11 Quantum Mechanical Treatment of Simple Molecules

One of the great achievements of quantum mechanics was a description of the stability of the chemical bond. It turns out that this is mainly a quantum mechanical effect; classical mechanics cannot fully account for its stability.

Consider the case of H_2. As you bring in two hydrogen atoms from infinity, their electron clouds begin to overlap, and at some point there is a buildup of electron probability between the nuclei; the electrons feel the attractive forces of both atoms. We want to see physically why this might occur.

First I will discuss the H_2 molecule itself, since it is one of the simplest examples of a chemical bond (H_2^+ is actually stable and is even simpler, but it doesn't display some of the more general principles that I would to demonstrate).

After discussing H_2 I will then talk about one-electron orbitals for molecules in the same way we had one-electron orbitals for atoms. These orbitals are appropriately called **Molecular Orbitals.**

We will only scratch the surface here, since the treatment of the electronic Schrödinger equation for molecules is a field in itself. My goals are (1) to be able to give you enough of a background in the quantum mechanics of simple molecules to be able to understand molecular spectroscopy, and (2) to give you some basis for understanding applications of these concepts to organic and inorganic chemistry.

The place to start a discussion of the quantum mechanical treatment of H_2 is with the **Born-Oppenheimer Approximation**.

The Hamiltonian for the Hydrogen molecule is

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\nabla_A^2 + \nabla_B^2\right) - \frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{Z^2e^2}{4\pi\varepsilon_0 R}$$

where *A* and *B* refer to the two nuclei and 1 and 2 to the two electrons.

As we discussed earlier in the course, because the nuclei are much more massive than the electrons, ($M/m_e \approx 1835$ for hydrogen and is higher for any other molecule), we can neglect the nuclear kinetic energy term from this Hamiltonian.

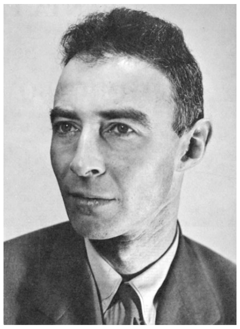
We are saying that on the timescale of electron motion, the nuclei are essentially fixed. One then solves the electronic part of the Schrödinger equation considering the internuclear separation *R* as a parameter (*i.e.* the Schrödinger equation is solved as a function of *R*).

The Hamiltonian for H_2 then becomes (in atomic units):

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

Our general approach to solving this equation will be to apply the variational method using various types of basis functions for the trial function.

Max Born



Robert Oppenheimer

11.1 Valence-Bond method for H_2

This approach was introduced by Heitler and London in 1927 and gave the first satisfactory explanation of the stability of a chemical bond. Later this method was extended by John Slater and Linus Pauling.

We will ignore spin in this treatment because as we have seen, for any two-electron system, the spin and spatial parts of the wave function are separable.

The valence bond method takes the following approach:

At large internuclear separation, an H_2 molecule looks like two separate hydrogen atoms. The ground state wave function in this case would be

$$\psi_1 = 1s_A(1)1s_B(2)$$

where $1s_A$ denotes a 1*s* hydrogen orbital centered on nucleus *A* and $1s_B$ a 1*s* hydrogen orbital centered on nucleus *B*.

Because the electrons are indistinguishable, an equally good wave function is

$$\psi_2 = 1s_A(2)1s_B(1)$$

Heitler and London's approach was to take a linear combination of these two functions as a variational trial function:

$$\psi = c_1\psi_1 + c_2\psi_2 = c_1 1s_A(1)1s_B(2) + c_2 1s_A(2)1s_B(1)$$

As we showed in our treatment of the variational principle, when we use a trial function that is a linear combination of functions with the expansion coefficients as variable parameters, the problem reduces to solving what we called the secular determinant,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

where I have used the fact that $H_{21}=H_{12}$.

Walter Heitler

Fritz London

John Slater

Linus Pauling

Solving this equation gives us an estimate to the lowest two energies (recall that the number of energies it estimates is determined by the number of terms included in the trial function).

One can also get the coefficients c_1 and c_2 by substituting the eigenvalues, E, back into the set of equations that gave rise to the determinant.

Recall that the S terms are what we call overlap integrals. Let's first look at those along the diagonal.

$$\begin{aligned} S_{11} &= \int\int 1s_A(1)1s_B(2)1s_A(1)1s_B(2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \\ &= \int 1s_A(1)1s_A(1)d\mathbf{r}_1 \int 1s_B(2)1s_B(2)d\mathbf{r}_2 \\ &= 1 \end{aligned}$$

These terms are equal to 1 because the orbitals are normalized. (note that $d\mathbf{r}_1$ and $d\mathbf{r}_2$ represent the volume element for electron 1 and 2, independent of the nucleus.)

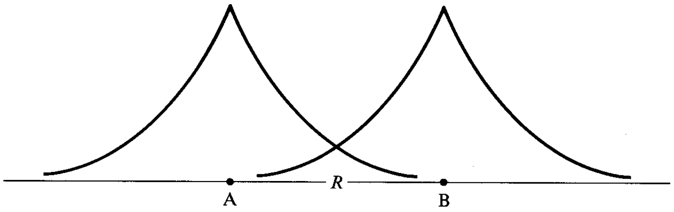
The value of the integrals S_{22} will be the same.

The off-diagonal overlap integrals are somewhat different, however.

$$\begin{aligned} S_{12} &= \int\int 1s_A(1)1s_B(2)1s_A(2)1s_B(2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \\ &= \int 1s_A(1)1s_B(1)d\mathbf{r}_1 \int 1s_B(2)1s_A(2)d\mathbf{r}_2 \end{aligned}$$

This is different from the diagonal term since the 1s orbitals in each integral are centered on different nuclei.

You can see that these two integrals are the same. Thus we can write $S_{12} = S^2$ where S is a single overlap integral. These integrals represent the overlap of the wave function on one nucleus with one on the other.



You can see that the region of overlap of these functions will be a strong function of *R*. Evaluation of the overlap integral as a function of *R* is a fairly long (but not difficult) procedure.

The result is

$$S(R) = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

We still need to evaluate the other terms in the determinant.

$$H_{11} = \int\int 1s_A(1)1s_B(2)\hat{H}1s_A(1)1s_B(2)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

Recall that

$$\hat{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

You can see that this Hamiltonian is comprised of two one electron Hamiltonians plus a few additional terms due to attraction of an electron by the opposite nucleus, the inter-electronic repulsion, and the nuclear repulsion.

Since the 1*s* functions are eigenfunctions of the one electron Hamiltonians, we can see that

$$H_{11} = -\frac{1}{2} - \frac{1}{2} + J = -1 + J$$

where

$$J = \int\int 1s_A(1)1s_B(2)\left(-\frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{r_{12}} + \frac{1}{R}\right)1s_A(1)1s_B(2)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

Recall that the energy of the H atom in atomic units is -1/2, so this looks like twice the H atom energy plus the integral.

We can break up this integral to see its physical significance.

$$J = -\int\frac{\left|1s_A(1)\right|^2}{r_{1B}}d\mathbf{r}_1 - \int\frac{\left|1s_B(2)\right|^2}{r_{2A}}d\mathbf{r}_2 + \int\int\frac{\left|1s_A(1)\right|^2\left|1s_B(2)\right|^2}{r_{12}}d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{R}$$

The first term is the coulomb interaction of the electron on nucleus A with nucleus *B*. The second term is the interaction of the electron on *B* with nucleus *A*. The third term is the inter-electronic repulsion. The last term is the nuclear repulsion. This integral is therefore called a ***coulomb integral.***

I will not take the time to evaluate this integral here. The result, which will be a function of the distance *R*, is

$$J = e^{-2R}\left(\frac{1}{R} + \frac{5}{8} - \frac{3}{4}R - \frac{R^2}{6}\right)$$

One could easily show that H_{22}=H_{11}.

The final term to evaluate is H_{12}

$$H_{12} = \int\int 1s_A(1)1s_B(2)\hat{H}1s_A(2)1s_B(1)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

If we were to substitute the Hamiltonian into the integral and use the fact that the 1*s* functions are eigenfunctions of the 1 electron Hamiltonians one obtains

$$H_{12} = -S^2 + K$$

where
$$K = \int\int 1s_A(1)1s_B(2)\left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}\right)1s_A(2)1s_B(1)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

K cannot be interpreted as a coulomb integral in the same way as *J*. We can rearrange this integral to get

$$K = \int\int 1s_A(1)1s_B(1)\left(-\frac{1}{r_{1A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}\right)1s_A(2)1s_B(2)\,d\mathbf{r}_1\,d\mathbf{r}_2$$

This integral arises because we are using a trial function that does not distinguish between the two electrons. (If we used only one of the two terms in the trial function, this *K* integral would not have arisen.) Because of this, *K* is called an ***exchange integral,*** and as such it is strictly a quantum mechanical property.

The evaluation of this exchange integral is pretty involved and I will not do it here. I will plot it as a function of *R* in a moment.

We are left with the following secular equation:

$$\begin{vmatrix} -1+J-E & -S^2+K-ES^2 \\ -S^2+K-ES^2 & -1+J-E \end{vmatrix} = 0$$

This gives us a quadratic equation with two roots.

$$E_\pm = -1 + \frac{J \pm K}{1 \pm S^2}$$

Note however that -1 is the energy of two isolated hydrogen atoms (in atomic units). We can define ΔE as the energy of H_2 relative to that of the isolated atoms. We then have

$$\Delta E_\pm = \frac{J \pm K}{1 \pm S^2}$$

If we take E_+ and put it back into the equations that gave us the secular determinant, we can get the constants c_1 and c_2 that go into our expression for the wave function.

We would find that

$$c_1 = c_2 = \frac{1}{\sqrt{2\left(1+S^2\right)}}$$

This gives us

$$\psi_+ = \frac{1}{\sqrt{2\left(1+S^2\right)}}\left(\psi_1 + \psi_2\right)$$

Recall that

$$\psi_1 = 1s_A(1)1s_B(2)$$

and

$$\psi_2 = 1s_A(2)1s_B(1)$$

You can see that this function is symmetric with respect to interchange of electrons 1 and 2, and hence its designation as ψ_+.

Similarly, E_- would give us

$$\psi_- = \frac{1}{\sqrt{2\left(1-S^2\right)}}\left(\psi_1 - \psi_2\right)$$

This function is antisymmetric with respect to particle interchange.

