c_B|$, consistent with the fact that there is partial ionic character to the bond due to partial electron transfer from the base to the acid.

We can determine the coefficients of $\psi_A(\mathbf{r})$ and $\psi_B(\mathbf{r})$ by finding the nontrivial solutions to the equation (cf. Eq. (4.117))

$$\begin{bmatrix} \varepsilon_A - E & \beta \\ \beta^* & \varepsilon_B - E \end{bmatrix} \begin{bmatrix} c_A \\ c_B \end{bmatrix} = 0. \tag{4.123}$$

Using the first equation, we have that

---

[28] Core orbitals feel a large effective nuclear charge, and are thus compact. As such, they are localized on their "home" atom, and have very little amplitude away from this atom. Consequently, they have a poor overlap with orbitals on different atoms.

[29] Recall that the orbital energy of the highest-occupied molecular orbital can be associated with minus the ionization potential of that orbital.

[30] Beware! When a quantum chemist talks about a second row atom, she normally means the Na-Ar row. First row atoms are usually considered Li-Ne, and H and He are considered "light atoms." (Everything heavier is a "heavy atom" to a quantum chemist; probably it is safe to say that a *real* heavy atom (e.g., an actinide) is just an "impossible atom" to a quantum chemist.) I've tried to use the more "official" language here—using the IUPAC numbering of the rows of the periodic table. But I—and many other quantum chemists—will often lapse into my wayward tendencies to call Li-Ne the "first row of the periodic table."

$$c_A = -\frac{\beta}{\varepsilon_A - E} c_B \tag{4.124}$$

Next, from Eq. (4.121), we have that for the binding orbital,

$$c_A \approx -\frac{\beta}{\varepsilon_A - \left(\varepsilon_A - \dfrac{|\beta|^2}{\varepsilon_B - \varepsilon_A}\right)} c_B \tag{4.125}$$

$$\approx \frac{\varepsilon_B - \varepsilon_A}{\beta^*} c_B$$

and then, from the Wolfsberg-Helmolz relation, we have that

$$c_A \approx \frac{\varepsilon_B - \varepsilon_A}{\frac{7}{4}\left(\frac{\varepsilon_A + \varepsilon_B}{2}\right) S_{AB}} c_B \tag{4.126}$$

$$\approx \frac{4}{7 S_{AB}^*} \frac{\varepsilon_B - \varepsilon_A}{\frac{\varepsilon_A + \varepsilon_B}{2}} c_B$$

and so

$$\left|\frac{c_A}{c_B}\right| \approx \frac{4}{7|S_{AB}|} \frac{\varepsilon_B - \varepsilon_A}{\frac{\varepsilon_A + \varepsilon_B}{2}} \tag{4.127}$$

Based on Eq. (4.127), we see that

- when the orbital energy difference is much larger than the average orbital energy, the bond is mostly ionic. This is unsurprising: when it is very favorable energetically to transfer an electron from the base to the acid, we expect to observe an ionic bond.

- when the orbital overlap, $|S_{AB}|$, is large, forming an ionic bond is unfavorable. This also is unsurprising. When two orbitals overlap very well, it is very favorable to form a covalent bond between them. Since the atoms can form a strong covalent bond, it is unlikely that ionic bonding would be favored.

- Conversely, bonds between orbitals with similar orbital energies tend to mostly covalent $\left(|c_A| \approx |c_B|\right)$ and bonds between orbitals that overlap very poorly tend to be mostly ionic $\left(|c_A| \gg |c_B|\right)$.

Again, this general line of argument explains many observed trends about ionic and covalent bonds. Ionic bonds tend to form when the electronegativity difference between the atoms is large is consistent with Eq. (4.127), because $\varepsilon_B - \varepsilon_A$ can be associated with the electronegativity difference.[31] Similarly, hard acids and bases tend to form ionic

---

[31] Recall that the orbital energy is associated with minus the ionization potential of the orbital, $\varepsilon_\phi = -I_\phi$. Consequently, it is very difficult to take an electron from an orbital with low orbital energy. That is,

compounds because hard molecules have small compact orbitals, which usually overlap poorly. As another example, consider that even though the electronegativity difference between iodine and cesium is about the same as the electronegativity difference between[32] hydrogen and fluorine, we say that *HF* is more covalent (recall that *HF* is a weak acid), while *CsI* is certainly ionic. In this case, the orbital energy differences between the atoms in the two compounds would be similar, but the orbital overlap between the orbitals in *CsI* is smaller (because the bonding orbitals are much more diffuse), leading to the preference for ionic character. In contrast, the orbital overlap between hydrogen and fluorine is quite pronounced: the hydrogen atom is actually almost "buried" in the electron cloud of the fluorine. This is consistent with the substantial covalent character of this chemical bond.

Sometimes it is convenient to have a quantitative measure of exactly "how ionic" or "how covalent" a given bond is. To do this, consider again the molecular orbital wave function, Eq. (4.96). The probability of observing an electron in this molecular orbital at a given point, $\boldsymbol{r}$, is given by

$$
\begin{aligned}
\left|\psi\left(\boldsymbol{r}\right)\right|^{2} &= \left|c_{A}\phi_{A}\left(\boldsymbol{r}\right)+c_{B}\phi_{B}\left(\boldsymbol{r}\right)\right|^{2} \\
&= \left|c_{A}^{2}\right|\left|\phi_{A}^{2}\left(\boldsymbol{r}\right)\right|+2\left(c_{A}c_{B}^{*}\phi_{A}\left(\boldsymbol{r}\right)\phi_{B}^{*}\left(\boldsymbol{r}\right)+c_{A}^{*}c_{B}\phi_{A}^{*}\left(\boldsymbol{r}\right)\phi_{B}\left(\boldsymbol{r}\right)\right)+\left|c_{B}^{2}\right|\left|\phi_{B}^{2}\left(\boldsymbol{r}\right)\right|
\end{aligned}
\tag{4.128}
$$

Integrating this expression with respect to $\boldsymbol{r}$ gives

$$
1 = \left|c_{A}\right|^{2}+2\operatorname{Re}\left(c_{A}c_{B}^{*}S_{AB}\right)+\left|c_{B}\right|^{2}.
\tag{4.129}
$$

The first term clearly corresponds to the probability that the electron is on atom A. The last term corresponds to the probability that the electron is on atom B. The middle term is related to the bonding/antibonding character of the density.

The implications of Eq. (4.129) are best understood with a series of examples.

---

when ε_{A} is small, we know that A is very electronegativity. Similarly, when ε_{B} is relatively large, then B is rather electropositive (it is relatively easy to remove electrons from B). When $\varepsilon_{B}-\varepsilon_{A}$ is large, the electronegativity difference between the atoms is large.

[32] The electronegativity difference in *CsI* is greater than that in *HF* if you use Mulliken electronegativities but less if you use the Pauling electronegativity scale.

A.   Bonding in Homonuclear Diatomic Molecules

The homonuclear diatomic molecule is the prototypical purely covalent bond. For cases where $S_{AB} > 0$ (e.g., σ bonds formed using s or d orbitals, and not p or f orbitals) bonding orbitals have the coefficients

$$c_A = \frac{1}{\sqrt{2\left(1 + S_{AB}\right)}} = c_B \tag{4.130}$$

and so

$$2c_A c_B S_{AB} = \frac{2S_{AB}}{2\left(1 + S_{AB}\right)} = \frac{S_{AB}}{1 + S_{AB}} > 0 \tag{4.131}$$

and

$$\left|c_A\right|^2 = \frac{1}{2\left(1 + S_{AB}\right)} = \left|c_B\right|^2 \tag{4.132}$$

For antibonding orbitals, we have instead that

$$c_A = \frac{1}{\sqrt{2\left(1 - S_{AB}\right)}} = -c_B \tag{4.133}$$

and so

$$2c_A c_B S_{AB} = \frac{-2S_{AB}}{2\left(1 - S_{AB}\right)} = -\frac{S_{AB}}{1 - S_{AB}} < 0 \tag{4.134}$$

This suggests that the middle term in Eq. (4.129) can be interpreted as a "bond density;" when the middle term is large and positive, the overlap between the atomic orbitals is large and orbitals are adding with the correct phase to produce a covalent bond. When the middle term is a large negative number, the overlap between the atomic orbitals is still large, but the orbitals are adding with the wrong phase to produce a covalent bond, giving an antibonding orbital. When the middle term is small, the orbital overlap is small, and there is not much covalent binding.

We thus define the *overlap density* as

$$n_{AB} = 2\,\mathrm{Re}\left(c_A c_B^* S_{AB}\right) \tag{4.135}$$

and conclude that

$$
\begin{array}{ll}
n_{AB} < 0 & \text{covalent antibonding orbital} \\
n_{AB} \approx 0 & \text{zero or weak covalent binding}\,. \\
n_{AB} > 0 & \text{covalent bonding orbital}
\end{array}
\tag{4.136}
$$

B.   Bonding in Purely Ionic Molecules

If a molecule was purely ionic, we would expect to observe complete electron transfer from the acid to the base. In this case, we would have

$$|c_A|^2 = 1$$
$$c_B = 0 \tag{4.137}$$

and, consequently, the overlap density, n_{AB}, is zero.

C.   Bonding in Partly Ionic Molecules

In practice, no molecule is purely ionic because the conditions for pure ionicity (an infinite difference in orbital energy and/or zero orbital overlap in Eq. (4.127)) are never exactly satisfied. Some compounds are highly ionic, however, and this is usually associated with a large dipole moment: the acid accepts most of the electron density from the base, but not all.

Referring back to Eq. (4.129), it is clear that the term $|c_A|^2$ is associated with electrons on atom A and the term $|c_B|^2$ are associated with electrons on atom B. But how should we divvy up the overlap density, n_{AB}? Mulliken proposed that one divide the overlap density equally between the two atoms. After the reaction, then, for every electron in the molecular orbital, the acidic fragment is assigned $\frac{1}{p_A}$ th of the electron and the base is assigned $\frac{1}{p_B}$ th of the electron, where

$$p_A = |c_A|^2 + \tfrac{1}{2} n_{AB} = |c_A|^2 + \mathrm{Re}\left(c_A c_B^* S_{AB}\right)$$
$$p_B = |c_B|^2 + \tfrac{1}{2} n_{AB} = |c_B|^2 + \mathrm{Re}\left(c_A c_B^* S_{AB}\right) \tag{4.138}$$

For a doubly-occupied molecular orbital, the acid will accept $2p_A - 1$ electrons from the base, and the base will donate $1 - 2p_B$ electrons to the acid. This leads to the interpretation that the bond in the heteronuclear diatomic molecule is

$$\% \text{ ionicity} = 100\left(2p_A - 1\right)$$
$$= 100\left(2|c_A^2| + n_{AB} - 1\right) \tag{4.139}$$

percent ionic in character. Note that Eq. (4.139) reproduces the reasonable result that homonuclear diatomics are 0% ionic, while if $|c_A| = 1$ then the molecule is 100% ionic.

The entire preceding analysis, which is often referred to as "Mulliken population analysis," is commonly used to assign bond orders and atomic charges in molecules. It should be emphasized, however, that Mulliken population analysis seems to work better at simpler levels of theory. If one writes ones molecular orbital as a linear combination of a

large number of atomic orbitals, then Mulliken analysis sometimes gives extraordinarily counterintuitive results.

