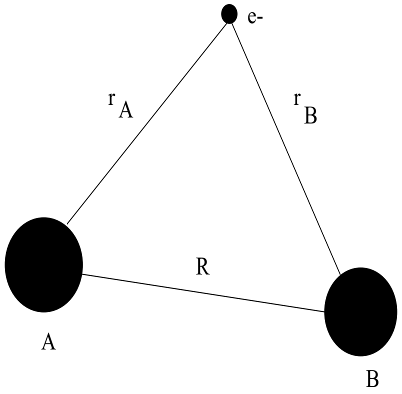
Lecture 26

We now turn to the **structure of molecules**. Our first cases will be the quantum mechanics of the two simplest molecules, the hydrogen molecule ion, H_2^+, a one electron molecule, and H_2, a two electron molecule. The **hydrogen molecule ion** consists of two hydrogen nuclei with a single electron. It is a new problem for us because **we have to deal simultaneously with the motion of the two heavy particles, the nuclei A and B, and the light particle, the electron. The potential energy function will contain terms for the attraction of the electron to each of the nuclei and a term for the repulsion between the two nuclei**. The Hamiltonian for this problem will contain this potential energy term, plus kinetic energy terms for each of the three particles, and is given by



Hydrogen Molecule Ion Coordinates

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m}\nabla_{el}^2 - \frac{e^2}{4\pi\varepsilon_0}(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R})$$

The Schrödinger equation for the hydrogen molecule ion is

$$\hat{H}\psi(r,R) = E\psi(r,R)$$

where **the dependence of the wavefunction on the distances between the electron and the nuclei and the internuclear distance serves to underscore the fact that we must consider both electronic and nuclear motion**.

Solving the Schrödinger equation for both types of motion simultaneously is exceedingly difficult. **The solution would be substantially easier if we could separate the problem into one dealing with nuclear motion, and one dealing with electronic motion.** This separation is accomplished not rigorously, as in our previous experiences with separation of variables, but by means of an approximation, the **Born-Oppenheimer approximation**, due to the German physicist Max Born, and the American physicist, J. Robert Oppenheimer. **The physical basis of the approximation is the observation that the masses of electrons in molecules are four orders of magnitude smaller than the masses of nuclei, and thus, at a given energy, their velocities will be far faster. Since the electrons are moving so much faster than nuclei, we can approximate the electrons as moving in the potential fields of stationary nuclei**. As the result of the approximation we do two things. First, we separate the wavefunction into a nuclear wavefunction and an electronic wavefunction by writing

$$\psi(r,R) = \psi_{nu}(R)\psi_{el}(r)$$

Now we separate our calculation into two separate calculations. First we solve an electronic Schrödinger equation,

$$[-\frac{\hbar^2}{2m_e}\nabla_{el}^2 - \frac{e^2}{4\pi\varepsilon_0}(\frac{1}{r_A}+\frac{1}{r_B}-\frac{1}{R})]\,\psi_{el} = E(R)\psi_{el},$$

treating R as a constant. When we solve this equation, we are determining the electronic energy at nuclear separation R. We can calculate the energy E as a function of R by repeating this process for all possible values of R. This will actually generate a family of E(R) vs. R curves that correspond to the electronic ground state and excited states for the molecule.