We have neglected spin up to this point. Remember we can do this because it is a two-electron system and the wave functions factor into a spatial and spin part. We can look at these functions and see what the spin parts need to be.

Since ψ_+ is symmetric with respect to interchange, the spin part must be antisymmetric.

Remember from our treatment of Helium, there is only one antisymmetric spin function involving α and β, but 3 symmetric functions:

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \qquad \text{antisymmetric}$$

$$\left.\begin{array}{c} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \end{array}\right\} \qquad \text{symmetric}$$

Thus, to have the correct overall symmetry behavior, ψ_+ must go with the antisymmetric spin function, and ψ_- goes with any of the symmetric spin functions.

Now let us look at the energy eigenvalues $\Delta E_\pm$ as a function of *R*. Recall that

$$\Delta E_\pm = \frac{J \pm K}{1 \pm S^2}$$

and that *J*, *K* and *S* are functions of *R*. If we plot these we see the following

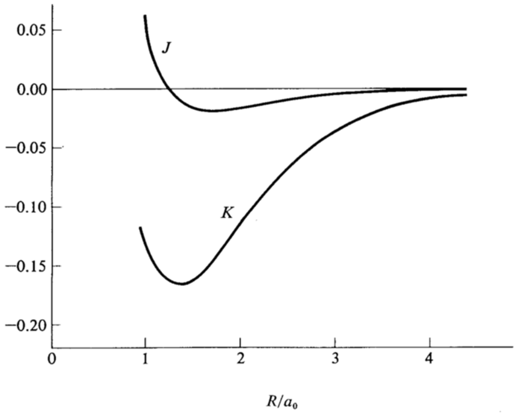
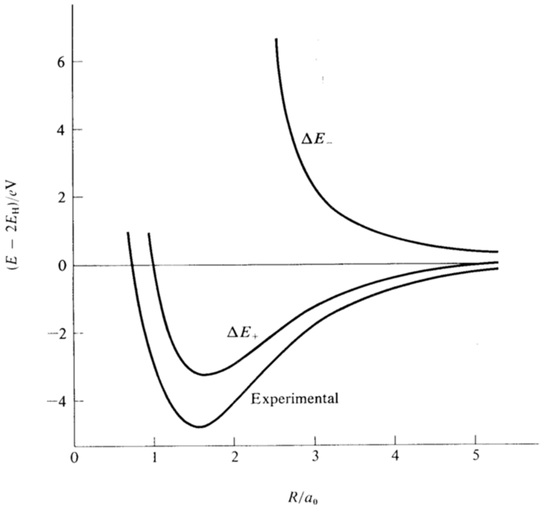


Figure 9-4. The Heitler-London valence-bond Coulomb (*J*) and exchange (*K*) integrals as a function of internuclear separation *R*. All quantities are expressed in atomic units.

As you can see, it is the exchange integral that accounts for most of the stability of the H_2 bond (in the context of the trial function we have chosen). Note that the overlap integral is a monotonically decaying function of R. Because the exchange integral is a quantum mechanical quantity, *the existence of the chemical bond is mainly a quantum mechanical effect.*

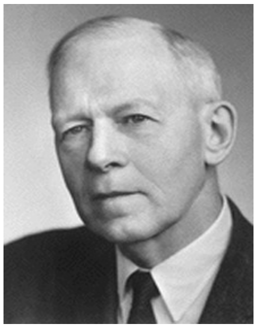


(The two curves in the figure above represent the electronic energy as a function of R. We could take this as a 1-dimensional function and solve the vibrational problem!)

While the valence bond approach doesn't give very good quantitative agreement, it gives us a good physical picture for the stability of the chemical bond.

We will now take a slightly different approach to solving the electronic Schrödinger equation for molecules. We will still use the variational principle, but rather than starting with wave functions that represent two hydrogen atoms at infinite distance (*i.e.* two atomic orbitals), we will construct one-electron molecular orbitals and then put electrons into these one-electron functions.

We will derive the molecular orbitals themselves by considering the H_2^+ molecule. It is a one-electron diatomic molecule, and will play the same role in molecular wave functions as H did for atomic wave functions. This way of describing molecular bonding was pioneered by Robert Mulliken.



Robert Mulliken

11.2 Molecular Orbital treatment of H_2^+

By using an approximate treatment of H_2^+, we develop the framework in which we can treat many electron molecules. We want to find functions to serve as *molecular orbitals* in the same way the H atom functions serve as atomic orbitals. We will begin by using the variational principle on H_2^+.

The Hamiltonian for H_2^+ is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

We will try a linear trial function of the form

$$\psi = c_1 1s_A + c_2 1s_B$$

This is called a LCAO-MO (linear combination of atomic orbitals-molecular orbital) where $1s_A$ and $1s_B$ are 1*s* H atom wave functions centered on nucleus *A* or *B*.

Remember from our discussion of the variational principle that the optimal values of c_1 and c_2 can be found from a solution of the secular equation.

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{BA} - ES & H_{BB} - E \end{vmatrix} = 0$$

where

$$H_{AA} = \int 1s_A \hat{H} \, 1s_A \, d\tau$$

$$H_{BB} = \int 1s_B \hat{H} \, 1s_B \, d\tau$$

$$S = \int 1s_A \, 1s_B \, d\tau$$

We can see that $H_{AA} = H_{BB}$ since the Hamiltonian is symmetrical with respect to interchange of r_a and r_b.

Also, $H_{AB} = H_{BA}$ by symmetry

$$H_{AB} = \int 1s_A \hat{H} 1s_B \, d\tau$$

Solving the secular equation (analogous to the way we did with the valence-bond method) yields two roots:

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

These two roots are <u>upper bounds</u> for the energies of the ground and first excited state of H_2^+.
(We get the first 2 states because we included 2 terms in our linear trial function)

We can get the coefficients c_1 and c_2 in our linear trial function by substituting the roots E_+ and E_- back into our system of linear equations (which we never wrote explicitly).

We get

$$\psi_{\pm} = \frac{1}{\sqrt{2 \pm 2S}}\left(1s_A \pm 1s_B\right)$$

What we have found here is basically a one electron analog of the valence bond wave function that we used earlier, however there is an important difference between the valence bond and molecular orbital approaches.

Let's digress for a moment to compare the wave function for H_2 using both the VB and MO approaches.

Recall the valence bond wavefunction for H_2 is given by

$$\psi_{VB} = 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)$$

Consider what the MO for H_2 might look like. If we put each of the two electrons in a one electron molecular orbital, the wave function would be a product of those one electron functions:

$$\begin{aligned}\psi_{MO} &= \big(1s_A(1) + 1s_B(1)\big)\big(1s_A(2) + 1s_B(2)\big)\\ &= 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2) + 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2)\end{aligned}$$

The first two terms here are just the terms in the valence-bond wave function. The second two terms correspond to electron configurations in which both electrons are on one atom.

Using electron dot formulas this would look like:

$\mathrm{H}_A\mathbf{:}\ \mathrm{H}_B$ and $\mathrm{H}_A\ \mathbf{:}\mathrm{H}_B$

or

$\mathrm{H}_A^-\mathrm{H}_B^+$ and $\mathrm{H}_A^+\mathrm{H}_B^-$

These last two terms represent ionic structures.

So $\psi_{MO} = \psi_{VB} + \psi_{ionic}$

Using a trial function like this gives a better estimate than the *VB* wavefunction alone. *This suggests that the true wave function has some ionic character.*

Getting back to the solution of our problem we find for the energy:

$$E_\pm = \frac{H_{AA} \pm H_{AB}}{1 \pm S}$$

If we were to look a little more closely at the integrals H_{AA} and H_{AB}, we would see that we could break them up into coulomb and exchange integrals in a similar manner to the valence-bond approach.

The result is

$$\Delta E_\pm = \frac{J' \pm K'}{1 \pm S}$$

where J' is given by

$$J' = \int 1s_A\left(-\frac{1}{r_B} + \frac{1}{R}\right)1s_A\,d\mathbf{r}$$

and K' by

$$K' = \int 1s_A\left(-\frac{1}{r_A} + \frac{1}{R}\right)1s_B\,d\mathbf{r}$$

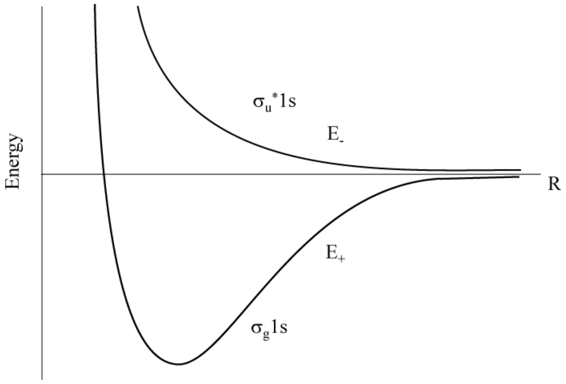
You can see these are basically the one-electron equivalents for the coulomb and exchange integrals we had earlier.

Note that the integrals are over the electron positions at a fixed value of *R*.

Thus $E_\pm$ is a function of *R*.

One can evaluate these integrals fairly easily, although we will not do it.

We can solve for different R and plot these as a function of *R*.



A brief digression about the notation of these states:

Each state of H_2^+ has a definite value of *m*. It turns out that $\left[\hat{L}_z, \hat{H}\right] = 0$. This will happen when the system has cylindrical symmetry. The electronic energy depends only on |*m*| since l_z^2 appears in the Hamiltonian. We did not write out the Hamiltonian explicitly to see this.

The absolute value of *m* is called λ: $\lambda = |m|$

One designates the states of H_2^+ by the value of λ in a similar way to the *s,p,d,f* notation for H atom states.

λ =	0	1	2	3	4
	σ	π	δ	φ	γ

The designation *s,p,d,f* for H atom states refers to the value of *l*. The designation $\sigma,\pi,\delta,\varphi$ for molecules indicates the value of $\lambda = |m|$.

Recall that *m* tells us how many nodes the wave function will have in the φ coordinate. We will later see that λ will also tell us something about the symmetry of the wave function.