X.   The Secular Equation

The results of the previous section hold when we form a molecular orbital from a linear combination of two atomic orbitals. However, as we observed for H_2^+, it is necessary to consider not only two atomic orbitals, but also all the other orbitals with suitable symmetry (see footnote 10). In general, for the Mth molecular orbital in a P-atom molecule, we can write

$$\psi_M\left(\boldsymbol{r}\right) = \sum_{\alpha=1}^{P}\sum_{i=1}^{\infty} c_{\alpha i, M}\phi_{\alpha i}\left(\boldsymbol{r}\right) \tag{4.140}$$

where the first sum runs over all the atoms in the molecule and the second sun runs over all the atomic orbitals of that atom, $\phi_{\alpha i}\left(\boldsymbol{r}\right)$.[33] In the general case, none of the coefficients in the linear combination of atomic orbitals, Eq. (4.140), will be zero. Some coefficients will be zero when the molecular orbital has a specified symmetry. For example, if $\psi_M\left(\boldsymbol{r}\right)$ is a σ_g orbital in a homonuclear diatomic molecule, we could rewrite Eq. (4.140) as

$$\psi_{\sigma_g}\left(\boldsymbol{r}\right) = \sum_{\alpha=1}^{2}\sum_{n=1}^{\infty}\sum_{l=0}^{n-1} c_{\alpha n l, M}\phi_{\alpha n l m=0}\left(\boldsymbol{r}\right) \tag{4.141}$$

where $\phi_{n,l,m=0}\left(\boldsymbol{r}\right)$ is the atomic orbital with principle quantum number n, orbital angular momentum quantum number l, and magnetic quantum number $m=0$. Orbitals with $m>0$ need not be included in the sum since they would have orbital angular momentum about the bond axis (chosen, by convention, to be the z axis), which is inconsistent with the fact we are examining a σ_g orbital. Similarly, we could write:

---

[33]   To be rigorously correct and highly accurate we must include the continuum eigenstates of the atom (corresponding to atomic cations in the presence of a free electron) in the sum. This is sometimes not done.

$$\psi_{\sigma_u}(\boldsymbol{r}) = \sum_{\alpha=1}^{2}\sum_{n=1}^{\infty}\sum_{l=0}^{n-1} c_{\alpha nl,M}\phi_{\alpha nlm=0}(\boldsymbol{r})$$

$$\psi_{\pi_u^+}(\boldsymbol{r}) = \sum_{\alpha=1}^{2}\sum_{n=1}^{\infty}\sum_{l=1}^{n-1} c_{\alpha nl,M}\phi_{\alpha nlm=1}(\boldsymbol{r})$$

$$\psi_{\pi_g^+}(\boldsymbol{r}) = \sum_{\alpha=1}^{2}\sum_{n=1}^{\infty}\sum_{l=1}^{n-1} c_{\alpha nl,M}\phi_{\alpha nlm=1}(\boldsymbol{r}) \qquad (4.142)$$

$$\psi_{\delta_g^-}(\boldsymbol{r}) = \sum_{\alpha=1}^{2}\sum_{n=1}^{\infty}\sum_{l=2}^{n-1} c_{\alpha nl,M}\phi_{\alpha nlm=-2}(\boldsymbol{r})$$

$$\psi_{\delta_u^-}(\boldsymbol{r}) = \sum_{\alpha=1}^{2}\sum_{n=1}^{\infty}\sum_{l=2}^{n-1} c_{\alpha nl,M}\phi_{\alpha nlm=-2}(\boldsymbol{r})$$

For molecules with no symmetry, one can choose *one* of the coefficients in the expansion to be zero in the case of accidental degeneracy. When two molecular orbitals, $\psi_M(\boldsymbol{r})$ and $\psi_N(\boldsymbol{r})$ have the same energy, we can choose a new set of molecular orbitals which are linear combinations of the old molecular orbitals,

$$\psi_M'(\boldsymbol{r}) = k\cdot\psi_M(\boldsymbol{r}) + \left(\sqrt{1-|k|^2}\right)\psi_L(\boldsymbol{r})$$
$$\psi_L'(\boldsymbol{r}) = \left(\sqrt{1-|k|^2}\right)\cdot\psi_M(\boldsymbol{r}) - k\psi_L(\boldsymbol{r}) \qquad (4.143)$$

so that one of the atomic-orbital coefficients is zero.[34] However, it should be emphasized again that, in general, none of the coefficients in the LCAO expansion will be zero.

Let us suppose that the molecular-orbital Hamiltonian is given by the expression

$$\hat{h}(\boldsymbol{r}) \equiv -\tfrac{\nabla^2}{2} + v(\boldsymbol{r}) + \hat{v}_{ee}^{(N)}(\boldsymbol{r}). \qquad (4.144)$$

The first term is the kinetic energy operator for the electron; the second term is the external potential, representing the nuclear-electron attraction;[35] the third term models the electron-electron repulsion between the electrons and is sometimes referred to as the internal potential. (The internal potential, $\hat{v}_{ee}^{(N)}(\boldsymbol{r})$, general depends on the number of electrons in the system, N, as denoted by the superscript (N).

If we want to find the molecular orbitals for an N-electron system with external potential $v(\boldsymbol{r})$, we need to solve the Schrödinger equation for the molecular orbitals,

---

[34] The reader may wish to verify this. Specifically, the reader may wish to verify that choosing

$$k = \frac{c_{\alpha i,K}}{c_{\alpha i,L}\sqrt{1 + \left|\frac{c_{\alpha i,K}}{c_{\alpha i,L}}\right|^2}}$$

in Eq. (4.143) serves to eliminate the coefficient of $\phi_{\alpha i}(\boldsymbol{r})$ in one of the molecular orbitals.

[35] More generally, the external potential models any effects that are not due to electrons in the molecule interaction with other electrons in the molecule. Such effects include the effects of an external electromagetic field, a molecular solvation environment, or a laser.

$$\hat{h}(\boldsymbol{r})\,\psi_M(\boldsymbol{r}) = \varepsilon_M \psi_M(\boldsymbol{r})$$

$$\hat{h}(\boldsymbol{r})\sum_{\alpha=1}^{P}\sum_{i=1}^{\infty} c_{\alpha i,M}\phi_{\alpha i}(\boldsymbol{r}) = \varepsilon_M \sum_{\alpha=1}^{P}\sum_{i=1}^{\infty} c_{\alpha i,M}\phi_{\alpha i}(\boldsymbol{r}) \tag{4.145}$$

$$\sum_{\alpha=1}^{P}\sum_{i=1}^{\infty} c_{\alpha i,M}\hat{h}(\boldsymbol{r})\phi_{\alpha i}(\boldsymbol{r}) = \varepsilon_M \sum_{\alpha=1}^{P}\sum_{i=1}^{\infty} c_{\alpha i,M}\phi_{\alpha i}(\boldsymbol{r}).$$

The last line follows from the fact that the molecular-orbital Hamiltonian, $\hat{h}(\boldsymbol{r})$, is a linear operator.

We now use the standard procedure to rewrite Eq. (4.145) as a generalized eigenvalue problem. First we multiply both sides of the equation by $\phi_{\beta j}^*(\boldsymbol{r})$ and integrate, obtaining

$$\sum_{\alpha=1}^{P}\sum_{i=1}^{\infty}\left\langle \phi_{\beta j}\left|\hat{h}\right|\phi_{\alpha i}\right\rangle c_{\alpha i,M} = \varepsilon_M \sum_{\alpha=1}^{P}\sum_{i=1}^{\infty}\left\langle \phi_{\beta j}\middle|\phi_{\alpha i}\right\rangle c_{\alpha i,M}. \tag{4.146}$$

Next, we define the Hamiltonian matrix, $\boldsymbol{H}$, with elements $h_{\alpha i,\beta j}$:

$$\boldsymbol{H} \Leftarrow \left[h_{\alpha i,\beta j}\right]$$

$$h_{\alpha i,\beta j} \equiv \left\langle \phi_{\beta j}\left|\hat{h}\right|\phi_{\alpha i}\right\rangle \tag{4.147}$$

and the overlap matrix, $\boldsymbol{S}$, with elements $s_{\alpha i,\beta j}$:

$$\boldsymbol{S} \Leftarrow \left[s_{\alpha i,\beta j}\right]$$

$$s_{\alpha i,\beta j} \equiv \left\langle \phi_{\beta j}\middle|\phi_{\alpha i}\right\rangle \tag{4.148}$$

In terms of these matrices, and the vector $\boldsymbol{c}_M$ with components $c_{\alpha i,M}$, Eq. (4.146) can be rewritten as

$$\boldsymbol{H}\boldsymbol{c}_M = \varepsilon_M \boldsymbol{S}\boldsymbol{c}_M \tag{4.149}$$

or, equivalently,

$$\left(\boldsymbol{H} - \varepsilon_M \boldsymbol{S}\right)\boldsymbol{c}_M = \boldsymbol{0} \tag{4.150}$$

Equations (4.149) and (4.150) are an example of a *generalized eigenvalue problem*, and these equations are often called the *secular equations* for the molecular orbitals. The generalized eigenvalue problem can be converted into a standard eigenvalue problem by multiplying both sides of Eq. (4.149) by the inverse of the overlap matrix, obtaining

$$\boldsymbol{S}^{-1}\boldsymbol{H}\boldsymbol{c}_M = \varepsilon_M \boldsymbol{S}^{-1}\boldsymbol{S}\boldsymbol{c}_M$$

$$\boldsymbol{S}^{-1}\boldsymbol{H}\boldsymbol{c}_M = \varepsilon_M \boldsymbol{I}\boldsymbol{c}_M \tag{4.151}$$

$$\boldsymbol{S}^{-1}\boldsymbol{H}\boldsymbol{c}_M = \varepsilon_M \boldsymbol{c}_M.$$

By solving any of Eqs. (4.149)-(4.151) for the coefficients, $\boldsymbol{c}_M$, we can obtain the LCAO expression for the molecular orbitals of a molecule. When someone says they are "running Gaussian," one part of the procedure they are implementing is almost always the solution

of a secular equation, most commonly the secular equation associated with the Hartree-Fock or Kohn-Sham density functional theory methods. The only difference between these two equations is model they use for the internal potential, $\hat{v}_{ee}^{(N)}(\boldsymbol{r})$. Most generally, because methods that rely on secular equations can be thought of as modeling independent electrons that move in an average "internal potential" due to the other electrons. For this reason, such models are called independent particle models or mean field methods.

XI. Molecular-Orbital Theory for H_2

As an example of how these ideas can be applied, we consider the hydrogen molecule. In the molecular-orbital picture, the ground state of H_2 will be modeled by a single doubly occupied σ_g molecular orbital, with a wave function given by Eq. (4.73). Just as for H_2^+,[36] the simplest LCAO approximation to the molecular orbital,

$$\psi_{\sigma_g}(\boldsymbol{r}) \propto \phi_{1s}^{(l)}(\boldsymbol{r}) + \phi_{1s}^{(r)}(\boldsymbol{r}), \tag{4.152}$$

where one just takes a linear combination of the 1s orbitals on the two hydrogen atoms, does not give good results. The resulting Slater determinant

$$\Psi_{H_2} = \left| \psi_{\sigma_g}^{LCAO}\alpha \quad \psi_{\sigma_g}^{LCAO}\beta \right| \tag{4.153}$$

underestimates the dissociation energy,

$$D_e = E_{H_2}(R_e) - 2E_H = E_{H_2}(R_e) - 1 \tag{4.154}$$

of the chemical bond by 40% and overestimates the bond length by 15%. To determine the bond length, we first determine the energy (both the electronic energy and the nuclear-nuclear repulsion energy must be included) as a function of the bond length, R. The minimum of this curve (R_e) is located by finding where the first derivative of the energy with respect to bond length is zero,

$$\left. \frac{\partial E_{H_2}(R)}{\partial R} \right|_{R=R_e} = 0. \tag{4.155}$$

The dissociation energy of the molecule is then obtained from Eq. (4.154), where the energy of the molecule is taken to be its energy at the optimum bond length. Some results for the dissociation energy and the equilibrium bond length are summarized in Table 4.2.

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[36] Based on Table 4.1, I would guess that the bond length in H_2 is less than 2.04 Bohr. (Why do I know this?) I would also suspect that the dissociation energy is less than .206 Hartree. (Why?)

For H_2^+ the key to obtaining the right bond length was to use an effective nuclear charge in the *1s* functions. If we do so, then the new molecular orbital can be conveniently denoted

$$\psi_{\sigma_g}^{\zeta}(\boldsymbol{r}) \propto \phi_{1s}^{(l)}(\zeta\boldsymbol{r}) + \phi_{1s}^{(r)}(\zeta\boldsymbol{r}), \tag{4.156}$$

where ζ is the effective nuclear charge.[37] This result is analogous to the Finkelstein-Horowitz treatment of H_2^+, and unsurprisingly has a very accurate bond length (the error is about .01 Angstroms) and a more accurate dissociation energy (it is "only" 25% too small). The optimum effective nuclear charge is about 1.20, in reasonable agreement with the value for H_2^+ (which was 1.23, cf. Table 4.1).

Obtaining good results for H_2^+ required mixing a contribution from the *2p* orbital into the wave function, à la Dickenson. Exact results were obtained only if we considered a linear combination of all the atomic orbitals and vary the coefficients, which allows us to determine the best molecular orbital description. Solving the secular equation for the appropriate linear combination of atomic orbitals (Eq. (4.141)) gives essentially the exact bond length, but the dissociation energy is still underestimated by more than 20%.