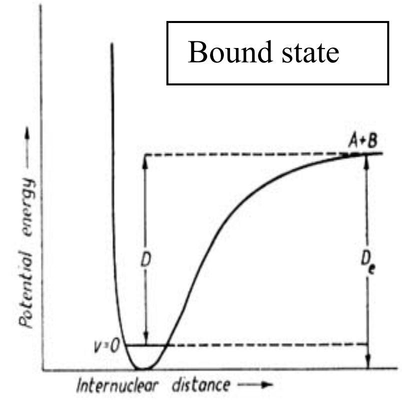


Fig. 3.1 Potential energy curve and the representation of thermal dissociation D

These states will fall into one of two classes, bound states and unbound states. **Bound states** are characterized by a decrease in potential energy until we reach a value which we call R_e, the **equilibrium bond length (the value of R at the energetic minimum in the figure to the right)**. This distance represents the stablest distance between the atoms in a bond. Any increase or decrease of the distance between the nuclei from this length results in an increase in the potential energy of the molecule. There are two dissociation energies that are used to characterize a bound state. **D_e is the energy necessary to break the bond from the minimum of the potential energy curve, and is called the equilibrium dissociation energy**, while **D_0 (D in the figure above) is the energy necessary to break the bond from the vibrational zero point**, the actual minimum energy the bond can have (and the actual dissociation energy that can be directly measured). If we express the dissociation energies in wavenumbers, the two dissociation energies are related by the equation

$$D_e = D_0 + \frac{\omega_e}{2} - \frac{\omega_e x_e}{4} + \frac{\omega_e y_e}{8}$$

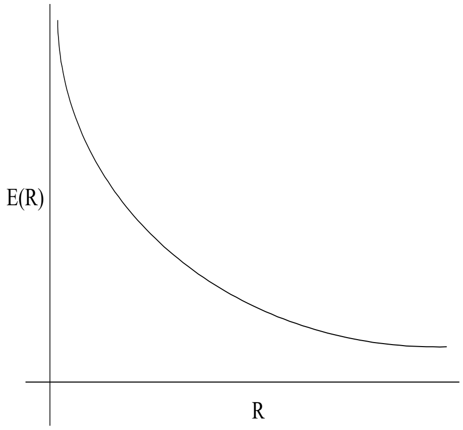
where ω_e is the harmonic vibrational wavenumber, equal to $\sqrt{\frac{k}{\mu}}$, and $\omega_e x_e$ and $\omega_e y_e$ are corrections to account for the fact that true potential energy curves are not really harmonic. **All stable molecules will have a bound state as their ground electronic state**. [Why did I specify stable molecules?]

As a quick but practical aside, notice that I talked of expressing energy in wavenumbers. Wavenumbers are not properly units of energy, but are often used to express relative energies because they are directly related to energy by the equation

$$E = hc\overline{\nu}$$

There are four common energy units you will find in use among physical chemists, the wavenumber, cm^{-1}; the electron volt, eV; the joule and the calorie. The relation between them is 1 eV = 8065.5 cm^{-1} = 23.01 kcal/mol = 96.485 kJ/mol. Other conversions can be found as an appendix in your book.

The other class of potential energy curve is the **unbound potential**. The minimum of this type of potential occurs only at internuclear distances so large that the molecule can be considered to be dissociated. Thus **this potential is purely repulsive**. Electronic excited states can be bound like the potential above, or repulsive, like this potential. A molecule that is excited to a repulsive electronic state will immediately dissociate, i.e., the bond will immediately break. I have used this fact in my experiments to precisely control the kinetic energy of hydrogen atoms, by photolyzing either HI or HBr with a precisely controlled wavelength obtained by frequency doubling the output of a pulsed dye laser. Both HI and HBr have this kind of repulsive excited state, so the H atoms had a kinetic energy equal to the difference between the photon energy and the energy at the asymptote of the potential.



Unbound Potential

Once the electronic Schrödinger equation has been solved to generate these

electronic states or electronic potentials, they are then used as the potential energy curves for the motion of the nuclei. In other words, we now solve a nuclear Schrödinger equation,

$$\hat{H}\psi_{nu} = E_{nu}\psi_{nu}$$

where the Hamiltonian operator is given by

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_R^2 + E(R)$$

The overall wavefunction, ψ(r, R) will be the product of the nuclear and electronic wavefunctions, while the total energy will be the sum of the nuclear and electronic energy eigenvalues.