We will also classify these states according to their properties upon inversion at the origin

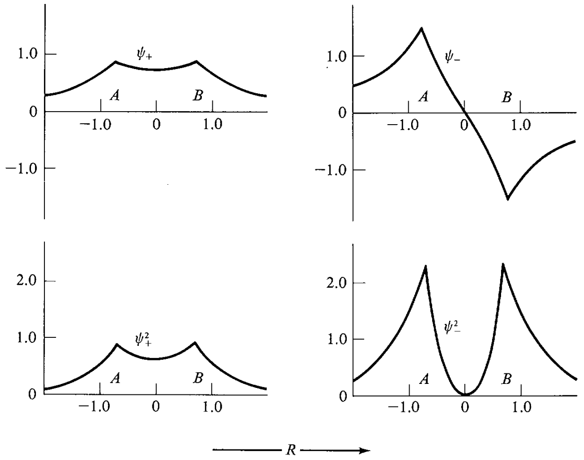
Even $\Rightarrow$ *g* for *gerade* Odd $\Rightarrow$ *u* for *ungerade*

Finally, the H_2^+ states are classified by the state of the H atom to which the molecule correlates at large *R*.

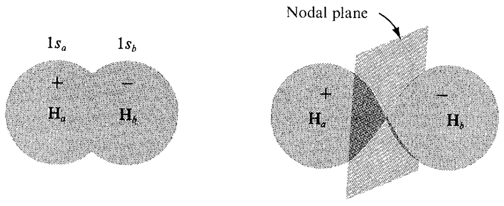
Thus, the lowest state of H_2^+ would be designated σ_g 1*s*.

Why we labeled the bonding σ_g and the antibonding σ_u will become clear in a moment.

If we look at the wavefunctions corresponding to these two potential curves, we can get a little better physical understanding of why one is bonding and the other is antibonding.



$\psi_+ = 1s_a + 1s_b$



$\psi_- = 1s_a - 1s_b$

If we look at $\psi_+ = 1s_A + 1s_B$

we see there is a buildup of electronic charge between the two nuclei, helping to cause mutual attraction. This arises from constructive interference between the two wave functions.

For $\psi_- = 1s_A - 1s_B$

we see that the probability goes to zero in between the two nuclei, *i.e.* the electron density is zero here, which gives rise to an antibonding orbital. (It will always be the case that antibonding orbital will have a nodal plane midway between the two nuclei.) Consequently the state is labeled $\sigma_u{}^*1s$

To determine whether an orbital is bonding or antibonding, one thus must look at the reflection of the wave function through a plane midway between the atoms. If the wavefunction changes sign, it must have a node.

⇒ This means there will be destructive interference and depleted electron density and will be antibonding

⇒ If the wavefunction does not change sign, it will be a bonding orbital.

From this simple LCAO-MO picture, we can get some reasonable insight into the nature of the chemical bond.

11.3 Higher MO's of H_2^+

We now only have orbitals for the 1st two states. This was because we included only two terms in our linear variational function.

We could have written

$$\psi = c_1\psi_{1s}(A) + c_2\psi_{2s}(A) + c_3\psi_{2p_0}(A) + c_4\psi_{1s}(B) + c_5\psi_{2s}(B) + c_6\psi_{2p_0}(B)$$

Because of the symmetry of H, we would get a similar result to what we obtained previously--the coefficients of the *B* orbitals will be ±1 times those of the *A* orbitals.

$$\psi = \left[c_1\psi_{1s}(A) + c_2\psi_{2s}(A) + c_3\psi_{2p_0}(A) \right] \pm \left[c_1\psi_{1s}(B) + c_2\psi_{2s}(B) + c_3\psi_{2p_0}(B) \right]$$

Consider for a moment the two electronic states that will dissociate to a 1s hydrogen atom. For this state, we would expect c_1 to be greater than c_2 or c_3. *Certainly at large R this is true.*

As a first approximation we can take

$$\psi = c_1 \left[\psi_{1s}(A) \pm \psi_{1s}(B) \right]$$

which is what we had done before.

We don't know for sure that this is the lowest state, but it is a good guess.

The same arguments hold for the two states that dissociate to a 2*s* H-atom

$$\psi = c_2 \left[\psi_{2s}(A) \pm \psi_{2s}(B) \right]$$

These functions are approximations to what we would get if we solved the secular equation of variational theory.

Another way to look at it, however, is from the point of view of perturbation theory. Taking the separated atoms as the unperturbed problem, these two wavefunctions are the correct zero-order wavefunctions. In general, molecular states will correlate with each state of the separated atoms, and rough approximations to their wave functions will be given by $f_A + f_B$ and $f_A - f_B$ where f_A and f_B are hydrogen like wave functions.

Thus

$$\psi = c_2 \left[\psi_{2s}(A) \pm \psi_{2s}(B) \right]$$

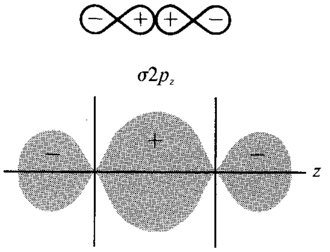
will give σ_g 2*s* and σ_u *2*s* molecular orbitals.

Think about what this zero-order picture means. In the case of atoms, the use of H atom orbitals as zeroth-order wave functions for many electron atoms says that to zeroth-order we are neglecting the inter-electronic repulsion. Once we have the zeroth-order function, we can use Perturbation Theory to improve our energy and wavefunction.

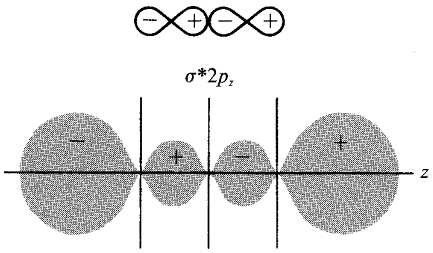
We are now doing the same thing for homonuclear diatomic molecules. Using H_2^+ *molecular orbitals*, we can put electrons in these orbitals in a manner consistent with the Pauli principle. This zeroth-order wavefunction neglects inter-electronic repulsion.

If you then use perturbation theory, the first-order correction to the wave function will mix in contributions from other functions in our basis set of atomic orbitals. However, only the functions closest in energy mix very strongly (remember the energy denominator in the first order perturbation theory correction to the wave function).
Let's look qualitatively at the few next higher MO's.

If we take the combinations of the $2p_0$ ($2p_z$) H atom state, we get the following:



$\psi_{2p0}(A) - \psi_{2p0}(B)$



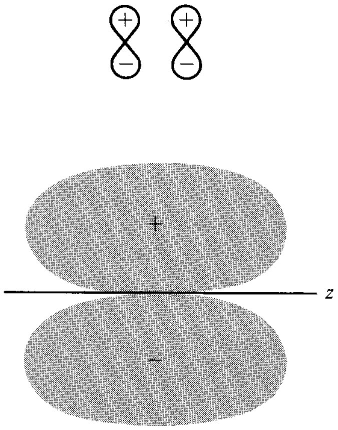
$\psi_{2p0}(A) + \psi_{2p0}(B)$

These orbitals are designated σ since we are taking linear combinations of atomic orbitals with $m = 0$. *These wave functions have cylindrical symmetry about the z-axis.*

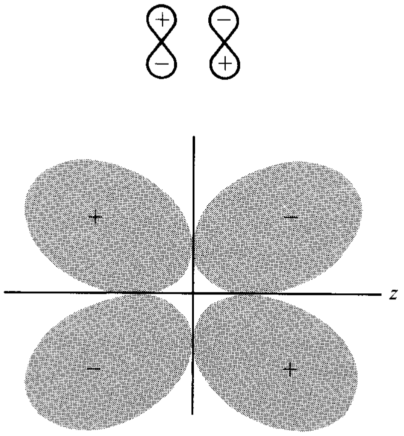
Orbitals with $m \neq 0$ are a little more difficult to visualize because the $2p_1$ and $2p_{-1}$ orbitals are complex.

We can use $2p_x$ and $2p_y$, however these are not eigenfunctions of $\hat{L}_z$. Remember $2p_x$ and $2p_y$ are linear combinations of $2p_1$ and $2p_{-1}$. Thus, they won't have cylindrical symmetry about the *z*-axis

When we draw the linear combinations $\psi = \psi_{2p_x}(A) \pm \psi_{2p_x}(B)$ we get things that look like:



$\pi_u 2p_x$



$\pi_g^* 2p_x$

These are not cylindrically symmetrical about *z*. They have an extra nodal surface. They are not eigenfunctions of $\hat{L}_z$. This is what one often sees as π orbitals. We can do this because any linear combination of eigenfunctions of H with the same energy is still an eigenfunction of $\hat{H}$. But it will not necessarily be an eigenfunction of $\hat{L}_z$.

We can now use these orbitals to discuss many-electron homonuclear diatomic molecules. If we ignore inter-electronic repulsion, we can take the zeroth-order wave function of homonuclear diatomics to be a Slater determinant of one electron H_2^+ spin orbitals, using the LCAO-MO's for spatial parts.

The approximate relative ordering of these orbitals is

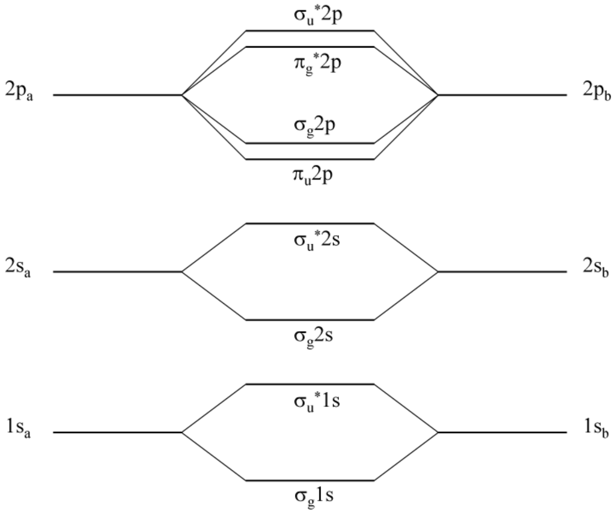
$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p_{+1}, \pi_u 2p_{-1} < \sigma_g 2p < \pi_g^* 2p_{+1}, \pi_g^* 2p_{-1} < \sigma_u^* 2p$$

Note that we have used the $2p_{+1}$ and $2p_{-1}$ atomic orbitals here to form our MO's rather than the $2p_x$ and $2p_y$. Note also that this order can be slightly different for different molecules.

Each bonding orbital fills before it's corresponding antibonding orbital (indicated by the *).