This last result, where all possible atomic-orbital contributions are considered, determines the molecular orbitals that minimize the energy. Recalling our treatment for atoms, whenever we minimize the energy of a Slater determinant of orbitals with respect to the form of the orbitals, we are performing the Hartree-Fock procedure. Thus, we can obtain the Hartree-Fock Energy by minimizing the energy of the Hydrogen molecule with respect to the coefficients in Eq. (4.141)

$$E_{H_2}^{HF}(R) = \min_{\underbrace{c_{\sigma nlm}=0}} \frac{\left\langle \left| \psi_{\sigma_g}^{(4.140)}\alpha \quad \psi_{\sigma_g}^{(4.140)}\beta \right| \left| -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{|r_1 - r_2|} \right| \left| \psi_{\sigma_g}^{(4.140)}\alpha \quad \psi_{\sigma_g}^{(4.140)}\beta \right| \right\rangle}{\left\langle \left| \psi_{\sigma_g}^{(4.140)}\alpha \quad \psi_{\sigma_g}^{(4.140)}\beta \right| \left| \psi_{\sigma_g}^{(4.140)}\alpha \quad \psi_{\sigma_g}^{(4.140)}\beta \right| \right\rangle}. \tag{4.157}$$

Hartree-Fock theory always neglects the effects of electron correlation, and the difference between the energy obtained from Eq. (4.157) and the exact energy is labeled the correlation energy,

$$E_{corr}(R) = E^{HF}(R) - E^{exact}(R). \tag{4.158}$$

We would expect the correlation energy to be negligible is when the bond length is very large. When $R \to \infty$, the hydrogen molecule dissociates into hydrogen atoms, and

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[37] Based on the form of the orbitals in atoms, why is introducing an effective nuclear charge equivalent to scaling the coordinates, $\boldsymbol{r} \to \zeta\boldsymbol{r}$?

there is no correlation energy in the hydrogen atom (since it has only one electron). This, alas, is not the case. To see why, let us rewrite the general molecular orbital expression in Eq. (4.141) in terms of its atomic contributions,

$$\psi_{\sigma_g}(\boldsymbol{r}) = \phi_1(\boldsymbol{r}) + \phi_2(\boldsymbol{r})$$

$$\phi_1(\boldsymbol{r}) \propto \sum_{n=1}^{\infty}\sum_{l=0}^{n-1} c_{1nl,M}\phi_{1nlm=0}(\boldsymbol{r}) \tag{4.159}$$

$$\phi_2(\boldsymbol{r}) \propto \sum_{n=1}^{\infty}\sum_{l=0}^{n-1} c_{2nl,M}\phi_{2nlm=0}(\boldsymbol{r})$$

Expanding out the Slater determinant, Eq. (4.153), we then obtain

$$\Psi_{H_2}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \big(\phi_1(\boldsymbol{r}_1) + \phi_2(\boldsymbol{r}_1)\big)\big(\phi_1(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_2)\big)\left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right)$$

$$= \begin{pmatrix}\phi_1(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) \\ +\phi_1(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2) + \phi_2(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2)\end{pmatrix}\left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right). \tag{4.160}$$

In the separated-atom limit, we can identify $\phi_1(\boldsymbol{r})$ and $\phi_2(\boldsymbol{r})$ with the $1s$ orbital of the Hydrogen atom (centered on the left and right-hand atoms, respectively). Thus,

$$\phi_1(\boldsymbol{r}) = \tfrac{1}{\sqrt{2}}\phi_{1s}^{(l)}(\boldsymbol{r})$$

$$\phi_2(\boldsymbol{r}) = \tfrac{1}{\sqrt{2}}\phi_{1s}^{(2)}(\boldsymbol{r}) \tag{4.161}$$

The factor of $\tfrac{1}{\sqrt{2}}$ ensures that the resulting wave function for H_2 is normalized. Thus, as the bond length goes to infinity, the wave function approaches

$$\Psi_{H_2}^{R\to\infty}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{2}\begin{pmatrix}\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2) + \phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2) \\ +\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2) + \phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2)\end{pmatrix}\left(\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right)$$

$$= \tfrac{1}{2}\left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(l)}\beta\right| + \tfrac{1}{2}\left|\phi_{1s}^{(r)}\alpha \quad \phi_{1s}^{(r)}\beta\right| \tag{4.162}$$

$$+ \tfrac{1}{2}\left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(r)}\beta\right| + \tfrac{1}{2}\left|\phi_{1s}^{(r)}\alpha \quad \phi_{1s}^{(l)}\beta\right|$$

This wave function is problematic. Note that one-half of the wave function (the first two terms) do not correspond to the correct dissociation products. Instead, they correspond to the hydrogen molecule dissociating to a hydride ion (with both electrons on either the left or right-hand atom) plus a proton. Consequently, when one evaluates the energy of the wave function in Eq. (4.162), one obtains

$$\left\langle \Psi_{H_2}^{R\to\infty}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)\left|\hat{H}\right|\Psi_{H_2}^{R\to\infty}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)\right\rangle = \tfrac{1}{4}\left\langle \left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(l)}\beta\right|\left|\hat{H}\right|\left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(l)}\beta\right|\right\rangle$$

$$+ \tfrac{1}{4}\left\langle \left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(l)}\beta\right|\left|\hat{H}\right|\left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(l)}\beta\right|\right\rangle$$

$$+ \tfrac{1}{4}\left\langle \left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(r)}\beta\right|\left|\hat{H}\right|\left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(r)}\beta\right|\right\rangle$$

$$+ \tfrac{1}{4}\left\langle \left|\phi_{1s}^{(r)}\alpha \quad \phi_{1s}^{(l)}\beta\right|\left|\hat{H}\right|\left|\phi_{1s}^{(r)}\alpha \quad \phi_{1s}^{(l)}\beta\right|\right\rangle \qquad (4.163)$$

$$= \tfrac{1}{2}\left(E_{H^-}\right) + \tfrac{1}{2}\left(E_H + E_H\right)$$

$$= \tfrac{1}{2}\left(E_{H^-}\right) + \tfrac{1}{2}(-1)$$

$$\approx -.5 \qquad (-1.0 \text{ is the desired answer})$$

(Because the hydride anion has almost zero ionization potential (the extra electron is barely bound), it is reasonable to assume that $E_{H^-} \approx E_H$. In fact, because of neither nuclear screening nor electron correlation is not included by this wave function, the extra electron is not bound, and so holding the extra electron in the "usual" 1s orbital is unfavorable, leading to $E_{H^-} > E_H$.)

XII. Valence Bond Theory for H$_2$

One way to avoid the dissociation energy problem in molecular orbital theory is to simply ignore the troublesome terms in Eq. (4.163); this guarantees that, whatever flaws the wave function may have, at least it will describe molecular dissociation correctly. This argument leads to the Heitler-London wave function,

$$\Psi_{H_2}^{HL}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right) = \left(\frac{\phi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\phi_{1s}^{(r)}\left(\boldsymbol{r}_2\right) + \phi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\phi_{1s}^{(l)}\left(\boldsymbol{r}_2\right)}{\sqrt{2}}\right)\left(\frac{\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)}{\sqrt{2}}\right)$$

$$= \tfrac{1}{\sqrt{2}}\left|\phi_{1s}^{(l)}\alpha \quad \phi_{1s}^{(r)}\beta\right| + \tfrac{1}{\sqrt{2}}\left|\phi_{1s}^{(r)}\alpha \quad \phi_{1s}^{(l)}\beta\right| \qquad (4.164)$$

Wave functions based on Eq. (4.164) (or other similar forms) are usually called *valence bond wave functions* and, broadly speaking, the methods associated with this type of wave functions are called *valence bond theory*. Looking at Table 4.2, one may argue that the Heitler-London wave function (Eq. (4.164)) is perhaps a little better than the simplest molecular-orbital wave function, though neither wave functions is any good. The predicted bond length in the Heitler-London wave function is particularly troublesome. By now, though, the reader knows how to get the bond length correct: insert an effective nuclear charge into the wave function. Wang did this, and the Heitler-London-Wang wave function

$$\Psi_{H_2}^{HLW}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\left(\frac{\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_1\right)\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_2\right)+\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_1\right)\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_2\right)}{\sqrt{2}}\right)\left(\frac{\alpha\left(1\right)\beta\left(2\right)-\alpha\left(2\right)\beta\left(1\right)}{\sqrt{2}}\right) \tag{4.165}$$

gives essentially exact results for the bond length and greatly improved results for the dissociation energy. The effective nuclear charge determined, $\zeta=1.17$, resembles the corresponding charge for H_2^+ and the effective nuclear charge in simple molecular orbital theory for H_2. In H_2^+, we observed that mixing a polarization function—typically a small contribution from the *2p* orbital—with the 1s orbital increased the "directionality" of the atomic orbitals, improving their overlap and increasing the strength of the chemical bond. Rosen did exactly this, using a wave function like

$$\Psi_{H_2}^{Rosen}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\left(\frac{\begin{array}{l}\left(c_{1s}\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_1\right)+c_{2p}\phi_{2p}^{(l)}\left(2\zeta\boldsymbol{r}_1\right)\right)\left(c_{1s}\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_2\right)+c_{2p}\phi_{2p}^{(r)}\left(2\zeta\boldsymbol{r}_2\right)\right)\\+\left(c_{1s}\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_1\right)+c_{2p}\phi_{2p}^{(r)}\left(2\zeta\boldsymbol{r}_1\right)\right)\left(c_{1s}\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_2\right)+c_{2p}\phi_{2p}^{(l)}\left(2\zeta\boldsymbol{r}_2\right)\right)\end{array}}{\sqrt{2}}\right)\left(\tfrac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\right) \tag{4.166}$$

Considering the simplicity of the model, this gives a quite good value for the dissociation energy, .148 Hartree.

Note that the dissociation energy in the Heitler-London-Wang and Rosen wave functions are *below* the Hartree-Fock value. These wave function, then, must include some electron correlation. Indeed they do; in these simple valence bond wave functions, if electron one is associated with the left atom, then electron two must be associated with the right atom, and vice versa. Thus, the Heitler-London wave function models *left-right correlation*, the tendency for the electrons composing a chemical bond to be divided equally between the atoms, rarely being observed on the same atom at the same time. Actually, according to these models, we expect to *never* observe two electrons on the same atom at the same time and, while we expect this to be improbable, at non-infinite bond distances we expect to occasionally observe both electrons on the same atom. We can express this possibility using the resonance structures,

$$\text{H-H}\leftrightarrow\text{H}^-\text{H}^+\leftrightarrow\text{H}^+\text{H}^-. \tag{4.167}$$
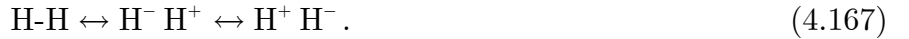
How can we include the possibility that both electrons will be on the same atom at the same time. We could decompose Eq. (4.162) into its covalent and ionic terms and multiply each by an appropriate weighting factor, thereby including a small "ionic" contribution as a correction to the Heitler-London form. This gives a wave function like

$$\Psi_{H_2}^{VB+ionic}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\frac{1}{2}\left[\begin{matrix}c_{ionic}\left(\phi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\phi_{1s}^{(l)}\left(\boldsymbol{r}_2\right)+\phi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\phi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)\right)\\+c_{covalent}\left(\phi_{1s}^{(l)}\left(\boldsymbol{r}_1\right)\phi_{1s}^{(r)}\left(\boldsymbol{r}_2\right)+\phi_{1s}^{(r)}\left(\boldsymbol{r}_1\right)\phi_{1s}^{(l)}\left(\boldsymbol{r}_2\right)\right)\end{matrix}\right]\left(\frac{\alpha\left(1\right)\beta\left(2\right)-\alpha\left(2\right)\beta\left(1\right)}{\sqrt{2}}\right)$$

$$=c_{covalent}\left(\tfrac{1}{2}\left|\phi_{1s}^{(l)}\alpha\quad\phi_{1s}^{(r)}\beta\right|+\tfrac{1}{2}\left|\phi_{1s}^{(r)}\alpha\quad\phi_{1s}^{(l)}\beta\right|\right) \qquad (4.168)$$

$$+c_{ionic}\left(\tfrac{1}{2}\left|\phi_{1s}^{(l)}\alpha\quad\phi_{1s}^{(l)}\beta\right|+\tfrac{1}{2}\left|\phi_{1s}^{(r)}\alpha\quad\phi_{1s}^{(r)}\beta\right|\right).$$

Wave functions with this form are said to be "Valence Bond + Ionic" wave functions. Looking in Table 4.2, we observe that the simple VB+ionic wave function does not give very good results for the bond distance. However, when Weinbaum included an effective nuclear charge in this wave function,

$$\Psi_{H_2}^{Weinbaum,\zeta}\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\frac{1}{2}\left[\begin{matrix}c_{ionic}\left(\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_1\right)\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_2\right)+\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_1\right)\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_2\right)\right)\\+c_{covalent}\left(\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_1\right)\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_2\right)+\phi_{1s}^{(r)}\left(\zeta\boldsymbol{r}_1\right)\phi_{1s}^{(l)}\left(\zeta\boldsymbol{r}_2\right)\right)\end{matrix}\right]\left(\frac{\alpha\left(1\right)\beta\left(2\right)-\alpha\left(2\right)\beta\left(1\right)}{\sqrt{2}}\right) \quad (4.169)$$

he obtained an excellent approximation to the geometry and, moreover, obtained a dissociation energy almost as good as the Rosen wave function (which includes a $2p$ orbital). The effective nuclear charge, $\zeta=1.19$, is about what one would expect. The ratio of the coefficients allows one to infer that the wave function is about 6% ionic, which would be consistent with the expectation that it is rare to observe two electrons on the same atom—this happens only about 5% of the time.[38] The next improvement is clear; include a polarization contribution, just as Rosen did for the valence-bond wave function (without ionic contributions). The resulting wave function is among the best simple wave functions for the hydrogen molecule. Continuing in this fashion one eventually approaches the exact result.