I'd like to **compare the experimental potential energy curves that have been obtained for the hydrogen molecule ion, H_2^+, and the hydrogen molecule, H_2**, before we go ahead with the calculation. First, note that the potential energy of the H_2 molecule is lower than that of the H_2^+ ion. This should make sense to you since to get H_2^+ from H_2 we need to ionize the molecule, which takes substantial energy. Note also that the H_2 molecule is stabler than the H_2^+ molecule. There are two pieces of evidence for this conclusion. First the spectroscopic dissociation energy for H_2, 4.477 eV, is almost twice as high as the spectroscopic dissociation energy for H_2^+, 2.650 eV. Second the equilibrium bond length, r_e, for H_2, about 80 pm, is substantially shorter than that of H_2^+, about 110 pm. Taken together, these tell us that the bonding in H_2

is stronger than the bonding in H_2^+. Finally, note that when we break the bond we get different products. When we break apart the H_2, we get two H atoms. When we break apart H_2^+, we get an H atom and a proton. The difference in energy between the two sets of products is the ionization energy of the H atom.

Lecture 27

Let's begin our detailed consideration of bonding by looking at the hydrogen molecule ion. Let's look at the potential we just drew for this molecule and try to develop a bit of physical insight before we begin to consider the theory. In general, the shape of any bound electronic surface for a molecule arises because of a balance between attraction and repulsion. It is the attraction that lowers the energy, and stabilizes the molecule as the atoms are brought together, and it is the repulsion that causes the rapid increase in energy when the distance between the atoms becomes less than the equilibrium bond length. The equilibrium bond length is the distance between the atoms where attraction and repulsion combine to yield the maximum stabilization.

The source of the repulsion is the coulomb repulsion between the hydrogen nuclei. The source of the attraction is the coulomb attraction between the lone electron and the two nuclei. In other words, the only thing that is holding the molecule together is the attraction of the nuclei for this single electron. This is the attractive force that is balanced against the repulsion of the two nuclei to generate the electronic potential energy for the molecule. Do all arrangements of nuclei and electrons result in this attractive force? No!! Consider for example the following arrangement, where we have the first the electron and then two hydrogen nuclei all in a straight line. In this configuration the two hydrogen nuclei repel each other, and there is nothing to oppose this repulsion. However, consider now a configuration in which we have a hydrogen nucleus, an electron, and then the other hydrogen nucleus, all in a straight line. In this case, nucleus A is attracted to the electron to its right and nucleus B is attracted to the same electron, which is to its left. The result is that the two nuclei, because they are simultaneously attracted to the electron which is between them, are also pulled toward each other.

This is a thread that should run through all of your thinking about chemical bonding. We start with a bunch of particles, the nuclei, whose interactions are purely repulsive. Some arrangements of electrons and nuclei, in which the electron density is concentrated between the nuclei, and in which each pair of nuclei has some electron density between them, will provide a strong enough attractive force that it will overcome this repulsion and hold the nuclei together, forming a molecule. Both the nuclear repulsion and the attractive force due to the electrons depend on the amount of separation between the nuclei and of the three dimensional arrangement of the nuclei. At some distance r and angles θ and φ, the combination of attraction and repulsion yields the lowest energy, and the nuclei are in their stablest geometry.

The wavefunctions of molecules can be determined using the variational method that we studied earlier. As usual, the first thing we need to do in using the variational method is to choose a trial function. One thing that we can guess about the ground state of the H_2^+ molecule is that since it consists of two nuclei and only one electron, that sometimes the electron will be on one nucleus and sometimes it will be on the other nucleus. Since the ground state wavefunctions of hydrogen atoms are 1s orbitals, we write this trial function as

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

where $1s_A$ and $1s_B$ are the 1s wavefunctions associated with atoms A and B. The constants c_1 and c_2 will be our variational parameters. Note that in this wavefunction, the two 1s orbitals are not centered on the same point in space, and therefore their product integrated over all space does not yield a value of one, unless the value of R is set to 0 so that the atoms are superimposed.