The energies of these orbitals indicated by the order shown above are determined using the variational principle. However for two closely spaced levels, the order may be reversed. The energies of such molecular orbitals can be verified experimentally using photoelectron spectroscopy.

Another way to think of the levels is in a diagram like this:



11.4 Molecular orbitals for multi-electron diatomic molecules

We can now begin to get some rough idea of molecular bonding in multi-electron diatomic molecules by simply placing electrons in these orbitals.

We saw that H_2^+ has one electron in a bonding orbital, $\sigma_g 1s$.

For H_2, one puts 2 electrons in σ_g1s with opposite spins. This gives $(\sigma_g 1s)^2$
The two bonding electrons give a single bond.

Consider $He_2 = (\sigma_g 1s)^2(\sigma_u{}^*1s)^2$ 2 bonding electrons 2 antibonding. $\Rightarrow$ No net bond.

Experimentally, He_2 shows no significant minimum in the potential energy curve.

In a more formal sense we could write:

 # bonds = ½ (# electrons in bonding orbitals - # electrons in anti-bonding orbitals)

Let us pursue this concept a little further. If you promote one of the antibonding electrons in helium to a higher state one has.

$$(\sigma_g 1s)^2(\sigma_u{}^*1s)^1(\sigma_g 2s)^1$$

This has 3 bonding and 1 anti-bonding electrons. It will therefore be chemically bound. This is correct. He_2 is called an *excimer* in that it is bound in the upper electronic state, but not in the lowest (ground) electronic state.

For Li_2 we have

$$(\sigma_g 1s)^2(\sigma_u{*}1s)^2(\sigma_g 2s)^2$$

Two net bonding electrons lead to a single bond. Experimentally Li_2 is a stable molecule.

Sometimes its configuration is written

$$KK(\sigma_g 2s)^2$$

where the *K* denotes filled *K* lithium atoms.

We did not talk about this notation when we did HF-SCF. *K*, *L*, *M* represent the quantum numbers *n* = 1, 2, 3. So the n. The *n*= 1 atomic orbitals constitute the *K* shell, *n*=2 the *L* shell, etc. . .

Let's jump to Nitrogen, N_2. The configuration is

$$KK(\sigma_g 2s)^2\,(\sigma_u^*\,2s)^2\,(\pi_u\,2p)^4\,(\sigma_g\,2p)^2$$

6 bonding electrons imply a triple bond, which is what is observed.

For O_2 $\quad KK(\sigma_g 2s)^2\,(\sigma_u^*\,2s)^2\,(\sigma_g\,2p)^2\,(\pi_u\,2p)^4(\pi_g^*\,2p)^2$

↑ ↑

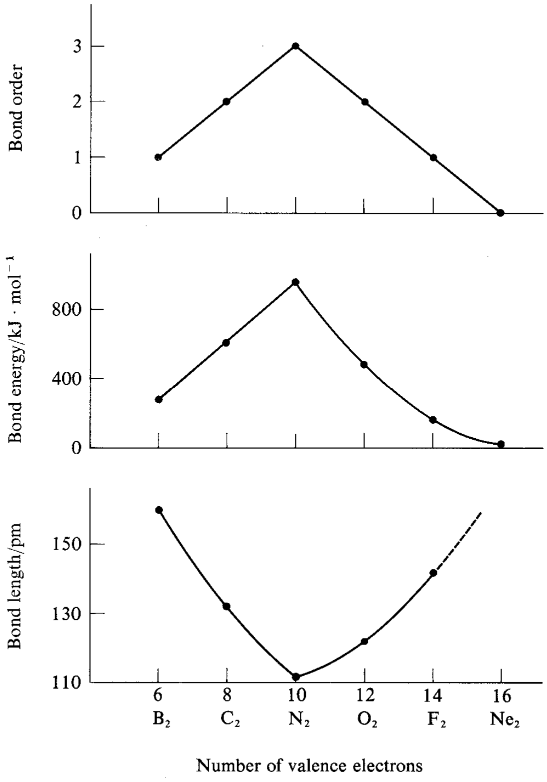
experimental evidence suggests these are reversed here.

In O_2 we have unfilled π orbitals. Hund's rule says that the triplet state has lower energy. The triplet state is the one in which the electrons are unpaired. Experimentally O_2 is paramagnetic because of the two unpaired electrons! One can use the magnetism of air to measure oxygen levels.

One usually uses the term *bond-order* to indicate the number of pairs of electrons are involved in the bond. A single bond has a bond order of 1. A double bond has a bond order of 2. etc.

As the table and figures below demonstrate, one can roughly correlate the bond order of a diatomic molecule with its bond length. The higher the bond order, the shorter (and stronger) the bond.

Species	Ground-state electron configuration	Bond order	Bond length/Å	Bond energy kJ mol^{-1}
H_2^+	$(\sigma 1s)^1$	1/2	1.06	255
H_2	$(\sigma 1s)^2$	1	0.74	431
He_2^+	$(\sigma 1s)^2(\sigma^* 1s)^1$	1/2	1.08	251
He_2	$(\sigma 1s)^1(\sigma^* 1s)^2$	0	-	-
Li_2	$KK(\sigma 2s)^2$	1	2.67	105
Be_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2$	0	-	-
B_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^2$	1	1.59	289
C_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4$	2	1.24	599
N_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2$	3	1.10	942
O_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^2$	2	1.21	494
F_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^4$	1	1.41	154
Ne_2	$KK(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^4(\sigma 2p_z)^2(\pi^* 2p)^4(\sigma^* 2p_z)^2$	0	-	-



You can clearly see that this simple molecular orbital picture allows us to make good qualitative predictions about the properties of molecules.

To be more quantitative, one can use the Hartree-Fock method for multi-electron diatomic molecules in an analogous way to its application to multi-electron atoms. (I won't discuss this in detail, but I would like to mention the terminology that is used.)

In using the HF method for molecules, we keep the concept of molecular orbitals that can be filled with two electrons each (consistent with the Pauli principle), however these orbitals are constructed from flexible functions that allow us to vary the parameters in such a way that we can reach the Hartree-Fock limit.

In our simple approach up to now, which is often called the LCAO-MO method (linear combination of atomic orbitals-molecular orbital), we took each molecular orbital to be a linear combination of an atomic orbital on each nucleus in such a way that the atomic orbitals maintain their identity.

As we started adding atomic orbitals to get higher molecular orbitals, I wrote things like

$$\psi = \left[c_1\psi_{1s}(A) + c_2\psi_{2s}(A) + c_3\psi_{2p_0}(A) + \ldots\right] \pm \left[c_1\psi_{1s}(B) + c_2\psi_{2s}(B) + c_3\psi_{2p_0}(B) + \ldots\right]$$

I indicated that to a good approximation, one coefficient would be dominant for each state of the separated atoms. To a first approximation we neglected the others.

Thus, I indicated that the first two states could be approximated as

$$\psi_{1,2} = c_1\left[\psi_{1s}(A) \pm \psi_{1s}(B)\right]$$

and hence we called this a $\sigma_g 1s$ molecular orbital.
The same arguments hold for the two states that dissociate to a 2*s* H-atom

$$\psi_{3,4} = c_2\left[\psi_{2s}(A) \pm \psi_{2s}(B)\right]$$

We called this a $\sigma_g 2s$ orbital.

However, if we want a more accurate estimate of the energy by using the HF method, we have to include not only the coefficients we neglected, but also make the atomic functions themselves flexible enough so that we can reach the HF limit. In doing this, the molecular orbitals lose their identity (in terms of the atomic orbitals) since the coefficients of many atomic orbitals can become significant. In this case, one often uses a different manner to label the molecular orbitals.

Correspondence between various notations for molecular orbitals

Simple LCAO-MO		HFSCF-LCAO-MO
$\sigma 1s$	$\sigma_g 1s$	$1\sigma_g$
$\sigma^* 1s$	$\sigma_u 1s$	$1\sigma_u$
$\sigma 2s$	$\sigma_g 2s$	$2\sigma_g$
$\sigma^* 2s$	$\sigma_u 2s$	$2\sigma_u$
$\pi 2p_x$	$\pi_u 2p_x$	$1\pi_u$
$\pi 2p_y$	$\pi_u 2p_y$	$1\pi_u$
$\sigma 2p_z$	$\sigma_g 2p_z$	$3\sigma_g$
$\pi^* 2p_x$	$\pi_g 2p_x$	$1\pi_g$
$\pi^* 2p_y$	$\pi_g 2p_y$	$1\pi_g$
$\sigma^* 2p_z$	$\sigma_u 2p_z$	$3\sigma_u$

11.5 Molecular term symbols for diatomic molecules

In a manner similar to that for atoms, the electronic states of diatomic molecules are designated by term symbols. In the case of atoms, I indicated that although the individual spin and orbital angular momentum quantum numbers of the electrons are no longer good quantum numbers (*i.e.*, the individual *l* and s are not conserved), the sum *L* and the sum *S* of all the electrons are still a good quantum number (if we ignore spin orbit coupling).

In the case of diatomic molecules, even if there is only one electron (*i.e.*, H_2^+), the *l* quantum number of the individual electrons is not a good quantum number. However, because of the cylindrical symmetry, m_l remains a good quantum number (for H_2^+) and $l_z = m_l \hbar$ is a conserved quantity.

Once we go to <u>multi-electron diatomic molecules</u>, l_z of the individual electrons is no longer conserved and thus m_l is no longer a good quantum number. However the sum, M_L of all the electrons is still a good quantum number. Also, the total *S* for the electrons is a good quantum number. Thus we can label the states of a diatomic molecule by M_L and *S*.

One constructs a molecular term symbol in an analogous way to the atomic term symbols:

$$^{2S+1}|M_L| \qquad \text{or since} \quad \Lambda = |M_L| \quad \text{we can write} \qquad ^{2S+1}\Lambda$$

Where $M_L = m_{l1} + m_{l2} + \ldots$ and $M_s = m_{s1} + m_{s2} + \ldots$

and *S* is determined from the values of M_s.

Note that the difference from the atomic case is that the main symbol represents a scalar quantity, $|M_L|$ rather than a vector quantity *L*.

The various values of $|M_L|$ are associated with capital Greek letters according to

$\|M_L\|$	Letter
0	Σ
1	Π
2	Δ
3	Φ

(Note that these letters correspond to the *S*, *P*, *D*, and *F* in the atomic case.)

Examples of molecular term symbols are $^1\Sigma$, $^3\Pi$, and $^2\Delta$.