Does one have to use the Valence-Bond approach to approach the exact result, or can one approach the exact result in molecular-orbital theory by doing something analogous to incorporating "ionic" configurations. Let us examine Eq. (4.168) once more. Rearranging terms, we have that

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[38] One should not read too much into this number; different ways of quantifying the probability of observing two electrons on the same atom will give different results. It is reasonable to infer, however, that it is much more likely for the two electrons in H_2 to be located on different atoms than it is for them to be located on the same atom.

$$\Psi_{H_2}^{VB+ionic}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{2}\begin{vmatrix} c_{ionic}\left(\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2)+\phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2)\right) \\ +c_{covalent}\left(\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2)+\phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2)\right) \end{vmatrix}\left(\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\right)$$

$$= \frac{1}{2}\begin{vmatrix} \dfrac{c_{covalent}+c_{ionic}}{2}\begin{pmatrix}\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2)+\phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2) \\ +\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2)+\phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2)\end{pmatrix} \\ \dfrac{c_{ionic}-c_{covalent}}{2}\begin{pmatrix}\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2)+\phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2) \\ -\phi_{1s}^{(l)}(\boldsymbol{r}_1)\phi_{1s}^{(r)}(\boldsymbol{r}_2)-\phi_{1s}^{(r)}(\boldsymbol{r}_1)\phi_{1s}^{(l)}(\boldsymbol{r}_2)\end{pmatrix}\end{vmatrix}\left(\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\right)$$

$$= \frac{1}{2}\begin{vmatrix} \dfrac{c_{covalent}+c_{ionic}}{2}\left(\phi_{1s}^{(l)}(\boldsymbol{r}_1)+\phi_{1s}^{(r)}(\boldsymbol{r}_1)\right)\left(\phi_{1s}^{(l)}(\boldsymbol{r}_2)+\phi_{1s}^{(r)}(\boldsymbol{r}_2)\right) \\ \dfrac{c_{ionic}-c_{covalent}}{2}\left(\phi_{1s}^{(l)}(\boldsymbol{r}_1)-\phi_{1s}^{(r)}(\boldsymbol{r}_1)\right)\left(\phi_{1s}^{(l)}(\boldsymbol{r}_2)-\phi_{1s}^{(r)}(\boldsymbol{r}_2)\right)\end{vmatrix}\left(\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\right) \quad (4.170)$$

$$= \left(\frac{c_{covalent}+c_{ionic}}{2}\right)\begin{vmatrix}\psi_{\sigma_g}\alpha & \psi_{\sigma_g}\beta\end{vmatrix} + \left(\frac{c_{ionic}-c_{covalent}}{2}\right)\begin{vmatrix}\psi_{\sigma_u}\alpha & \psi_{\sigma_u}\beta\end{vmatrix}$$

$$\equiv \Psi_{H_2}^{MO+CI}(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

When we write the wave function in this form, we say that we are considering a molecular-orbital + configuration interaction (MO+CI) wave function. Molecular orbital theory + configuration interaction is equivalent to Valence-Bond theory + resonance structures.[39]

The MO+CI wave function is best understood from the perspective of the non-crossing rule. According to the noncrossing rule, potential energy surfaces for electronic states with the same symmetry cannot cross (excepting conical intersections). This "avoided crossing" is effected by a "repulsion" between the two potential energy curves: given two wave functions with the same symmetry, e.g., the wave function for H_2 where the ground state is doubly occupied ($\begin{vmatrix}\psi_{\sigma_g}\alpha & \psi_{\sigma_g}\beta\end{vmatrix}$) and the wave function for H_2 where the first excited state is doubly occupied ($\begin{vmatrix}\psi_{\sigma_u}\alpha & \psi_{\sigma_u}\beta\end{vmatrix}$),[40] we can take a linear combination of these Slater determinants to find improved wave functions for the ground and excited state of the system, just as we did when deriving the noncrossing rule (cf. Eq. (4.27)). The resulting ground state approximation will be lower than before and the resulting excited-state approximation will be higher than before (cf. Eq. (4.31)), and so the effect of

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[39] A desirable effect is that as the bond length goes to infinity, the valence-bond wave function can now be recovered, avoiding the previously troublesome dissociation behavior from molecular-orbital theory.

[40] Both these wave functions have zero angular momentum about the bond axis and are gerade (because the product of two ungerade functions is gerade). Thus, they have the same symmetry. We often denote the symmetry of this ground state as $^1\Sigma_g^+$.

including configuration interaction is to "shove down" the ground state potential energy surface and "force up" the excited-state potential energy surface. Not only does this ensure keep the potential energy curves of the two states in question from crossing, it improves the approximation to the ground state wave function.

How does one approximate the exact energy in terms of configuration interaction? One can write the exact wave function as[41]

$$\Psi_{H_2,exact}^{MO+CI}\left(\boldsymbol{r}_1, \boldsymbol{r}_2\right) = \sum_{\substack{\text{all Slater} \\ \text{determinants}}} c_{ij} \left| \psi_i \alpha \quad \psi_j \beta \right|$$

$$\approx \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_{nm}^{(g)} \left| \psi_{n\sigma_g} \alpha \quad \psi_{n\sigma_g} \beta \right| \qquad (4.171)$$

$$+ \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_{nm}^{(u)} \left| \psi_{n\sigma_u} \alpha \quad \psi_{m\sigma_u} \beta \right|$$

where the $n\sigma_g$ and $m\sigma_u$ molecular orbitals are the nth molecular orbital of σ_g symmetry and the mth molecular orbital of σ_u symmetry, respectively. Note that in order to use Eq. (4.171), one must solve the secular equation not only for the occupied molecular orbital, but also all of the excited-state molecular orbitals (or as many of these as one can afford to compute).

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[41] You might think that the expansion in terms of the Slater determinants containing σ_g and σ_u orbital would be exact. However, there are $^1\Sigma_g^+$ terms that also arise from the π^2, δ^2, ϕ^2, . . . configurations. These terms, however, cannot be expressed as Slater determinants, but is instead associated with a linear combination of Slater determinants. (We observed a similar phenomenon for atoms; there was a ^1S term associated with the p^2 configuration, but this term did not correspond to a simple Slater determinant but, instead, a linear combination of Slater determinants.) This linear combination of Slater determinants is often called a "configuration state function" (CSF). Historically, many computer programs computed wave functions in terms of CSFs. These days, Slater determinants are often used directly, instead. Actually, the approximation in Eq. (4.171) is not even all that good; the neglected terms (involving linear combinations of electron configurations like $\left(n\pi^-\right)\left(m\pi^+\right)$, $\left(n\delta^+\right)\left(m\delta^-\right)$, etc.) are rather important.

Table 4.2. Summary of computational methods for H_2.

Type	Method	Bond Length (Bohr)	Bond Dissociation Energy (Hartree)	Parameters
MO	Simple Linear Combination of Atomic Orbitals	1.61	.099	
MO	Simple LCAO + effective nuclear charge	1.38	.128	$\zeta = 1.20$
MO	Full MO Theory including all atomic orbitals	1.40	.133	
VB	Simple Valence Bond *Heitler-London*	1.64	.115	
VB	Simple Valence Bond + effective nuclear charge *Heitler-London-Wang*	1.40	.139	$\zeta = 1.17$
VB	Valence Bond + effective nuclear charge + Polarization (2p) *Rosen*	1.40	.148	$\zeta = 1.17$ $\sim 2\%\ 2p$
VB+ionic MO+CI	VB + ionic (or MO + CI) (1s orbitals only) *Weinbaum*	1.67	.118	$\frac{c_{\text{ionic}}}{c_{\text{covalent}}} = .158$
VB+ionic MO+CI	VB + ionic (or MO + CI) + effective nuclear charge *Weinbaum*	1.41	.147	$\frac{c_{\text{ionic}}}{c_{\text{covalent}}} = .257$ $\zeta = 1.19$
VB+ionic MO+CI	VB + ionic (or MO + CI) + effective nuclear charge + polarization (2p) *Weinbaum*	1.40	.151	$\zeta = 1.19$ $\sim .35\%\ 2p$
exact		**1.4011**	**.174**	

XIII. MO and VB Theory for Bigger Molecules

A. LiH

As an example of how the molecular-orbital and valence-bond theories can be applied to bigger molecules, let us first consider Lithium Hydride. In molecular orbital theory, we would expect that the $1s$ orbitals of Lithium are essentially inert; they are not involved in binding. The bonding molecular orbital would be expected to include the $2s$ orbital of Lithium and the $1s$ orbital of Hydrogen,

$$\psi_{\sigma_g}^{LiH}(\boldsymbol{r}) = c_{1s,\sigma_g}^{H}\psi_{1s}^{H}(\boldsymbol{r}) + c_{2s,\sigma_g}^{Li}\psi_{2s}^{Li}(\boldsymbol{r}) \tag{4.172}$$

with

$$c_{1s,\sigma_g}^{H} > c_{2s,\sigma_g}^{Li} > 0\,. \tag{4.173}$$

The coefficients of the $\psi_{1s}^{H}(\boldsymbol{r})$ and $\psi_{2s}^{Li}(\boldsymbol{r})$ have the same sign (it is a bonding orbital), so they can both be chosen to be positive. Moreover, because hydrogen is more electronegative than Lithium, we infer (cf. Eq. (4.127)) that the molecular orbital will be polarized towards the hydrogen atom (and away from the Lithium atom). This leads to Eq. (4.173). Similarly, because the antibonding orbital must be orthogonal to the bonding orbital, we have that

$$\psi_{\sigma_u}^{LiH}(\boldsymbol{r}) = c_{1s,\sigma_u}^{H}\psi_{1s}^{H}(\boldsymbol{r}) - c_{2s,\sigma_u}^{Li}\psi_{2s}^{Li}(\boldsymbol{r}) \tag{4.174}$$

with

$$c_{2s,\sigma_u}^{Li} > c_{1s,\sigma_u}^{H} > 0\,. \tag{4.175}$$

The antibonding orbital is polarized towards the Lithium atom.

The simple molecular-orbital theory approximation to the wave function for Lithium Hydride will be

$$\Psi_{LiH}^{MO}\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4\right) = \left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{\sigma_g}^{LiH}\alpha \quad \psi_{\sigma_g}^{LiH}\beta\right| \tag{4.176}$$

and we can improve this result with configuration interaction, giving

$$\Psi_{LiH}^{MO+CI}\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4\right) = c_1\left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{\sigma_g}^{LiH}\alpha \quad \psi_{\sigma_g}^{LiH}\beta\right| + c_2\left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{\sigma_u}^{LiH}\alpha \quad \psi_{\sigma_u}^{LiH}\beta\right|. \tag{4.177}$$

We can also treat LiH using valence-bond theory. Our wave function looks rather like

$$\left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta\right|\left(\psi_{2s}^{Li}(\boldsymbol{r}_3)\psi_{1s}^{H}(\boldsymbol{r}_4) + \psi_{2s}^{Li}(\boldsymbol{r}_4)\psi_{1s}^{H}(\boldsymbol{r}_3)\right)\left(\tfrac{\alpha(3)\beta(4)-\alpha(4)\beta(3)}{\sqrt{2}}\right) \tag{4.178}$$

except that this wave function is not allowable, because the $1s$ electrons are distinguishable from the binding electrons in this wave function, but we know that electrons are indistinguishable particles. We let $\mathcal{A}$ denote the antisymmetrizer, which takes Eq. (4.178) and adds to it all the various equivalent arrangements of electrons, each with the appropriate factor of $+1$ or -1.[42] Thus

$$\Psi_{LiH}^{VB}\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_4\right) = \mathcal{A}\left(\left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta\right|\left(\psi_{2s}^{Li}\left(\boldsymbol{r}_3\right)\psi_{1s}^{H}\left(\boldsymbol{r}_4\right)+\psi_{2s}^{Li}\left(\boldsymbol{r}_4\right)\psi_{1s}^{H}\left(\boldsymbol{r}_3\right)\right)\left(\tfrac{\alpha(3)\beta(4)-\alpha(4)\beta(3)}{\sqrt{2}}\right)\right)$$
$$= \left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \widehat{\psi_{2s}^{Li} \quad \psi_{1s}^{H}}\right|. \tag{4.179}$$