Remember that in the variational method, we calculate a variational energy,

$$E(\alpha,\beta)=\frac{\int\psi(\alpha,\beta)^{*}\hat{H}\psi(\alpha,\beta)d\tau}{\int\psi(\alpha,\beta)^{*}\psi(\alpha,\beta)d\tau}$$

where α and β are our variational parameters. We will, for simplicity's sake, dispense with the complex conjugate notation. In this case our variation energy is

$$E\left(c_1,c_2\right)=\frac{\int[c_1 1s_A+c_2 1s_B]\hat{H}[c_1 1s_A+c_2 1s_B]d\tau}{\int[c_1 1s_A+c_2 1s_B]^2 d\tau}$$

Expanding these integrals yields,

$$E\left(c_1,c_2\right)=\frac{\int(c_1^{2}1s_A\hat{H}1s_A+2c_1c_2 1s_A\hat{H}1s_B+c_2^{2}1s_B\hat{H}1s_B)d\tau}{\int(c_1^{2}1s_A^{2}+2c_1c_1 1s_A 1s_B+c_2^{2}1s_B^{2})d\tau}$$

When we deal with larger numbers of electrons, this integral will become even bulkier, and to compress the notation somewhat, the following abbreviations have been introduced.

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

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

$$S_{AA}=\int 1s_A 1s_A d\tau=\int 1s_B 1s_B d\tau=S_{BB}=1$$

$$S_{AB}=\int 1s_A 1s_B d\tau=\int 1s_B 1s_A d\tau=S.$$

The integrals abbreviated by S are called overlap integrals, because they, especially S_{AB}, are the best measure of the degree that the orbitals are overlapping. The integrals H_{AA} and H_{AB} are called the coulomb integrals. H_{AA} represents the total energy due to the coulomb attraction between the electron sitting in the 1s orbital of atom A and the two nuclei, plus the repulsion between the two nuclei. Similarly, H_{BB} represents the total energy due to the coulomb attraction between the electron sitting in the 1s orbital of atom B and the two nuclei, plus the repulsion between the two nuclei. The energy H_{AB} is called the resonance energy. It represents the energy due to the coulomb attraction between the electron and the nuclei if the electron is in a portion of space created by the overlap of 1s orbitals on the two H atoms.

Now our variational energy becomes

$$E(c_1,c_2)=\frac{c_1^{\,2}H_{AA}+2c_1c_2H_{AB}+c_2^{\,2}H_{BB}}{c_1^{\,2}+2c_1c_2S+c_2^{\,2}}$$

The next step in the variational method is to differentiate with respect to the variational parameters, set them equal to zero and solve for them, in order to find the minimum energy that goes with this configuration. Taking the derivative with respect to c_1 and setting equal to zero yields

$$c_1(H_{AA} - E) + c_2\ (H_{AB} - ES_{AB}) = 0$$

and taking the derivative with respect to c_2 and setting equal to zero yields

$$c_1\ (H_{AB} - ES_{AB}) + c_2\ (H_{BB} - E) = 0.$$

This is a pair of simultaneous equations in c_1 and c_2. It turns out that there will be solutions other than $c_1 = c_2 = 0$, only if the determinant of a matrix made up of the coefficients is equal to zero, i.e.

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

This equation is called a secular determinant, and can be generalized to an n atom system. Expanding out this determinant yields a quadratic equation in the energy, with two solutions, which are labeled E_g or E_u. The values of the energy that are required for c_1 and

c_2 to be nonzero are:

$$E_g = \frac{H_{AA} + H_{AB}}{1 + S_{AB}}$$

and $$E_u = \frac{H_{AA} - H_{AB}}{1 - S_{AB}}.$$

When these energies are substituted back into our simultaneous equation, we get two different solutions. The first is $c_1 = c_2$, and the second is $c_1 = -c_2$. If we substitute these results into our trial function,

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

and normalize it, we get two different wavefunctions for the hydrogen molecule ion,

$$\psi_g = \frac{1}{[2(1+S_{AB})]^{1/2}}[1s_A + 1s_B]$$

and $$\psi_u = \frac{1}{[2(1-S_{AB})]^{1/2}}[1s_A - 1s_B].$$

Note that in both of these cases the two hydrogen-like wavefunctions contribute equally. This should make sense since there is no intrinsic reason why the electron should prefer one nucleus to the other. When we evaluate H_{AA} and H_{AB} we find that H_{AB} is negative, so ψ_g is lower in energy than ψ_u. In fact, ψ_g will have a lower energy than the unbonded hydrogen 1s orbital, and ψ_u will have a higher energy than the unbonded hydrogen 1s orbital. Since a bonding interaction results in a lower energy than the separated atoms, this leads us to conclude that ψ_g is a bonding molecular orbital, and ψ_u, which destabilizes the system compared to the original hydrogen orbitals, is an antibonding molecular orbital.