The determination of the molecular terms symbols from molecular-orbital electron configurations is simpler than the atomic case since M_L is a scalar quantity. However, it is important to remember that *S* is still a vector quantity. I illustrate this procedure below with 3 examples.

Consider the case of H_2, which has an electron configuration of $(\sigma 1s)^2$.

The occupied σ orbitals have $m_l = 0$.

Thus $M_L = 0 + 0 = 0$

The two electrons must have opposite spins in order to satisfy the Pauli principle, thus

$$M_S = +\frac{1}{2} - \frac{1}{2} = 0$$

Because there is only one value of M_S, then *S* must equal 0.

The terms symbol will therefore be: $^1\Sigma$

Now consider the case of He_2^+. The ground state electronic configuration is $(\sigma 1s)^2(\sigma^* 1s)^1$.
One can construct a table of the possible values of m_l and m_s.

m_{l1}	m_{s1}	m_{l2}	m_{s2}	m_{l3}	m_{s3}	M_L	M_S
0	+ ½	0	- ½	0	+ ½	0	+ ½
0	+ ½	0	- ½	0	- ½	0	- ½

The fact that $M_L = 0$ says that we have a Σ state.

The $M_S = \pm 1/2$ corresponds to the two projections of $S = 1/2$. This means $2S+1 = 2$ and we have a doublet state.

So the term symbol for He_2^+ is $^2\Sigma$.

These first two examples are quite simple since there is only one possible value of *S*.

The next example, B_2, is a little more complicated and illustrates the general scheme that one should use.
The electron configuration for B_2 is

$$(\sigma 1s)^2(\sigma^* 1s)^2 (\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p)^2$$

The first 4 molecular orbitals in B_2 have M_L=0 and M_S=0, and thus we need to consider only the last two electrons. (Recall that in the atomic case, we also ignored filled subshells.)

Each of these last two electrons is in a π orbital and can have $m_l = \pm 1$ and $m_s = \pm 1/2$. One can construct a table of the possible values, keeping in mind the indistinguishability of the electrons and the Pauli principle.

	m_{l1}	m_{s1}	m_{l2}	m_{s2}	M_L	M_S
1	+1	+ ½	+1	- ½	2	0
2	+1	+ ½	-1	+ ½	0	1
3	+1	+ ½	-1	- ½	0	0
4	+1	- ½	-1	+ ½	0	0
5	+1	- ½	-1	- ½	0	-1
6	-1	+ ½	-1	- ½	-2	0

Entries 1 and 6 in the table correspond to $|M_L|$ = 2 and M_S = 0. This gives rise to a $^1\Delta$ (singlet delta) state.

Entries 2, 3, and 5 correspond to M_L=0 and S=1, and so we have a $^3\Sigma$ (triplet sigma) state.

Entry number 4 has to M_L=0 and M_S=0, an thus it corresponds to a $^1\Sigma$ state.

Thus we have 3 possible molecular states for this electronic configuration of B_2: $^1\Delta$, $^3\Sigma$, and $^1\Sigma$.

Hund's rules apply to molecular electronic states as well as to atomic states. Hund's rule says that the state with the largest spin multiplicity will be the ground state. Thus, we predict that the ground state of B_2 is a $^3\Sigma$ state.

(For the Σ states of homonuclear diatomics, there is also a right superscript of + or - that indicates the symmetry of the wave function with respect to reflection in a plane containing the internuclear axis. We will not concern ourselves with this for the moment.)

11.6 MO treatment of Heteronuclear Diatomics

The treatment of heteronuclear diatomic molecules is similar to that of homonuclear diatomics.

In the case where the two atoms in a diatomic have atomic number that differ only slightly, such as in CO, we could consider the molecule being formed from the isoelectronic molecule N_2 by a gradual transfer of nuclear charge from one nucleus to the other. During this hypothetical transfer, the original N_2 MO's would slowly vary to give finally the CO MO's. We therefore expect the CO molecular orbitals to bear some resemblance to those of N_2.

In a case such as this, the symbols used for the MO's are similar to those for homonuclear diatomics.

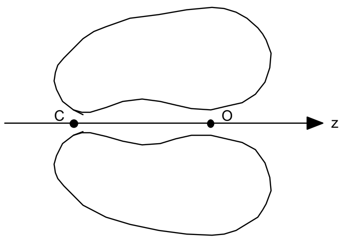
However, in the heteronuclear case, the electronic Hamiltonian lacks the symmetry of the homonuclear diatomic case, and hence the *g*, *u* property of the molecular orbitals disappears.

The correlation between the N_2 and CO subshell designations is

N_2	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$3\sigma_u$
CO	1σ	2σ	3σ	4σ	1π	5σ	2π	6σ

The MO's of the same symmetry are numbered in order of increasing energy. Because of the absence of the g, u property, the numbers of corresponding homonuclear and heteronuclear MO's differ.

Shown below is a a sketch of a contour of the CO 1π MO taken from an SCF calculation. Note its resemblance to the π MO that I had drawn earlier for homonuclear diatomics.



A Hartree-Fock SCF calculation for the expansion coefficients of this molecular orbital in terms of Slater atomic orbitals gives

$$1\pi = 0.469\,(2p\pi_C) + 0.771\,(2p\pi_O)$$

This can be compared to the corresponding bonding orbital of N_2 which is given by

$$1\pi_u = 0.624\,(2p\pi_a + 2p\pi_b)$$

You can see both from the picture of the orbital as well as in the SCF calculation that the amount of atomic orbital centered on the carbon and the oxygen are not the same. This makes sense since the symmetry is now broken and the charge is different on the two nuclei. (Note, however, that the wave functions are not normalized).

11.7 More on Valence-Bond Theory

I would like to say a bit more about valence-bond theory. Although this approach is not accurate enough to be used for computations, it provides some important qualitative notions about chemical bonding. More specificially, valence-bond theory guides our intuitive ideas regarding Lewis formulas, resonance formulas, etc. In our treatment of H_2, we constructed a wave function that had one electron on each atom.

If we let

$$\psi_1 = \begin{vmatrix} 1s_A\alpha(1) & 1s_B\beta(1) \\ 1s_A\alpha(2) & 1s_B\beta(2) \end{vmatrix}$$

and

$$\psi_2 = \begin{vmatrix} 1s_A\beta(1) & 1s_B\alpha(1) \\ 1s_A\beta(2) & 1s_B\alpha(2) \end{vmatrix}$$

each of which represent H_2 with one electron on each atom, then we can use

$$\psi = c_1\psi_1 + c_2\psi_2$$

as a trial function and minimize the energy with respect to c_1 and c_2.

The ground state wave function is given by

$$\psi = \frac{1}{\sqrt{2\left(1+S^2\right)}}\left(\psi_1 - \psi_2\right)$$

(Note that the problem is formulated differently than our original treatment, and the definition of ψ_1 and ψ_2 are different, but if you multiply out these determinants and compare the result to the one we had before, you will see that it is the same).

Consider now the molecule LiH. One of the (unnormalized) Slater determinants in the valence bond wave function of LiH is of the form

$$\psi_1 = \begin{vmatrix} \psi_{1s\mathrm{Li}}\alpha(1) & \psi_{1s\mathrm{Li}}\beta(1) & \psi_{2s\mathrm{Li}}\alpha(1) & \psi_{1s\mathrm{H}}\beta(1) \\ \psi_{1s\mathrm{Li}}\alpha(2) & \psi_{1s\mathrm{Li}}\beta(2) & \psi_{2s\mathrm{Li}}\alpha(2) & \psi_{1s\mathrm{H}}\beta(2) \\ \psi_{1s\mathrm{Li}}\alpha(3) & \psi_{1s\mathrm{Li}}\beta(3) & \psi_{2s\mathrm{Li}}\alpha(3) & \psi_{1s\mathrm{H}}\beta(3) \\ \psi_{1s\mathrm{Li}}\alpha(4) & \psi_{1s\mathrm{Li}}\beta(4) & \psi_{2s\mathrm{Li}}\alpha(4) & \psi_{1s\mathrm{H}}\beta(4) \end{vmatrix}$$

We can abbreviate these Slater determinants by only listing the elements on the diagonal. This would give the notation:

$$\psi_1 = \left| \psi_{1s\mathrm{Li}}\alpha(1) \quad \psi_{1s\mathrm{Li}}\beta(2) \quad \psi_{2s\mathrm{Li}}\alpha(3) \quad \psi_{1s\mathrm{H}}\beta(4) \right|$$

The other contribution to the valence-bond wave function that is distinct (not just changing labels on the electrons) is

$$\psi_2 = \left| \psi_{1s\mathrm{Li}}\alpha(1) \quad \psi_{1s\mathrm{Li}}\beta(2) \quad \psi_{2s\mathrm{Li}}\beta(3) \quad \psi_{1s\mathrm{H}}\alpha(4) \right|$$

Thus we can write the valence-bond wave function as

$$\psi_{cov} = c_1\psi_1 + c_2\psi_2$$

where I have used the subscript ψ_{cov} to indicate that we have chosen configurations that correspond to covalent bonding where the electrons are equally shared between the bonded atoms.

A variational calculation would give $c_1 = -c_2$, since there should be no preference for which electron has spin up or down. Thus we have

$$\psi_{cov} = \left| \psi_{1s\mathrm{Li}}\alpha(1) \quad \psi_{1s\mathrm{Li}}\beta(2) \quad \psi_{2s\mathrm{Li}}\alpha(3) \quad \psi_{1s\mathrm{H}}\beta(4) \right| - \left| \psi_{1s\mathrm{Li}}\alpha(1) \quad \psi_{1s\mathrm{Li}}\beta(2) \quad \psi_{2s\mathrm{Li}}\beta(3) \quad \psi_{1s\mathrm{H}}\alpha(4) \right|$$

If we were to use this function to calculate the bond length and bond energy, we would get values of 3.01 au and -215.98 au respectively.

This should be compared to the experimental values of 3.02 au and -219.71 au.

One reason for the poor agreement in the energy is that we have not allowed for any ionic character in our valence-bond wave function.

We can include the ionic structure $\mathrm{Li^+H^-}$ into our valence-bond treatment by using

$$\psi_{ionic} = \left| \psi_{1s\mathrm{Li}}\alpha(1) \quad \psi_{1s\mathrm{Li}}\beta(2) \quad \psi_{1s\mathrm{H}}\alpha(3) \quad \psi_{1s\mathrm{H}}\beta(4) \right|$$

Note that this wave function describes $\mathrm{Li^+H^-}$ in that there are two electrons on $\mathrm{Li^+}$ and two electrons on $\mathrm{H^-}$.