The last equation is a convenient shorthand for the valence-bond wave function. Referring to the expression for the Heitler-London wave function in terms of Slater determinants (cf. Eq. (4.164)) we have that

$$\Psi_{LiH}^{VB}\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_4\right) = \left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \widehat{\psi_{2s}^{Li} \quad \psi_{1s}^{H}}\right|$$
$$\propto \left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{2s}^{Li}\alpha \quad \psi_{1s}^{H}\beta\right| + \left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{1s}^{H}\alpha \quad \psi_{2s}^{Li}\beta\right| \tag{4.180}$$

Equation (4.180) is called the perfect-pairing valence-bond wave function. The perfect pairing valence bond wave function represents the "most important" of the covalently bound structures, in this case Li-H. In order to improve the valence-bond wave function, we should recall that the hydrogen in Lithium Hydride is negatively charged, and therefore include a suitable ionic structure. Ergo,

$$\Psi_{LiH}^{VB+ionic}\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_4\right) = c_{\text{cov}}\left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \widehat{\psi_{2s}^{Li} \quad \psi_{1s}^{H}}\right| + c_{ionic}\left|\psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{1s}^{H}\alpha \quad \psi_{1s}^{H}\beta\right| \tag{4.181}$$

Equation (4.181) corresponds to the resonance structures

$$\text{Li-H} \leftrightarrow \text{Li}^+\text{H}^-. \tag{4.182}$$

Now, recall that when we did configuration interaction in the molecular-orbital picture, we mixed in a molecular that was polarized towards the Lithium atom—this is (roughly) comparable to mixing in the Li^-H^+ configuration. Thus, in order to reproduce the wave function in Eq. (4.177) in the valence-bond picture, we generally must consider the Slater determinant that corresponds to the Li^-H^+ resonance structure, ergo:

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[42] For example, $\left|\psi_1\alpha \quad \psi_1\beta \quad \psi_2\alpha\right| = \mathcal{A}\left(\psi_1\left(\boldsymbol{r}_1\right)\alpha\left(1\right)\psi_1\left(\boldsymbol{r}_2\right)\beta\left(2\right)\psi_2\alpha\left(3\right)\right).$

$$\Psi_{LiH}^{VB+2\times ionic}\left(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_4\right) = c_{\mathrm{cov}} \left| \psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \widehat{\psi_{2s}^{Li} \quad \psi_{1s}^{H}} \right|$$

$$+ c_{Li^+H^-} \left| \psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{1s}^{H}\alpha \quad \psi_{1s}^{H}\beta \right| \qquad (4.183)$$

$$+ c_{Li^-H^+} \left| \psi_{1s}^{Li}\alpha \quad \psi_{1s}^{Li}\beta \quad \psi_{2s}^{Li}\alpha \quad \psi_{2s}^{Li}\beta \right|.$$

Equation (4.183) is consistent with the fact that the valence-bond + ionic wave function for Hydrogen was associated with four Slater determinants of atomic orbitals (Eq. (4.168)) but only two Slater determinants of molecular orbitals (Eq. (4.170)). In general, then, the molecular orbital approach is more efficient. It takes fewer Slater determinants to make the first reasonable approximation: the single Slater determinant in Eq. (4.176) is already reasonable because the σ_g orbital is polarized towards the more electronegative Hydrogen atom in molecular orbital theory; by contrast, the simple perfect-pairing wave function has no ionic contribution. Moreover, because the molecular orbitals are orthogonal (atomic orbitals on different atoms are not), the equations associated with molecular-orbital calculations are simpler than those associated with valence-bond calculations. We conclude that the molecular orbital method is a more practical computational technique.

B.   BeH$_2$

When we consider polyatomic molecules, we determining the molecular-orbital diagram is sometime difficult. When several atoms (or functional groups) are bonded to a "central" atom, the "generator orbital" technique proposed by Ruedenberg is a powerful method for determining the shapes and relative energies of the molecular orbitals. The basic idea is that when you form a bond to an atom, that atom "attracts" electrons. For the purposes of determining the shapes of the molecular orbitals and the order of their orbital energies, then, you can take one atom and model the other atoms by small point charges (which, similarly, attract electrons).[43]

For example, we can determine the symmetries of the molecular orbitals in BeH_2 by modeling the Hydrogen atoms as a positive charges. Then, we can construct molecular

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[43]   This method is most straightforward to apply when you have a "central" atom surrounded by lighter atoms, though it can be generalized to other cases.

orbitals by symmetry matching.[44]   Figures 4.11-4.13 shows how one constructs molecular-orbitals and their orbital energies for BeH_2, H_2O, and NH_3 using this method.
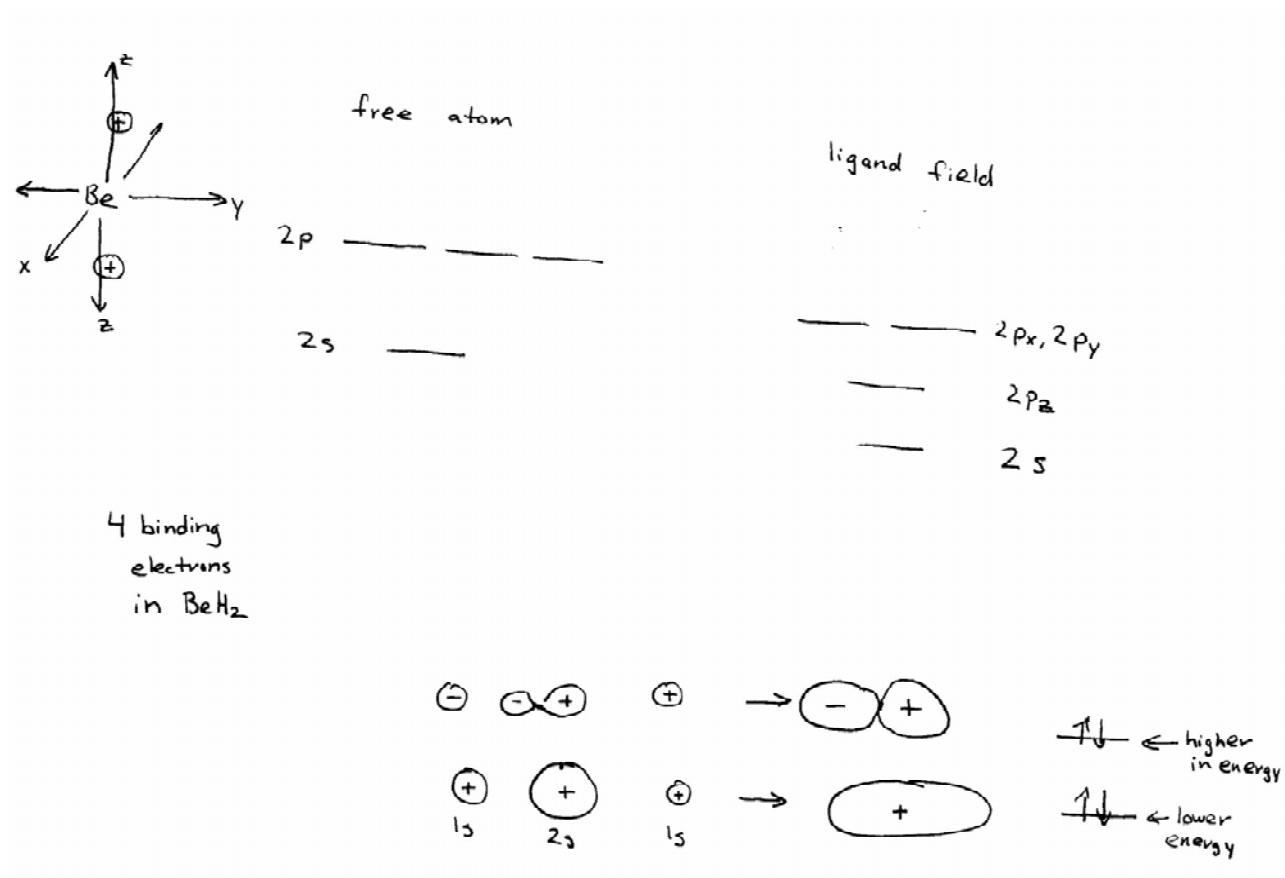

Figure 4.11   Constructing the molecular orbitals for BeH_2.

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[44]   It is admittedly strange to use positive charges to model the hydrogen atoms since that the hydrogen atoms in BeH_2 will be negatively charged. The reason is that, because of its electronegativity, the Hydrogen atom tends to attract electric charge. Similarly, a positive charge attracts negative charge (but a negative charge repels it). The opposite case holds in ligand field theory: in typical mononuclear transition metal complexes, the d-orbitals are not directly involved in chemical binding and so the "electrostatic" effects of the ligands (rather than their ability to withdraw charge from the metal's d-orbitals) are important for determining the energetic ordering of the orbitals; we then model the ligands with negative point charges. Of course, in actuality, there is a small (and sometimes not-so-small) effect from covalent bonding, and this partially accounts for the deficiencies in ligand-field theory.

free atom

ligand field

$2p$ —— —— —— ——

$2s$ ——

—— $2p_z$

—— $2p_x$ } these orbitals
—— $2p_y$ } are degenerate
if the bond
angle is 90°.

—— $\overline{E}_{2p_x} < E_{2p_y}$
if $\Theta < 90°$

$\overline{E}_{2p_y} > E_{2p_x}$
if $\Theta > 90°$

$2p_z$

$1b_1$

$2p_x$

$3a_1$

$2p_y$

$1b_2$

$\uparrow\downarrow$ $1b_1$

$\uparrow\downarrow$ $3a_1$

$\uparrow\downarrow$ $1b_2$

$2s$

$2a_1$

$\uparrow\downarrow$ $2a_1$
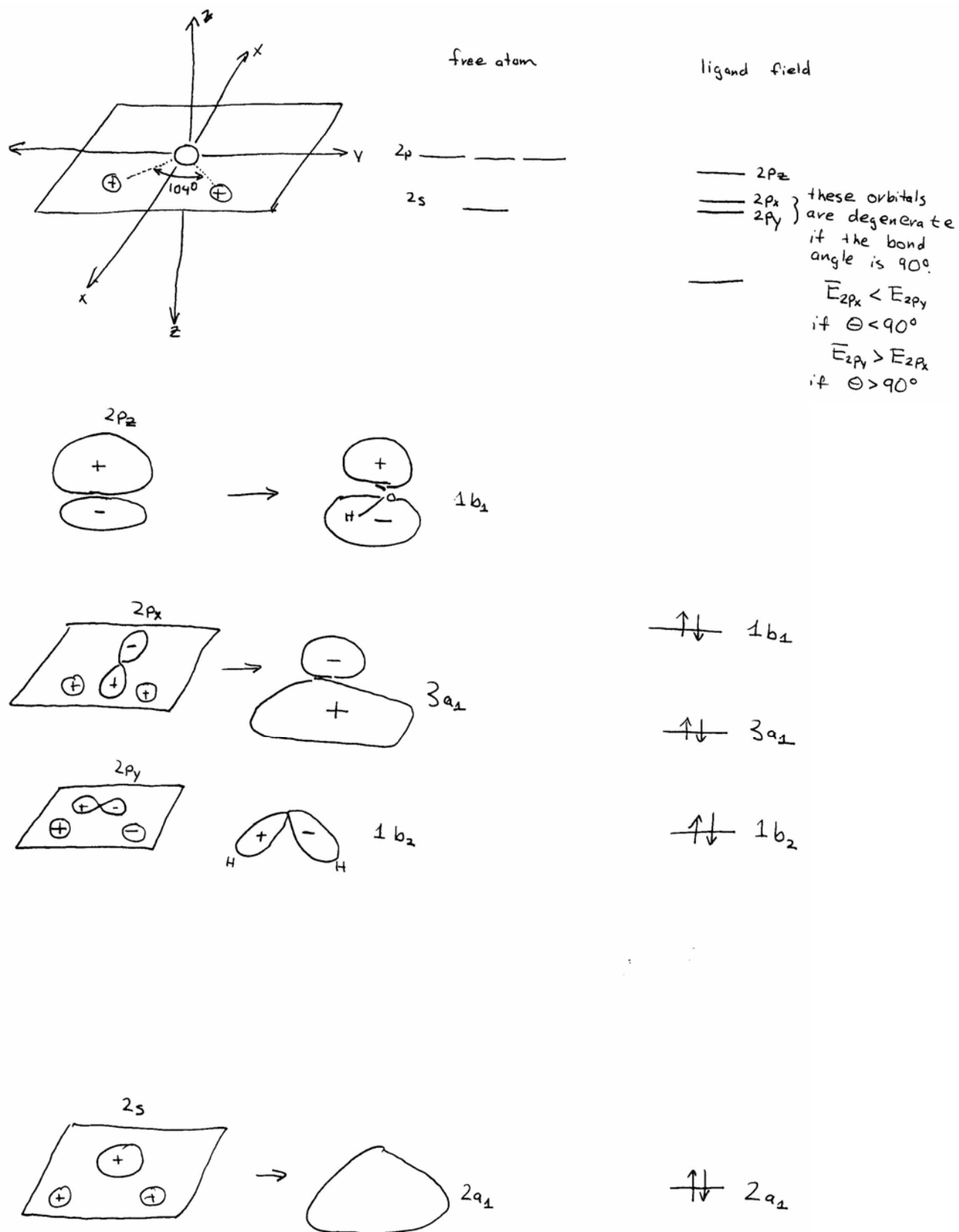
Figure 4.12 Constructing the molecular orbitals for H_2O.