The g and u labels on the wavefunctions refer to properties of wavefunctions of molecules that have inversion symmetry, when a wavefunction is inverted. **Inversion symmetry** means that **when all of the nuclei in the molecule are reflected through a point in the exact center of the molecule that the exact same molecule in the same position is produced.** One example of a molecule with inversion symmetry is H_2. If we place a point in the center of the molecule, reflecting each nucleus in the molecule through that point results in an identical H_2. From this we see that all homonuclear diatomic molecules will have inversion symmetry. Another example is ethylene, C_2H_4. If a point is placed in the center of the molecule, and all of the nuclei are reflected through that point, each hydrogen will be exactly in the place of the hydrogen directly across from it and the carbons merely switch places. In contrast two molecules which do not have inversion symmetry are HCl and C_2H_3I. If we reflect the H and the Cl through a point in the middle of the molecule, we get an HCl that is reversed in direction. Similarly reflection of all nuclei of vinyl iodide through a point in the center of the molecule will yield a vinyl iodide which is reversed in direction.

To invert a wavefunction $\psi(x,y,z)$, we merely change the sign of all of its coordinates. Thus the inversion of $\psi(x,y,z)$ is $\psi(-x, -y, -z)$. Inverting the wavefunction of a molecule which has inversion symmetry may or may not change the sign of the wavefunction. **If $\psi(x,y,z) = \psi(-x,-y,-z)$, the wavefunction is said to have *even parity* and is given the subscript g**, which stands for gerade, the German word for even. **If $\psi(x,y,z) = -\psi(-x,-y,-z)$, then the wavefunction is said to have *odd parity*, and is given the subscript u**, which stands for ungerade, the German work for odd. Note that the designations g and u are applied only to the wavefunctions of molecules with inversion symmetry.

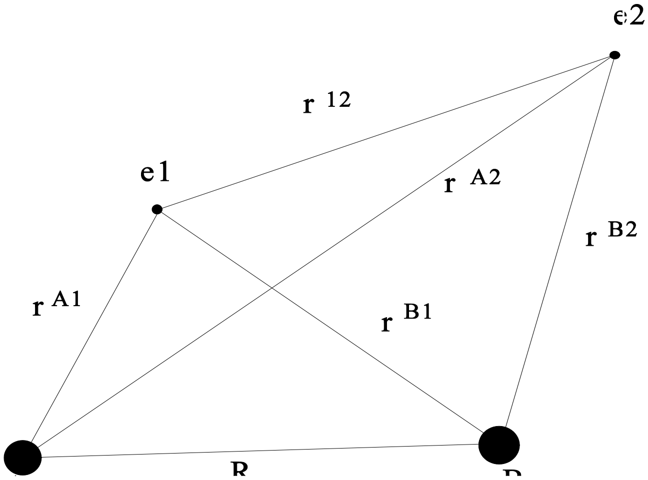
The probability densities for our two wavefunctions, ψ_g and ψ_u, are given below. Note that **for ψ_g, the electronic probability density is higher between the two hydrogen nuclei than would be the case for the sum of two non-interacting hydrogen atoms at the same positions.** Therefore there is a net negative charge between the two nuclei, and the net interaction will be attractive and a bond will form. We call this a **bonding orbital**. Since it is symmetrical around the internuclear axis, we call it a **σ orbital**. Since it is made up from two 1s orbitals we call it a $1s\sigma_g$ orbital.