We can now take a linear combination of ψ_{cov} and ψ_{ionic} and write

$$\Psi_{VB} = c_{cov}\Psi_{cov} + c_{ionic}\Psi_{ionic}$$

The inclusion of the ionic term improves the energy calculation to a value of -217.0 au.

Because the two 1*s* electrons in the lithium atom do not play a great role in the formation of the bond in LiH, it is a convenient, common approximation to ignore inner-core electrons in the valence-bond wave function and to consider only the bonding, or valence, electrons. In this approximation we would have

$$\psi_{cov} = |\psi_{2s\mathrm{Li}}\alpha(1) \quad \psi_{1s\mathrm{H}}\beta(2)| - |\psi_{2s\mathrm{Li}}\beta(1) \quad \psi_{1s\mathrm{H}}\alpha(2)|$$

and

$$\psi_{ionic} = |\psi_{1s\mathrm{H}}\alpha(1) \quad \psi_{1s\mathrm{H}}\beta(2)|$$

The neglect of these inner-core electrons is not so important for LiH, since this is a small enough molecule that it can be solved to a high degree of accuracy. However as we will see shortly, this approach becomes very useful when discussing larger systems.

The square of the expansion coefficients, c_{cov}^2 and c_{ionic}^2, give some indication of the ionic and covalent character in the molecule. However, one must be careful with this interpretation. The precise values of these coefficients depend on the form of the atomic orbitals that are used.

The idea of introducing ionic terms into valence-bond wave functions nicely illustrates the concept of resonance that you learned in first year chemistry and organic chemistry. Quantum mechanically, we see that if we can write two or more sensible Lewis structural formulas for a molecule, then the wave function for that molecule is a linear combination of these structures and the “true” picture is some intermediate structure. The variational principle, which gives the numerical values of the coefficients in the linear combination, provides an indication of the relative importance of various possible Lewis formulas.

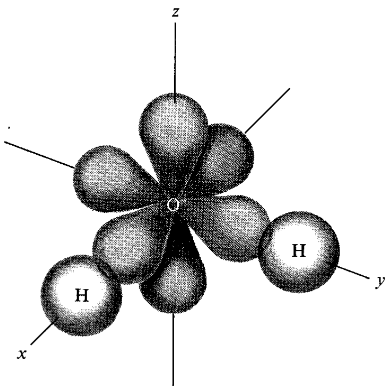
Thus, the qualitative ideas about resonance structures have a quantitative basis in quantum chemistry. (This is true about many of the qualitative ideas presented in organic chemistry.)

The extension of the valence-bond method to non-linear polyatomic molecules is straightforward in principle.

Consider the molecule H_2O. The electron configuration of the oxygen atom is

$$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^2$$

suggesting that the unpaired $2p_x^1$ and $2p_y^1$ electrons are available for bonding with the hydrogen atoms.



From this simple valence-bond picture considering only covalent terms, one would expect the bond angle in H_2O to be 90°, since the $2p_x^1$ and $2p_y^1$ orbitals lie along the x and y axes and we would expect the hydrogen $1s$ orbitals to maximize the overlap with the oxygen $2p$ orbitals.

The prediction of a 90° H-O-H bond angle is in poor agreement with the measured bond angle of 104°.

However, if one introduces ionic terms in the wave function, the hydrogen atoms will develop some positive character and repel each other, giving a bond angle closer to 104°.

For the corresponding molecules H_2S, H_2Se, and H_2Te, the electronegativities of the sulfur, selenium, and tellurium atoms are such that the ionic terms contribute progressively less. In this case, the predicted angle becomes progressively closer to the prediction of 90°.

If we go on to the case of NH_3, the valence-bond approach predicts that the H-N-H bond angles are 90° as compared to the experimental value of 107°. Once again, the situation can be improved by introducing ionic terms, however, this approach clearly fails us when we get to methane, CH_4.

Clearly, the carbon electron configuration of $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ does not explain (using a valence-bond picture) the well-known tetrahedral bonding in methane and other saturated hydrocarbons.

An approach that better describes the directionality of chemical bonding involves a consideration of hybrid orbitals , a subject that you will have likely discussed both in introductory chemistry and in organic chemistry. We will treat this subject from a quantum mechanical point of view.

11.8 Hybrid Orbitals

Like valence bond theory, the concept of hybrid orbitals is not particularly accurate in a computational sense, but it provides an important qualitative picture from which we can make predictions about the geometries of simple molecules. I will briefly introduce some of the mathematical background behind hybrid orbitals.

11.8.1 sp hybrid orbitals

Consider first the molecule beryllium hydride, BeH_2. The two Be-H bonds in this molecule are equivalent and the H-Be-H bond angle is 180°.

The ground state electron configuration of Be is: $1s^2\ 2s^2$

To represent the two equivalent Be-H bonds in BeH_2 that make an angle of 180° with respect to one another, we will take a linear combination of the beryllium 2s orbital and one of the beryllium 2*p* orbitals (*i.e.*, the $2p_z$). We can do this for each of the 2*s* electrons since the orbital holds two electrons. Thus, we have

$$\xi = a_1\, 2s_{Be} + b_1\, 2p_{zBe}$$

$$\xi' = a_2\, 2s_{Be} + b_2\, 2p_{zBe}$$

Linear combinations of orbitals on the same atom are called ***hybrid orbitals.***

(Recall that if we neglect inter-electronic repulsion, the s and p orbitals on an atom would have the same energy, so in this limit, these hybrid orbitals would still be eigenfunctions of the atomic Hamiltonian. In reality, the *s* and *p* do not have the same energy, however this approach still provides a useful qualitative picture of molecular bonding.)

The two bonds in BeH_2 are described by the following bond orbitals:

$$\phi = c_1 1s_A + c_2 \xi$$

$$\phi' = c_1' 1s_B + c_2' \xi'$$

where the $1s_A$ and $1s_B$ are the 1*s* orbitals of the two hydrogen atoms.

So the bond orbitals are linear combinations of an atomic orbital on the hydrogen atom and a hybrid orbital on the beryllium.

We will now determine the form of the two hybrid orbitals ξ and ξ' so that ϕ and ϕ' describe two equivalent bond orbitals that are directed 180° from one another.

We can approximate the 2*s* and 2p_z orbitals of the beryllium atom by the Slater orbitals

$$\psi_{2s} = \sqrt{\frac{1}{4\pi}} R(r)$$
$$\psi_{2p_z} = \sqrt{\frac{3}{4\pi}} \cos\theta\, R(r)$$

where for simplicity I have used the same functional form for the radial part of the wave functions. (Recall that the angular part is simply given by the spherical harmonics). The constants in front insure that the functions are normalized.

If we substitute these functions into the expression for ξ we get

$$\xi = \frac{R(r)}{\sqrt{4\pi}}\left(a_1 + \sqrt{3}b_1 \cos\theta\right)$$

If a_1 and b_1 are both positive, then ξ is directed along the positive *z*-axis, and we can choose this to be the case since we are free to orient the molecule in space as we wish.

The other hybrid orbital, ξ' is then given by

$$\xi' = \frac{R(r)}{\sqrt{4\pi}}\left(a_2 + \sqrt{3}b_2 \cos\theta\right)$$

Recall that the original *s* and *p* functions are orthogonal, and when we take a linear combination of these orbitals to get another set of two orbitals, ξ and ξ', it is convenient to require that ξ and ξ' be orthogonal.

In this case we have that:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \xi(r,\theta)\xi'(r,\theta) r^2 \sin\theta\, dr\, d\theta\, d\varphi = 0$$

If we have chosen our radial function to be normalized, then

$$\int_0^\infty R^2(r) r^2 dr = 1$$

Combining this with the expressions for ξ and ξ' gives us for the first integral

$$\int_0^\pi \left(a_1 + \sqrt{3}b_1 \cos\theta\right)\left(a_2 + \sqrt{3}b_2 \cos\theta\right) \sin\theta d\theta = 0$$

The evaluation of this integral is straightforward and gives

$$a_1 a_2 + b_1 b_2 = 0$$

Because we have taken a_1 and b_1 to be positive, then a_2 and b_2 must have opposite signs, and this causes ξ' to be directed along the negative *z*-axis, 180° from ξ.

Because the two Be-H bonds in BeH_2 are equivalent, we require that the two hybrid orbitals have the same shape.

Thus we require that $a_1 = a_2$ and that $b_1 = -b_2$.

Furthermore, because $a_1 a_2 + b_1 b_2 = 0$

we find that $a = \pm b$

Finally, if the two equivalent orbitals are normalized, then

$$\xi = \frac{1}{\sqrt{2}}(2s + 2p_z)$$
$$\xi' = \frac{1}{\sqrt{2}}(2s - 2p_z)$$

Because these hybrid orbitals are made up of a 2*s* orbital and one 2*p* orbital, they are called *sp* hybrid orbitals.

The BeH_2 molecule is formed by overlapping a hydrogen 1*s* orbital with each of the sp hybrid orbitals.
The electron configuration of BeH_2 in this bond-orbital description is therefore

$$K\,(\phi)^2\,(\phi')^2$$

where ϕ and ϕ' are the bond orbitals described earlier. In this picture, a chemical bond is described as two electrons of opposite spin occupying a bond orbital.

11.8.2 sp^2 hybrid orbitals

Consider now the case of BH_3. The three B-H bonds in BH_3 are equivalent and lie in a plane, directed 120° from each other.

To describe the three equivalent bonds in BH_3, we must construct three hybrid orbitals on the boron atom. We will construct each of these orbitals as a linear combination of one *s* and two *p* orbitals

$$\xi_1 = a_1 2s + b_1 2p_z + c_1 2p_x$$

$$\xi_2 = a_2 2s + b_2 2p_z + c_2 2p_x$$

$$\xi_3 = a_3 2s + b_3 2p_z + c_3 2p_x$$

where the 2*s* and $2p_z$ orbitals are the same we used in the previous example, and the $2p_x$ is a Slater orbital given by:

$$\psi_{2p_x} = \sqrt{\frac{3}{4\pi}} \sin\theta \cos\varphi R(r)$$

Because these hybrid orbitals are constructed from one 2*s* and two 2*p* orbitals, they are called *sp*^{2} hybrid orbitals.