Ammonia

free atom

ligand field

2p — — — —

2s —

2p_z

2p_x, 2p_y

molecular orbitals

2p_z

3a_1

2p_x

1e_x

1e_y

2p_y

2s

2a_1

1e_x, 1e_y

2a_1
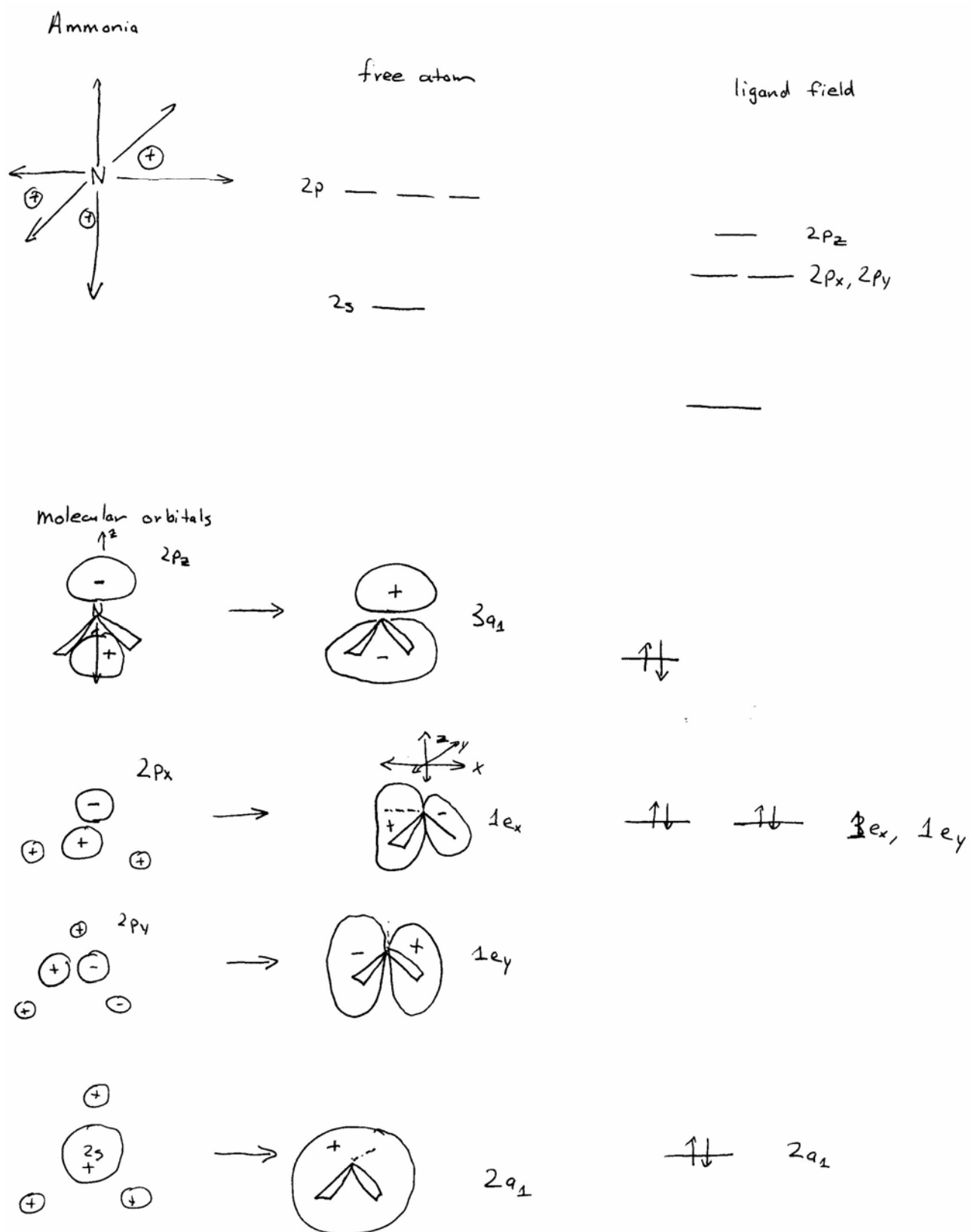
Figure 4.13 Constructing the molecular orbitals for NH_3.

Based on Figure 4.11, we can write an approximate molecular-orbital wave function for BeH_2:

$$\Psi_{BeH_2}^{MO} = \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \psi_{\sigma_g[2s]}^{BeH_2}\alpha \quad \psi_{\sigma_g[2s]}^{BeH_2}\beta \quad \psi_{\sigma_u[2p]}^{BeH_2}\alpha \quad \psi_{\sigma_u[2p]}^{BeH_2}\beta \right|. \tag{4.184}$$

The lowest-energy "molecular" orbital is essentially the 1s atomic orbital of the Beryllium, which mixes only minimally with the 1s orbital of the hydrogen atoms because of poor overlap and the large difference in orbital energy. From Figure 4.11, it is clear that the next lowest-energy orbital is associated with the 2s orbital of Beryllium and the "symmetric" combination of the two hydrogen atoms, giving

$$\psi_{\sigma_g[2s]}(\boldsymbol{r}) = c_{Be}\psi_{2s}^{Be}(\boldsymbol{r}) + c_H\left(\frac{1}{\sqrt{2}}\right)\left(\psi_{2s}^{H,right}(\boldsymbol{r}) + \psi_{1s}^{H,left}(\boldsymbol{r})\right). \tag{4.185}$$

Based on the fact that Hydrogen is more electronegative than Beryllium (and, similarly, based on the fact that Hydrogen has a higher ionization potential than Beryllium), we expect that $|c_{1s}| > |c_{2s}|$ in Eq. (4.185). Again referring to Figure 4.11, the next lowest-energy orbital is associated with the 2p orbital of Beryllium, namely

$$\psi_{\sigma_u[2p]}(\boldsymbol{r}) = c_{Be}\psi_{2p_z}^{Be}(\boldsymbol{r}) + c_H\left(\frac{1}{\sqrt{2}}\right)\left(\psi_{2s}^{H,right}(\boldsymbol{r}) - \psi_{1s}^{H,left}(\boldsymbol{r})\right) \tag{4.186}$$

Again, we expect that $|c_H| > |c_{Be}|$. The unoccupied orbitals of BeH_2 include the 2p orbitals of the Beryllium atom; these orbitals do not have the right symmetry to mix with the Hydrogen 1s orbitals, though they could mix with the unoccupied 2p orbitals of the Hydrogen atoms. These orbitals are essentially nonbonding. The form of the antibonding orbitals can be inferred from the form of the bonding orbitals, giving

$$\psi_{\sigma_u[2s]}(\boldsymbol{r}) = c_{Be}\psi_{2s}^{Be}(\boldsymbol{r}) - c_H\left(\frac{1}{\sqrt{2}}\right)\left(\psi_{2s}^{H,right}(\boldsymbol{r}) + \psi_{1s}^{H,left}(\boldsymbol{r})\right) \tag{4.187}$$

$$\psi_{\sigma_g[2p]}(\boldsymbol{r}) = c_{Be}\psi_{2p_z}^{Be}(\boldsymbol{r}) - c_H\left(\frac{1}{\sqrt{2}}\right)\left(\psi_{2s}^{H,right}(\boldsymbol{r}) - \psi_{1s}^{H,left}(\boldsymbol{r})\right). \tag{4.188}$$

with $|c_{Be}| > |c_H|$ in this case, so that the antibonding orbitals are polarized towards the Beryllium atom. We can summarize the situation by listing the molecular orbitals in order of increasing energy, with

$$\varepsilon\left[\psi_{1s}[Be]\right] < \varepsilon\left[\psi_{\sigma_g[2s]}\right] < \varepsilon\left[\psi_{\sigma_u[2p]}\right] < \varepsilon\left[\psi_{2p_{x,y}}[Be]\right] < \varepsilon\left[\psi_{\sigma_u[2s]}\right] < \varepsilon\left[\psi_{\sigma_g[2p]}\right] \tag{4.189}$$

Can we describe BeH_2 using Valence-Bond Theory? We can, but first we must introduce the sp-hybrid orbitals,

$$\psi_{sp}^{Be,+}(\boldsymbol{r}) = \psi_{2s}^{Be}(\boldsymbol{r}) + \psi_{2p_z}^{Be}(\boldsymbol{r})$$
$$\psi_{sp}^{Be,-}(\boldsymbol{r}) = \psi_{2s}^{Be}(\boldsymbol{r}) - \psi_{2p_z}^{Be}(\boldsymbol{r}) \tag{4.190}$$

These orbitals are directed towards the hydrogen atoms in BeH_2; the $\psi_{sp}^{Be,+}(\boldsymbol{r})$ hybrid orbital points at the rightmost Hydrogen atom and the $\psi_{sp}^{Be,+}(\boldsymbol{r})$ hybrid orbital points at the leftmost Hydrogen atom. This allow us to write the valence-bond wave function

$$\Psi_{BeH_2}^{VB} = \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \overbrace{\psi_{sp}^{Be,+} \quad \psi_{1s}^{H,right}} \quad \overbrace{\psi_{sp}^{Be,-} \quad \psi_{1s}^{H,left}} \right|$$

$$= \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \psi_{sp}^{Be,+}\alpha \quad \psi_{1s}^{H,right}\beta \quad \psi_{sp}^{Be,-}\alpha \quad \psi_{1s}^{H,left}\beta \right|$$

$$+ \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \psi_{sp}^{Be,+}\beta \quad \psi_{1s}^{H,right}\alpha \quad \psi_{sp}^{Be,-}\alpha \quad \psi_{1s}^{H,left}\beta \right| \quad (4.191)$$

$$+ \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \psi_{sp}^{Be,+}\alpha \quad \psi_{1s}^{H,right}\beta \quad \psi_{sp}^{Be,-}\beta \quad \psi_{1s}^{H,left}\alpha \right|$$

$$+ \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \psi_{sp}^{Be,+}\beta \quad \psi_{1s}^{H,right}\alpha \quad \psi_{sp}^{Be,-}\beta \quad \psi_{1s}^{H,left}\alpha \right|$$

Note that even the simple perfect-pairing wave function, which does not include any polarization of the bonds, requires four Slater determinants. An improved valence-bond wave function would include ionic resonance structures like $H^- Be^{+2} H^-$

$$\Psi_{BeH_2}^{VB+ionic} = c_{cov} \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \overbrace{\psi_{sp}^{Be,+} \quad \psi_{1s}^{H,right}} \quad \overbrace{\psi_{sp}^{Be,-} \quad \psi_{1s}^{H,left}} \right|$$

$$+ c_{ionic} \left| \psi_{1s}^{Be}\alpha \quad \psi_{1s}^{Be}\beta \quad \psi_{1s}^{H,right}\alpha \quad \psi_{1s}^{H,right}\beta \quad \psi_{1s}^{H,left}\alpha \quad \psi_{1s}^{H,left}\beta \right| \quad (4.192)$$

and an adequate description requires considering even more resonance structures,

$$\text{H-Be-H} \leftrightarrow H^- Be^{+2} H^- \leftrightarrow \text{H-Be}^+ H^- \leftrightarrow H^- Be^+\text{-H} . \quad (4.193)$$

XIV.   Orbital Hybridization

The valence-bond description of BeH_2 shows that the idea of orbital hybridization is, at its heart, a concept associated with valence-bond theory. Hybrid orbitals localize electrons between atoms, giving rise to a picture of bonding that is consistent with Lewis-dot diagrams and the theory of resonance. The introduction of hybrid orbitals is consistent with the emphasis placed on electron pairing in valence-bond theory.

By contrast, the molecular orbitals in BeH_2 are delocalized, stretching over all three centers. The concept of the "electron pair bond" plays a much smaller role in molecular orbital theory.