Notice that in contrast, **the probability density between the two nuclei in the ψ_u state is less than would be the case for two hydrogen atoms**. In fact there is a slight increase in density to the outside of the two nuclei. This means that there will be a net positive charge between the two nuclei. The net interaction will be repulsive, and not only will no bond form, but the nuclei will be forced away from each other. An orbital that has this effect is called an **antibonding orbital**. Since it is both symmetric about the internuclear axis, and composed of 1s orbitals, we call this a **$1s\sigma_u$ orbital**.

How good are the results based on this theory? Quite frankly they are mediocre. The calculation we have just summarized yields a D_0 of 1.77 eV, which is far weaker than the experimental value of 2.793 eV, and an equilibrium bond length of 123 pm, which is far longer than the experimental value of 106 pm. The weaknesses of these results are not due to a major flaw in the theory but rather to oversimplified trial functions. In particular, the weakness lies in attempting to construct cylindrical molecular wavefunctions from spherical atomic wavefunctions. (Try it and you'll see the problem.) Nonetheless, this simple calculation shows us important qualitative results. **In every case, bonding occurs when electron density is concentrated between the two nuclei. Bonding fails to occur when the electron density is highest outside the nuclei.**

Lecture 28

Let’s look at the molecular orbital approach to H_2 in detail to see the advantages and disadvantages of such an approach. H_2 is identical to H_2^+ in every way except the presence of the second electron. However, even the simple addition of the second electron increases the number of potential terms drastically. If we draw the molecule and its coordinate system we see that adding this second electron increases the number of potential energy terms from three to six. The six are the attraction of the first electron to both proton A and proton B, the attraction of the second electron to both protons, the interelectron repulsion, and the internuclear repulsion.



As we will always do in calculating the energies and structures of molecules, we will begin with the Born-Oppenheimer approximation, which yields the electronic Hamiltonian for H_2,

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}(\nabla_1^2+\nabla_2^2)+\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{A1}}-\frac{1}{r_{A2}}-\frac{1}{r_{B1}}-\frac{1}{r_{B2}}+\frac{1}{r_{12}}+\frac{1}{R}\right)$$

Just as when we added the second electron in the helium atom, the interelectron repulsion term here prevents us from attempting an exact solution. As before, we'll try an approximate solution.

The simplest approximate solution is to take the molecular orbitals that we calculated for H_2^+, i.e., without considering the interelectron repulsion, and place electrons in them according to the aufbau principle and the Pauli exclusion principle. Since hydrogen has two electrons this means putting two electrons in the $1s\sigma_g$ orbital, a configuration we denote $1s\sigma_g^2$. The configuration in full would be $\psi_{MO} = 1s\sigma_g\alpha(1)\ 1s\sigma_g\beta(2)$, where 1 and 2 stand for electron 1 and electron 2 respectively. DOES ANYONE SEE ANYTHING WRONG WITH THE WAVEFUNCTION AS I'VE WRITTEN IT? [Electrons are distinguishable] Just as was the case for multielectron atoms, the electrons in a molecule must be indistinguishable, and their wavefunctions must be antisymmetric. To achieve both of these goals we use Slater determinants. The only difference in using Slater determinants to construct antisymmetric orbitals for molecules is that we use molecular orbitals in the determinant instead of atomic orbitals.

The Slater determinant for the ground state of hydrogen is

$$\psi_{MO}[(1\sigma_g)^2] = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) \end{vmatrix}$$

where the single electron molecular orbital $1\sigma_g$ is given by

$$1\sigma_g(1) = \frac{1}{[2(1+S)]^{1/2}}[1s_A(1) + 1s_B(1)]$$

Expanding out the determinant gives us

$$\psi_{MO}[(1\sigma_g)^2] = (1/2)^{1/2}[1\sigma_g(1)1\sigma_g(2)\alpha(1)\beta(2) - 1\sigma_g(1)1\sigma_g(2)\beta(1)\alpha(2)].$$

while substituting our formula for the $1\sigma_g(1)$ orbital yields

$$\psi_{MO}[(1\sigma_g)^2)] = \frac{1}{\sqrt{2}}\frac{[1s_A(1)+1s_B(1)][1s_A(2)+1s_B(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]}{2(1+S_{AB})}$$