Because we can choose the overall orientation of the molecule with respect to the axis system, we can let one hybrid orbital lie along the *z*-axis. In this case, the contribution of the p_x orbital will be zero, and

$$\xi_1 = a_2 2s + b_1 2p_z$$

In analogy to the case of BeH_2, because the *s* orbital is spherically symmetric and the three hybrid orbitals are equivalent, we shall take equal contribution of the 2*s* orbital to each hybrid orbital.

This means that $a_1 = a_2 = a_3$

Furthermore, because there is one 2*s* orbital to be distributed among the three hybrids, it must be true that

$$a_1^2 + a_2^2 + a_3^2 = 1$$

(Note: This expresses the conservation of the 2*s* orbital. Whenever we take three orthogonal functions and take linear combinations to make three others, there will always be both a normalization condition and what I call a conservation condition, meaning that the total amount of the original orbitals must be conserved.)

From these two conditions we find that

$$a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$$

If we now substitute a_1 into ξ_1 we have

$$\xi_1 = \frac{1}{\sqrt{3}} 2s + b_1 2p_z$$

Because ξ_1 is normalized, we have that

$$\frac{1}{3} + b_1^2 = 1$$

$$b_1 = \sqrt{\frac{2}{3}}$$

Thus

$$\xi_1 = \frac{1}{\sqrt{3}} 2s + \sqrt{\frac{2}{3}} 2p_z$$

The second hybrid orbital is

$$\xi_2 = \frac{1}{\sqrt{3}} 2s + b_2 2p_z + c_2 2p_x$$

The requirement that ξ_1 and ξ_2 be orthogonal leads to the condition that

$$a_1 a_2 + b_1 b_2 + c_1 c_2 = 0$$

Note that this is the same condition that we had in the previous example. If we have a set of orthogonal functions and take linear combinations of them to get a new set of orthogonal functions, this condition will always arise. It is simply the condition of two orthogonal vectors.

With $c_1 = 0$, this condition leads to

$$\frac{1}{3}+\sqrt{\frac{2}{3}}b_2=0$$

$$b_2=-\frac{1}{\sqrt{6}}$$

Thus

$$\xi_2=\frac{1}{\sqrt{3}}2s-\frac{1}{\sqrt{6}}2p_z+c_2 2p_x$$

By requiring ξ_2 to be normalized we have

$$\frac{1}{3}+\frac{1}{6}+c_2^2=1$$

$$c_2=\frac{1}{\sqrt{2}}$$

We therefore have that

$$\xi_2=\frac{1}{\sqrt{3}}2s-\frac{1}{\sqrt{6}}2p_z+\frac{1}{\sqrt{2}}2p_x$$

Once we have ξ_1 and ξ_2, we can find many expressions that relate the remaining coefficients to those that are not yet determined.

For example, we have

$$b_1^2+b_2^2+b_3^2=1$$

$$c_1^2+c_2^2+c_3^2=1$$

together with the orthogonality conditions

$$a_1a_3+b_1b_3+c_1c_3=0$$

$$a_2a_3+b_2b_3+c_2c_3=0$$

and the normalization condition

$$a_3^2+b_3^2+c_3^2=1$$

At this point, we have an over determined system, and we need not use all of these relations. I will use the orthogonality conditions.

From the first of the two orthogonality conditions, we have

$$a_1a_3 + b_1b_3 + c_1c_3 = 0$$

$$\frac{1}{3} + \sqrt{\frac{2}{3}}b_3 + 0 = 0$$

$$b_3 = -\frac{1}{\sqrt{6}}$$

From the second orthogonality condition

$$a_2a_3 + b_2b_3 + c_2c_3 = 0$$

$$\frac{1}{3} + \frac{1}{6} + \frac{1}{\sqrt{2}}c_3 = 0$$

$$c_3 = -\frac{1}{\sqrt{2}}$$

Thus

$$\xi_3 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x$$

I will leave it as an exercise for you to demonstrate that these three hybrid orbitals lie 120° apart from each other.

11.8.3 sp^3 hybrid orbitals

From what we have done up to this point, the development of the four *sp*^{3} hybrid orbitals should directly follow. By choosing the first to lie along the *z*-axis and using the orthogonality and normalization relations, you can easily find the coefficients of the following orbitals.

$$\xi_1 = a_1 2s + b_1 2p_x + c_1 2p_y + d_1 2p_z$$

$$\xi_2 = a_2 2s + b_2 2p_x + c_2 2p_y + d_2 2p_z$$

$$\xi_3 = a_3 2s + b_3 2p_x + c_3 2p_y + d_3 2p_z$$

$$\xi_4 = a_4 2s + b_4 2p_x + c_4 2p_y + d_4 2p_z$$

You can then show that they have the shape of a tetrahedron. I will leave this as an optional exercise.

11.9 π-electron approximation and Hückel molecular orbital theory

I would like to take our discussion of simple molecules one step further to relate the quantum mechanical treatment that we have developed to some of the concepts that you will encounter in organic chemistry. I will not give a very sophisticated treatment but rather introduce some of the basic notions that will help you to better understand what you do in organic chemistry.

Our discussion of hybrid orbitals leads us to consider the case of unsaturated hydrocarbons. Consider, for example, the molecule ethylene, C_2H_4. It is planar and has all of its bond angles equal to 120°. One can describe the structure of the molecule by assuming that all the carbon atoms form *sp*^{2} hybrid orbitals as shown in the figure below:

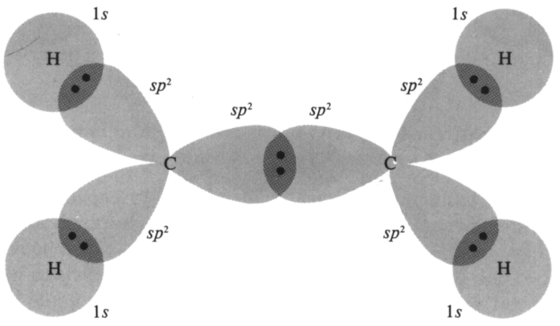


Figure 9-28. The σ-orbital framework of the ethylene molecule.

The CH bonds result from the overlap of the 1*s* hydrogen orbital with an sp^2 carbon hybrid orbital. Part of the CC bond results from the overlap of the two sp^2 carbon hybrid orbitals.

Each of the bonds shown in the figure above are σ bonds. This is because the carbon sp^2 hybrid orbitals are planar with no nodes about their respective bond axis and the hydrogen 1*s* orbitals have no nodes since l=0 and m=0. (Note that when we are considering the symmetry of these bonds, in the present case a σ bond, we are considering the local symmetry of each bond and not of the overall molecule)

The representation in the figure above is therefore called the σ bond framework of the ethylene molecule. If we let this framework be in the *x-y* plane, the carbon atomic orbitals used to construct the hybrid orbitals would have been the $2p_x$ and the $2p_y$ orbitals. This leaves the two carbon $2p_z$ orbitals available for further bonding, and their overlap can contribute to the C-C bond, as shown below:

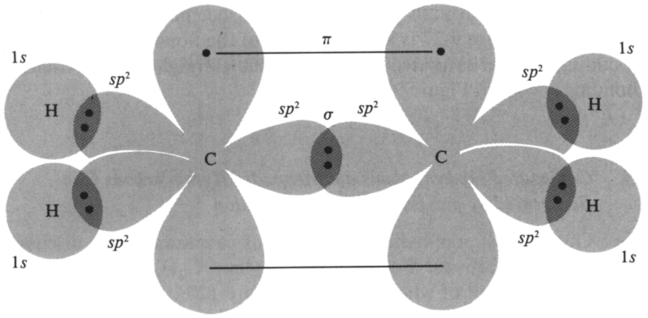


Figure 9-29. A schematic representation of the π bond in the ethylene molecule.

The charge distribution along the C-C bond due to the overlap of the $2p_z$ orbitals produces a π bond.

We are developing here a σ–π description of unsaturated hydrocarbons. It turns out to be a fairly good approximation to treat the π electrons as moving in a fixed, effective, electrostatic potential due to the electrons in the □ framework. This approximation is called the ***π-electron approximation.*** It can be developed from the Schrödinger equation, but we will simply accept it as being physically intuitive.

In 1930, Eric Hückel developed a treatment of conjugated and aromatic molecules that has found wide success in organic chemistry. This theory, which is referred to as ***Hückel molecular orbital theory*** , is based upon the π-electron approximation. The σ electrons are described as localized hybrid bond orbitals and the π electrons are described by molecular wave functions that extend over each of the atoms that contribute a π electron. Thus, the π electrons are delocalized.

I will illustrate this technique by considering some specific examples.

11.9.1 Ethylene

Let us first consider the simple case of ethylene.

The σ framework of ethylene is shown on the previous pages. Each carbon atom contributes a $2p_z$ orbital to the delocalized π orbital, and as in the case of the molecular orbital treatment of H_2 we write

$$\psi_\pi = c_1\chi_1 + c_2\chi_2$$

where χ_1 and χ_2 are the carbon $2p_z$ orbitals. It is important to realize that the Hamiltonian operator in this theory involves the effective potential due to the electrons in the σ framework of the molecule and so itself is an effective Hamiltonian. A principal advantage of Hückel theory is that it is not necessary to ever specify this effective Hamiltonian.

The secular determinantal equation associated with the molecular orbital above is

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

where the H_{ij} are integrals involving the effective Hamiltonian. Because the carbon atoms in ethylene are equivalent, $H_{11} = H_{22}$.

These diagonal elements of the secular determinant, called *Coulomb integrals*, are customarily denoted by α.

The off-diagonal H's in the secular determinant are called *resonance integrals* or *exchange integrals* and are customarily denoted by β. Note that β is a two-center integral because it involves the atomic orbitals from two different carbon atoms. Although it is not necessary, one often neglects the overlap integrals in Hückel theory and so the S_{ij} are given by

$S_{ij} = 0$ if $i \neq j$
$= 1$ if $i = j$

Thus, the Hückel secular determinantal equation describing the ethylene molecule is

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

The two roots of this secular determinant are:

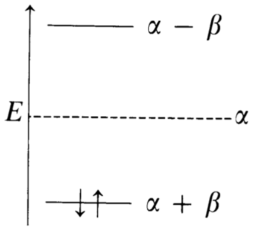
$$E = \alpha \pm \beta.$$

In principle, to evaluate α and β we would have to know the effective Hamiltonian operator. However, we do not have to do this in Hückel theory because α and β are assigned empirical values.