Despite their very different perspectives on chemical bonding, molecular-orbital theory and valence-bond theory are equivalent paths towards enlightenment in quantum chemistry: if we include ionic structures in valence-bond theory or include excited-state configurations in molecular-orbital theory, then we will obtain the same wave function. We expect, then, that there is some way to "localize" molecular orbitals so that hybrid orbitals and electron-pair bonds are recovered. This is usually, but not always, true. It is unsurprising that there are some cases where localized molecular-orbitals cannot be found. For example, we would not expect to be able to describe the 3-center, 2-electron bridging

bonds in diborane with orbitals that were localized between only two atoms. Similarly, we would not expect to be able to completely describe an aromatic molecule like benzene with localized orbitals. These requirements form the basis of the Hund's localization criterion:

Hund's Localization Criterion: *Consider a P-atom molecule. For each atom in the molecule, determine:*

- b_i, *the number of atomic orbitals available for bonding.*
- n_i, *the number of "unpaired valence electrons" used for bonding.*
- e_i, *the number of atoms to which the atom is bonded.*

If $b_i = n_i = e_i$ for every atom in the molecule, then all the bonds can be localized. More generally, if $b_i = n_i = e_i$ for any specific atom, then the bonds involving that atom can be localized.

A useful supplement to Hund's localization criterion is the Gritsenko, Ensing, Schipper, Baerends (GESB) rule,

GESB rule: *Consider a P-atom molecule. For each atom in the molecule, determine:*

- n_i, *the number of electrons involved in bonding to the adjacent atoms.*
- c_i, *the number of atomic centers over which the bond extends.*

If $\frac{n_i}{c_i}$ is an integer, then the bonds in the molecule are "conventional."

The GESB rule is useful for characterizing "conventional" electron-pair bonding. (Simple aromatic molecules satisfy the GESB rule,[45] but more complex bonding situations—for example, the two-electron three-center bonds in diborane, the four-electron three-center bonds associated with the transition state of $S_N 2$ reactions—do not satisfy the GESB rule. As a general rule, valence-bond theory works best when Hund's localization criterion is satisfied and molecular-orbital theory works best when the GESB rule is satisfied. When the GESB rule is not satisfied, neither molecular-orbital theory nor valence-bond theory is entirely reliable.

It is instructive to consider how molecular orbitals can be "localized." For this purpose, we reconsider the BeH_2 molecule. Manipulating the Slater determinant wave function, we obtain

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[45] In benzene, a carbon atom forms (a) a two-electron two-center bond with a hydrogen atom and (b) a three-electron three-center bond with the adjacent carbon atoms.

$$\Psi_{\text{BeH}_2}^{\text{MO}} = \begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \psi_{\sigma_g[2s]}^{BeH_2}\alpha & \psi_{\sigma_g[2s]}^{BeH_2}\beta & \psi_{\sigma_u[2p]}^{BeH_2}\alpha & \psi_{\sigma_u[2p]}^{BeH_2}\beta \end{vmatrix}$$

$$= \begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \psi_{\sigma_g[2s]}^{BeH_2}\alpha & \psi_{\sigma_g[2s]}^{BeH_2}\beta & \left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right)\alpha & \left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right)\beta \end{vmatrix}$$

$$= \begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \left((-\tfrac{1}{2})\left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right) + \psi_{\sigma_g[2s]}^{BeH_2}\right)\alpha & \left((-\tfrac{1}{2})\left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right) + \psi_{\sigma_g[2s]}^{BeH_2}\right)\beta \\ \cdots & \left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right)\alpha & \left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right)\beta \end{vmatrix} \quad (4.194)$$

$$= \tfrac{1}{2}\begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \left(\psi_{\sigma_g[2s]}^{BeH_2} - \psi_{\sigma_u[2p]}^{BeH_2}\right)\alpha & \left(\psi_{\sigma_g[2s]}^{BeH_2} - \psi_{\sigma_u[2p]}^{BeH_2}\right)\beta \\ \cdots & \left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right)\alpha & \left(\psi_{\sigma_u[2p]}^{BeH_2} + \psi_{\sigma_g[2s]}^{BeH_2}\right)\beta \end{vmatrix}$$

The equalities in the above equation are based on the theorem that the determinant of a matrix is not changed by adding a constant times one column (or row) to another column (or row) of the matrix. Thus,

$$\begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{vmatrix} = \begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} + \lambda a_{1m} \\ a_{21} & a_{22} & \cdots & a_{2n} + \lambda a_{2m} \\ \vdots & & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} + \lambda a_{nm} \end{vmatrix}. \quad (4.195)$$

Repeated application of Eq. (4.195) yields the result in Eq. (4.194), which can then be simplified to

$$\Psi_{\text{BeH}_2}^{\text{MO}} = \tfrac{1}{2}\begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \left(2c_{Be}\psi_{sp}^{Be,-} - \tfrac{2}{\sqrt{2}}c_H\psi_{1s}^{left}\right)\alpha & \left(2c_{Be}\psi_{sp}^{Be,-} - \tfrac{2}{\sqrt{2}}c_H\psi_{1s}^{left}\right)\beta \\ \cdots & \left(2c_{Be}\psi_{sp}^{Be,+} + \tfrac{2}{\sqrt{2}}c_H\psi_{1s}^{right}\right)\alpha & \left(2c_{Be}\psi_{sp}^{Be,+} + \tfrac{2}{\sqrt{2}}c_H\psi_{1s}^{right}\right)\beta \end{vmatrix}$$

$$= 8\begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \left(c_{Be}\psi_{sp}^{Be,-} - \tfrac{1}{\sqrt{2}}c_H\psi_{1s}^{left}\right)\alpha & \left(c_{Be}\psi_{sp}^{Be,-} - \tfrac{1}{\sqrt{2}}c_H\psi_{1s}^{left}\right)\beta \\ \cdots & \left(c_{Be}\psi_{sp}^{Be,+} + \tfrac{1}{\sqrt{2}}c_H\psi_{1s}^{right}\right)\alpha & \left(c_{Be}\psi_{sp}^{Be,+} + \tfrac{1}{\sqrt{2}}c_H\psi_{1s}^{right}\right)\beta \end{vmatrix} \quad (4.196)$$

In the last line we use the fact that multiplying a row or column of a matrix by a constant causes the determinant of the matrix to be multiplied by a constant. In Eq. (4.196), the localized "hybrid" orbitals are evident. If we choose $c_{Be} = 1$ and $c_H = \sqrt{2}$ and then ignore all the Slater determinants containing doubly-occupied atomic orbitals, then Eq. (4.196) reduces to the perfect-pairing valence-bond wave function.

For a molecule like BeH_2^+, Hund's localization criterion is no longer satisfied. Thus, it is impossible to form localized orbitals. Revisiting our previous analysis, we observe that we lack the β-spin molecular orbital we need in order to rearrange the determinant into its localized orbital form:

$$\Psi_{BeH_2^+}^{MO} = \begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \psi_{\sigma_g[2s]}^{BeH_2^+}\alpha & \psi_{\sigma_g[2s]}^{BeH_2^+}\beta & \psi_{\sigma_u[2p]}^{BeH_2^+}\alpha \end{vmatrix}$$

$$= \begin{vmatrix} \psi_{1s}^{Be}\alpha & \psi_{1s}^{Be}\beta & \left(c_{Be}\psi_{sp}^{Be,-} - \tfrac{1}{\sqrt{2}}c_H\psi_{1s}^{left}\right)\alpha & \psi_{\sigma_g[2s]}^{BeH_2^+}\beta & \left(c_{Be}\psi_{sp}^{Be,+} + \tfrac{1}{\sqrt{2}}c_H\psi_{1s}^{right}\right)\alpha \end{vmatrix} \quad (4.197)$$

Thus, we can write localized orbitals for the α-spin bonding electrons, but not for the β-spin electron. This is consistent with the fact that BeH_2^+ has a 3-center 2-electron bond. Clearly, we cannot localize the orbitals in BeH_2^{+2} either.[46]

From the preceding, it is clear that when we can localize molecular orbitals, orbital hybridization of atomic orbitals naturally follows. Probably the most important cases of orbital hybridization (other than the sp-hybridization, which we have already considered in great detail) are sp^2 hybridization, with hybrid orbitals of the form

$$\psi_x = \tfrac{1}{\sqrt{3}}\psi_{2s} + \sqrt{\tfrac{2}{3}}\psi_{2p_x}$$
$$\psi_{x+y} = \tfrac{1}{\sqrt{3}}\psi_{2s} - \left(\tfrac{1}{\sqrt{6}}\psi_{2p_x} + \tfrac{1}{\sqrt{2}}\psi_{2p_y}\right) \quad (4.198)$$
$$\psi_{x-y} = \tfrac{1}{\sqrt{3}}\psi_{2s} - \left(\tfrac{1}{\sqrt{6}}\psi_{2p_x} - \tfrac{1}{\sqrt{2}}\psi_{2p_y}\right)$$

and sp^3 hybridization, with hybrid orbitals of the form

$$\psi_1 = \tfrac{1}{2}\left(\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z}\right)$$
$$\psi_2 = \tfrac{1}{2}\left(\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z}\right)$$
$$\psi_3 = \tfrac{1}{2}\left(\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z}\right) \quad (4.199)$$
$$\psi_4 = \tfrac{1}{2}\left(\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z}\right)$$

Because hybrid orbitals are associated with localized molecular orbitals and electron-pair bonds, they are associated most strongly with valence-bond theory.

After all of this analysis, the burning question arises as to whether the "delocalized" or "localized" describing of the electrons in molecules is most appropriate. The answer depends largely on what one is seeking to describe. The localized-orbital picture is most strongly associated with Lewis structures, and so in some sense is the most useful tool for describing molecular geometries. The delocalized molecular-orbital picture is most useful for spectroscopy: the spectrum of BeH_2 clearly indicates that there are three doubly occupied molecular orbitals, each of which has a different energy. This is consistent with the molecular-orbital picture (cf. Eq. (4.184)) but not with the valence-bond picture, where the sp-hybrid orbitals are equivalent (and would thus be expected to have equivalent orbital energies). In the molecular-orbital picture, electronic transitions can be

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[46]   We can, however, localize the electrons in BeH_2^-. Can you explain why?

approximated by exciting an electron from an occupied molecular orbital to an unoccupied molecular orbital;[47] the method for describing electronic spectra using the valence-bond formalism is more complicated. (By analogy, to obtain a "chemical structure" of bonds and lone pairs from the valence-bond method is simple, but obtaining similar information from molecular-orbital theory requires localization of the molecular orbitals.)

XV. Summary: Pros and Cons of the Molecular-Orbital and Valence-Bond Approaches

- **Molecular Orbital Theory is more useful for spectroscopy.** In molecular-orbital theory, you can approximate electronic transitions by promoting electrons from occupied to unoccupied orbitals.

- **Valence Bond Theory gives a more intuitive picture of molecular structure and chemical binding.** In valence-bond theory, electron pairing is emphasized. This makes direct contact with the concept of a chemical bond.

- **Primitive Molecular Orbital Theory tends to give an incorrect description of molecular dissociation.** Valence Bond Theory usually does predict dissociation satisfactorily.

- **Valence-Bond Theory is more difficult computationally.** Most computational techniques are based on molecular-orbital theory and corrections thereto. Tthere are simple "secular equations" to solve in molecular-orbital theory, the multideterminant nature of the Valence-Bond wave function is less amenable to solution by standard methods. In addition, molecular orbitals are all orthogonal, while the atomic orbitals in Valence-Bond theory are usually nonorthogonal.

- **Primitive Valence-Bond Theory includes a little bit of electron correlation.** Simple Valence-Bond theory includes a little electron correlation, notably the fact that it is

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[47] Recall that we described molecular orbitals as being eigenfunctions of an effective one-electron molecular Hamiltonian; moving an electron from a "occupied" state of this effective one-electron Hamiltonian to an "unoccupied" state corresponds to excitation. Valence bond theory, by contrast, relies on atomic orbitals—eigenfunctions of the *atomic* Hamiltonians, rather than an approximate molecular Hamiltonian. Unless the energy levels of the constituent atoms correspond to the energy levels of the molecule (this is only true in the united atom limit), valence-bond theory is not as useful as molecular-orbital theory for spectroscopy.

unlikely for both of the electrons composing a chemical bond to be on the same atom at the same time.

- **Primitive Molecular-Orbital Theory describes bond polarity better.** We can describe the "partial ionic" character of a heteronuclear molecule in the simplest (single Slater determinant) Molecular-Orbital Theory description. However, the "perfect pairing" description in Valence-Bond theory assumes that the atoms composing a bond share the electrons equally and requires "ionic terms" to describe the asymmetric sharing of electrons when bonded atoms have different electronegativities.

XVI.   Bent's Rule

As a "special topic," I will mention in this context is Bent's rule, which states that the more electronegative groups tend to have smaller bond angles (all else being equal). Thus, if we consider the $2s$ and $2p$ orbitals to be degenerate, and form the sp^2 hybrids,

$$
\begin{aligned}
\psi_x &= \tfrac{1}{\sqrt{3}}\psi_{2s} + \sqrt{\tfrac{2}{3}}\psi_{2p_x} \\
\psi_{x+y} &= \tfrac{1}{\sqrt{3}}\psi_{2s} - \left(\tfrac{1}{\sqrt{6}}\psi_{2p_x} + \tfrac{1}{\sqrt{2}}\psi_{2p_y}\right) \\
\psi_{x-y} &= \tfrac{1}{\sqrt{3}}\psi_{2s} - \left(\tfrac{1}{\sqrt{6}}\psi_{2p_x} - \tfrac{1}{\sqrt{2}}\psi_{2p_y}\right)
\end{aligned}
\tag{4.200}
$$

and consider how these degenerate orbitals are split if the charge on the x-axis, q_x is increased, so that it is larger than the other charges q_{x+y} and q_{x-y}. We see that the $\psi_x(\boldsymbol{r})$ orbital becomes lower in energy and, moreover, it is favorable to increase the $2p_x$ character in this orbital. But this decreases the $2p_x$ character in the ψ_{x+y} and ψ_{x-y} hybrids, which causes the 120° bond angle to tend towards 90° (which is what happens in the limit where $q_x \gg q_{x+y}, q_{x-y}$).
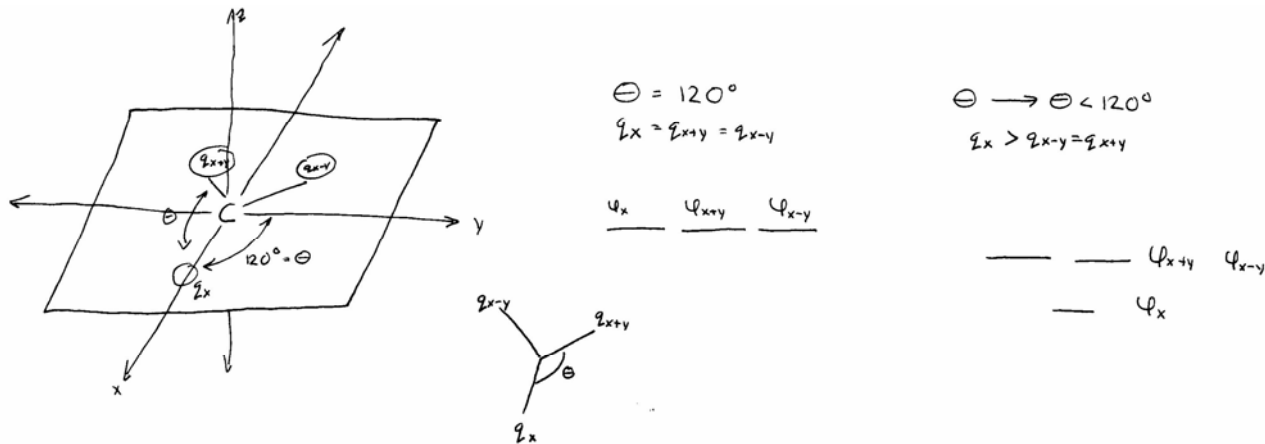
This is the argument for Bent's rule, which states that more electronegative substituents favor hybrid orbitals with less s character, and thus tend to have smaller bond angles. Thus electronegative substituents prefer the axial sites in trigonal bipyramidal complexes (except when steric effects predominate) and lone pairs and other electropositive groups prefer the equatorial sites. Similarly, the bond angle between the fluorine atoms in difluoromethane is less than the classic tetrahedral bond length of $109.5°$, as is the bond angle in ammonia and water (because the electron pairs are more electropositive than hydrogen).

XVII. Ligand Field Theory

While it does not depend directly on the methods of the preceding section, the effect of imposing a ligand field on a transition metal is conceptually and methodologically similar. For example, suppose we are given an octahedral metal complex. In general, the ligands are negatively charged and the d-orbitals are not heavily involved in covalent bonding to the ligands, so we can model the ligands with negative point charges at the points $(0,0,\pm d),(0,\pm d,0),(\pm d,0,0)$. Since, in the absence of the ligands' field, all the metal d-orbitals are degenerate, this is a task for degenerate perturbation theory. In particular, we model the complex with the Hamiltonian,

$$\hat{H} = \hat{H}_{atom} + V_{\substack{ligand \\ field}}, \tag{4.201}$$

where

$$V_{\substack{ligand \\ field}} \equiv \sum_{i=1}^{N} \left(\begin{array}{c} \dfrac{-q}{\|\boldsymbol{r}_i - [0,0,d]\|} + \dfrac{-q}{\|\boldsymbol{r}_i - [0,0,-d]\|} + \dfrac{-q}{\|\boldsymbol{r}_i - [0,d,0]\|} \\ + \dfrac{-q}{\|\boldsymbol{r}_i - [0,-d,0]\|} + \dfrac{-q}{\|\boldsymbol{r}_i - [d,0,0]\|} + \dfrac{-q}{\|\boldsymbol{r}_i - [-d,0,0]\|} \end{array} \right). \tag{4.202}$$

Here, $-q$ approximates the charge on the ligand.
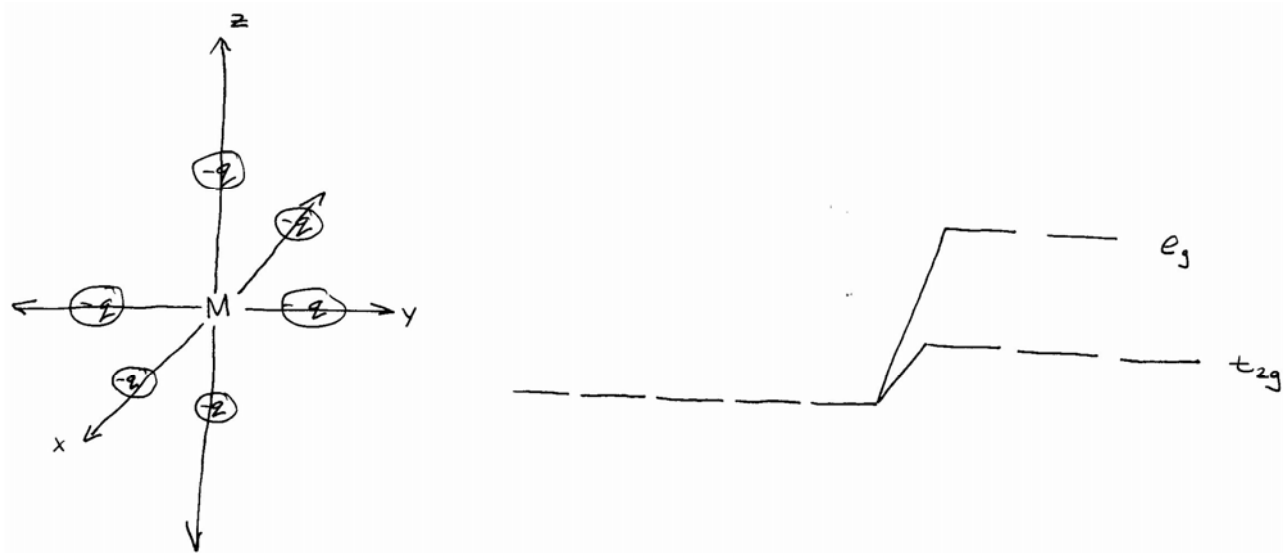
In keeping with degenerate perturbation theory, we need to evaluate the effect of this perturbation on the d-orbitals of the system. (The other orbitals are also affected, but we are primarily interested in the splitting.) To do this, we evaluate the elements of the perturbation matrix,

$$V_{m,m'} \equiv \left\langle R_{3d}(r)Y_2^m(\theta,\phi) \left| V_{\substack{ligand \\ field}} \right| R_{3d}(r)Y_2^{m'}(\theta,\phi) \right\rangle \qquad (4.203)$$

where $R_{3d}(r)$ is the radial component of the orbital, which can be taken from accurate calculations.

These integrals are very tedious, but the way in which they are worked is generally useful, and thus worthy of mention. The key is the expansion of $\frac{1}{|r-r'|}$ in terms of the spherical harmonics. In particular,

$$\frac{1}{|r-r'|} \equiv \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \left(\frac{\min(r,r')}{\max(r,r')} \right)^{\lambda} \frac{Y_\lambda^\mu(\theta,\phi)Y_\lambda^\mu(\theta',\phi')}{\max(r,r')} \qquad (4.204)$$

where $Y_\lambda^\mu(\theta,\phi)$ and $Y_\lambda^\mu(\theta',\phi')$ are the spherical harmonics centered at the location of the particle at r and the particle at r', respectively. Just as before, $\min(r,r')$ and $\max(r,r')$, are the smaller and larger of r and r', respectively.

For example, if we assume that the electrons in a d-orbital are rarely as far away from the molecule as the position of the ligands, then we can approximate the terms in the perturbation matrix using expansions of the form:

$$\frac{1}{|\mathbf{r}_i - [0,0,d]|} \approx \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \left(\frac{r_i}{d}\right)^{\lambda} \frac{Y_{\lambda}^{\mu}(\theta,\phi) Y_{\lambda}^{\mu}(\theta',\phi')}{d}$$
$$\approx \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{4\pi}{2\lambda+1} \frac{r^{\lambda}}{d^{\lambda+1}} Y_{\lambda}^{\mu}(\theta,\phi) Y_{\lambda}^{\mu}(\theta',\phi').$$

(4.205)

Let's suppose we do this, and examine what we learn.

- First of all, all the d-orbitals are shifted up in energy, but there is a splitting, with $\psi_{d_{x^2+y^2}}$ and $\psi_{d_{z^2}}$ lying higher in energy (thus shifted more) and $\psi_{d_{xy}}, \psi_{d_{xz}}, \psi_{d_{yz}}$ lying lower in energy (and thus shifted less). Any linear combination of $\psi_{d_{x^2+y^2}}$ and $\psi_{d_{z^2}}$ is also acceptable, as is any linear combination of $\psi_{d_{xy}}, \psi_{d_{xz}}, \psi_{d_{yz}}$. But the "Cartesian d-orbitals" are the usual choice.

- For a reasonable choice for the magnitude of the ligand charge ($q \approx 1$) and the distance of the ligand from the central metal ($d \approx 2.4\text{Å} = 4\,\text{Bohr}$) the splitting between the orbitals is observed to be about $1000\ cm^{-1}$, which is about 10 times less than is experimentally observed. Simple revisions to the model tend to give worse results, not better results, and an "orbital picture" is required to give quantitative accuracy.

Based on its inability reproduce experimental data, one might ask whether ligand field theory is useful at all. It is important that the ligand field approach tends to predict the splitting of the orbitals qualitatively, with a doubly degenerate e_g set of orbitals at "high energy" and a triply degenerate set of t_{2g} orbitals at lower energy. Similarly, the appropriate splitting of the d-orbitals in square planar and tetrahedral complexes is also predicted, as is the alteration of splitting associated with distortions (e.g., the Jahn-Teller distortion), inequivalent ligands, etc.. All of these effects are determined by the location of the ligands—not by the ligands' specific properties—and ligand field theory describes the *qualitative* effects of this symmetry and the distortion thereof quite well.

There is another important application, and that is to describe the orbitals in compounds that have complicated symmetry. For example, a metal atom that is chelated will generally not feel a field with any well-defined symmetry, yet we can describe the d-orbital splitting in a qualitative way with crystal field theory. Crystal field theory is also useful for identifying the key molecular orbitals. For example, one can consider the unconventional choice of a square pyramidal complex where the ligands are positioned in

the xz-plane (usually the xy-plane is chosen). Constructing the appropriate "perturbing" ligand-field potential,

$$V_{\substack{ligand \\ field}} \equiv \sum_{i=1}^{N} \left(\frac{-q}{|r_i - [0,0,d]|} + \frac{-q}{|r_i - [0,0,-d]|} + \frac{-q}{|r_i - [d,0,0]|} + \frac{-q}{|r_i - [-d,0,0]|} \right), \tag{4.206}$$

and then evaluating and finding the eigenvectors and eigenvalues of the perturbation matrix (Eq. (4.203)), we find that the orbitals are split, with the lowest energy level being doubly degenerate ($\psi_{3d_{xy}}$ and $\psi_{3d_{yz}}$), the next highest-orbital being the unconventional $\psi_{3d_{y^2}} = \frac{1}{2}\psi_{3d_{z^2}} + \frac{\sqrt{3}}{2} \cdot \psi_{d_{x^2-y^2}}$, followed by the $\psi_{3d_{xz}}$. Finally, the highest-energy orbital is the unconventional $\psi_{3d_{z^2-x^2}} = \frac{\sqrt{3}}{2}\psi_{3d_{z^2}} - \frac{1}{2}\psi_{3d_{x^2-y^2}}$. All of these results follow from a simple ligand field treatment, and emphasize that, whatever its quantitative deficiencies, the ligand field approach is useful for determining the splitting pattern for energy levels and the symmetries of the orbitals.