Because α is essentially the energy of an electron in an isolated carbon $2p_z$ orbital, we can use it to set our zero of energy. The quantity β has been determined from a consideration of a variety of data and can be assigned a value of approximately -75 kJ mol^{-1}.

There are two π electrons in ethylene. In the ground state, both electrons occupy the lowest energy orbital. Because β is negative, the lowest energy is $E = \alpha + \beta$.

An energy-level diagram showing the ground state of ethylene is shown below:



The π electronic energy of ethylene is simply the sum of the energies of the two π electrons and is given by $E = 2\alpha + 2\beta$. But because α is used to specify the zero of energy, the π electronic energy of ethylene is simply 2β.

Because α is essentially the energy of an isolated *p* orbital, the two energies, $E = \alpha \pm \beta$ must correspond to bonding and antibonding orbitals.

Let us determine the wave functions for the Hückel molecular orbitals.

Recall that the secular determinantal equation originates from the pair of linear algebraic equations for the expansion coefficients c_1 and c_2

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0$$

$$(H_{12} - ES_{12})c_1 + (H_{22} - ES_{22})c_2 = 0$$

where c_1 and c_2 came from our trial wave function in which we approximated the orbitals as linear combinations of π orbitals on the two atoms.

Upon using the Hückel approximations for the H and S, we have

$$(\alpha - E)c_1 + \beta c_2 = 0$$

$$\beta c_1 + (\alpha - E)c_2 = 0$$

To find the *c*'s associated with each value of *E*, we substitute one value of *E* into either of the two linear algebraic equations above.

For example, for the value $E = \alpha + \beta$, either equation yields $c_1 = c_2$, so that

$$\psi_1 = c_1(\chi_1 + \chi_2)$$

The value of c_1 is found by requiring that ψ_1 be normalized. Because we are using $S_{12} = 0$, we find that $c_1 = \frac{1}{\sqrt{2}}$.

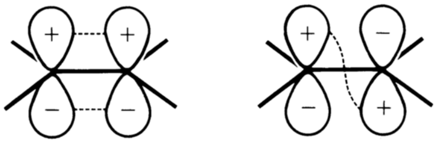
Thus,

$$\psi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2)$$

It is not difficult to show that the root $E = \alpha - \beta$ yields

$$\psi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2)$$

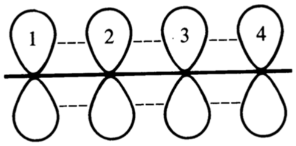
The figure below shows the two molecular orbitals schematically:



Note that it would not be difficult to extend this treatment to the case where we do not assume that the overlap integrals, S_{ij} to be zero for i≠j.

11.9.2 Butadiene

The case of butadiene is more interesting than that of ethylene. Although butadiene exists in cis or trans configuration, we will picture this molecule as simply a linear sequence of four carbon atoms, each of which contributes a $2p_z$ orbital to a π-electron orbital.



Because we have a linear combination of four atomic orbitals, we are going to have a 4 x 4 secular determinant, four different energies, and four different π-molecular orbitals.
We can introduce the notation

$$\psi_i = \sum_{n=1}^{4} c_{in}\chi_n$$

where c_{in} is the coefficient of the atomic orbital of the n^{th} atom in the i^{th} molecular orbital.

The secular determinantal equation for the butadiene molecule is

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} \\ H_{12}-ES_{12} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} \\ H_{13}-ES_{13} & H_{23}-ES_{23} & H_{33}-ES_{33} & H_{34}-ES_{34} \\ H_{14}-ES_{14} & H_{24}-ES_{24} & H_{34}-ES_{34} & H_{44}-ES_{44} \end{vmatrix} = 0$$

Because we are taking the four carbon atoms in the butadiene molecule to be equivalent, all the H_{ii} in this determinant are equal, and as in the case of ethylene, we denote them by α.

The H_{ij} , on the other hand, are two-center integrals. They involve the $2p_z$ orbital centered on carbons *i* and *j*. In the simplest version of Hückel theory, one sets $H_{ij} = \beta$ if the i and j carbon atoms are adjacent and $H_{ij} = 0$ if they are not adjacent. The justification of this is that the overlap of the $2p_z$ orbitals from two carbon atoms decreases with their separation. Following this argument, one might set $S_{ij} = S$ for adjacent carbon atoms and $S_{ij} = 0$ for nonadjacent carbon atoms. In the simplest version of Hückel theory, one goes even one step further and sets $S = 0$.

Under these approximations and assumptions, the Hückel theory secular determinantal equation for butadiene becomes

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

If we factor β from each column and let $x = (\alpha - E)/\beta$, then the determinant above becomes

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$

If we expand this determinant, then the secular equation is

$$x^4 - 3x^2 + 1 = 0$$

We can solve this equation for x^2 to obtain

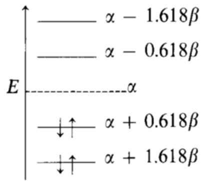
$$x^2 = \frac{3 \pm \sqrt{5}}{2}$$

We therefore find the four roots to be

$$x = \pm 1.61804$$

$$x = \pm 0.61804$$

Recalling that $x = (\alpha - E)/\beta$ and that β is a negative quantity, we can construct a Hückel theory energy-level diagram for butadiene. There are four π electrons in butadiene. In the ground state, these four π electrons occupy the two orbitals of lowest energy as shown below



The total π electronic energy of butadiene is

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$

$$= 4\alpha + 4.472\beta$$

It is interesting to compare the energy given in this equation to the energy of the localized structure in which the two double bonds are localized between carbon atoms 1 and 2 and carbons atoms 3 and 4 in butadiene.

In the simple Hückel theory, this localized structure is equivalent to two isolated ethylene molecules. We have shown above that $E_\pi = 2\alpha + 2\beta$ for ethylene, and so we can define a delocalization energy by

$$E_D = E_\pi(butadiene) - 2E_\pi(ethylene)$$

$$= 0.472\beta$$

If β is given the value -75 kJ mol^{-1}, then we see that the delocalization energy in butadiene is about -35 kJ mol^{-1}. This is the energy by which butadiene is stabilized relative to two isolated double bonds, or in other words, the stability that butadiene derives because its π electrons are delocalized over the entire length of the molecule instead of being localized to the two end bonds.

Associated with each of the four molecular orbital energies of butadiene is a wave function given by the expansion coefficients.

Recall that the molecular orbital wave functions are given by

$$\psi_i = \sum_{n=1}^{4} c_{in}\chi_n$$

where the c_{in} are determined by the set of linear algebraic equations that lead to the secular determinantal equation. The algebra is a little bit longer than in the case of ethylene although straightforward. The resulting wave functions are

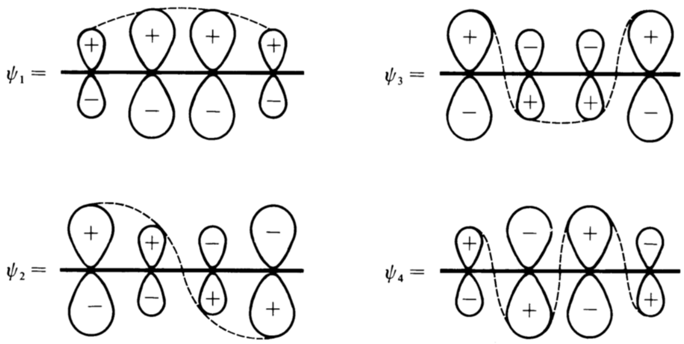
$$\psi_1 = 0.3717\chi_1 + 0.6015\chi_2 + 0.6015\chi_3 + 0.3717\chi_4$$

$$\psi_2 = 0.6015\chi_1 + 0.3717\chi_2 - 0.3717\chi_3 - 0.6015\chi_4$$

$$\psi_3 = 0.6015\chi_1 - 0.3717\chi_2 - 0.3717\chi_3 + 0.6015\chi_4$$

$$\psi_4 = 0.3717\chi_1 - 0.6015\chi_2 + 0.6015\chi_3 - 0.3717\chi_4$$

These wave functions are presented schematically below:



Notice that the energy increases as the number of nodes increases.

Because we have set $S_{ij} = \delta_{ij}$, we have in effect assumed that the χ_n are orthonormal. Using this fact, one can see that

$$\sum_{n=1}^{4} c_{in}^2 = 1$$

This allows us to interpret c_{in}^2 as the fractional π electronic charge on the n^{th} carbon atom due to an electron in the i^{th} molecular orbital. Thus, the total π electronic charge on the n^{th} carbon atom is

$$q_n = \sum_i n_i c_{in}^2$$

Where n_i is the number of π electrons in the i^{th} molecular orbital. For butadiene, you will find that all the *q*'s are 1, indicating that the *p* electrons are uniformly distributed over the molecule. You can see this schematically by putting 2 electrons in each of the first two molecular orbitals and adding the electron probabilities.

One can also use Hückel theory to define the π bond order. We can interpret the product $c_{ir}c_{is}$ as the π electron charge in the ith molecular orbital between the adjacent carbon atoms *r* and *s.* The π bond order can be defined as:

$$P_{rs}^{\pi} = \sum_i n_i c_{ir} c_{is}$$

Where n_i is the number of π electrons in the i^{th} molecular orbital.

For butadiene, one gets

$$P_{12}^{\pi} = 2c_{11}c_{12} + 2c_{21}c_{22} + 0c_{31}c_{32} + 0c_{41}c_{42}$$

$$= 2(0.3717)(0.6015) + 2(0.6015)(0.3717)$$

$$= 0.8942$$

$$P_{23}^{\pi} = 2c_{12}c_{13} + 2c_{22}c_{23}$$

$$= 2(0.6015)(0.6015) + 2(0.3717)(-0.3717)$$

$$= 0.4473$$

You can see by symmetry that

$$P_{12}^{\pi} = P_{34}^{\pi}$$

Remember that this is the π bond order. To find the total bond order, we must remember that there is a σ bond between each carbon atom. So we can write:

$$P_{rs} = 1 + P_{rs}^{\pi}$$

For butadiene, this leads to

$$P_{12} = P_{34} = 1.894$$

$$P_{23} = 1.447$$

These values are in good agreement with the relative reactivity of these bonds.