The energy of this approximate wavefunction for the hydrogen molecule is given by

$$E = \int \psi^*_{MO}[(1\sigma_g)^2]\hat{H}_{el}\psi_{MO}[(1\sigma_g)^2]d\tau \int \psi^*_{MO}[(1\sigma_g)^2]\hat{H}_{el}\psi_{MO}[(1\sigma_g)^2]d\tau.$$

Your book in a rather understated way says simply that this integration leads to a rather complicated equation and goes on from there. It is right. But rather than just tell you this, I'll show you. The equation itself is

$$E = 2E_{1s} + \frac{e^2}{4\pi\varepsilon_0 R} - 2\left(\frac{j' + k'}{1+S}\right) + \left(\frac{j + 2k + m + 4l}{2(1+S)^2}\right)$$

The actual integrals represented by the letters j, j', k, k', l and m are shown below. I am including them only for the sake of completeness. They are:

$$j'/j_0 = \int s_A^2(1)\left(\frac{1}{r_{1b}}\right)d\tau_1 = \left(\frac{1}{R}\right)\left\{1-(1+s)e^{-2s}\right\}$$

$$k'/j_0 = \int s_A(1)s_B(1)\left(\frac{1}{r_{1b}}\right)d\tau_1 = \left(\frac{1}{a_0}\right)\left\{1+s\right\}e^{-s}$$

$$S = \int s_A(1)s_B(1)d\tau_1 = \left\{1+s+\tfrac{1}{3}s^2\right\}e^{-s}$$

$$j/j_0 = \int\int s_A^2(1)\left(\frac{1}{r_{12}}\right)s_B^2(2)d\tau_1 d\tau_2 = \frac{1}{R} - \left(\frac{1}{2a_0}\right)\left\{\frac{2}{s}+\frac{11}{4}+\frac{3s}{2}+\frac{s^2}{3}\right\}e^{-2s}$$

$$k/j_0 = \int\int s_A(1)s_B(1)\frac{1}{r_{12}}s_A(2)s_B(2)d\tau_1 d\tau_2 = \frac{1}{5a_0}\left(A-B\right)$$

$$l/j_0 = \int\int s_A^2(1)\left(\frac{1}{r_{12}}\right)s_A(2)s_B(2)d\tau_1 d\tau_2 = \left(\frac{1}{2a_0}\right)\left\{\left(2s+\frac{1}{4}+\frac{5}{8s}\right)e^{-s} - \left(\frac{1}{4}+\frac{5}{8s}\right)e^{-3s}\right\}$$

$$m/j_0 = \int\int s_A^2(1)\left(\frac{1}{r_{12}}\right)s_A^2(2)d\tau_1 d\tau_2 = \frac{5}{8a_0}$$

with

$$A = \left(\frac{6}{s}\right)\left\{S^2\left(\gamma + \ln s\right) - S'^2 E_1(4s) + 2SS' E_1(2s)\right\}$$

$$B = \left\{-\frac{25}{8}+\frac{23s}{4}+3s^2+\frac{s^3}{3}\right\}e^{-2s}$$

and

$$S'(s) = S(-s),$$

$$\text{where } j_0 = \frac{e^2}{4\pi\varepsilon_0} \text{ and } s = \frac{R}{a_0}.$$

However, what is more important for our goals than the details of the actual integrals is what they represent physically. The main point is that as your book says, **there are three components to this energy integral**. The first is the energy two hydrogen atoms would have if they were not involved in a bond. The second term is the internuclear repulsion. The other six terms are integrals that represent the various interactions. Of these six terms, the two grouped as $-2(\frac{j'+k'}{1+S})$ are simply twice the energy of the electron in the hydrogen molecule ion. The sum of the four unprimed terms is the total of the various contributions to the interelectron repulsion. The potential energy for a given state depends on the way that these two terms and the internuclear repulsion vary as a function of the distance between the nuclei. When these integrals are evaluated the solution we obtain has a value of r_e = 84 pm and a dissociation energy of 255 kJ/mol. The actual experimental values are 74.1 pm and 458 kJ mol^{-1}.

What can we do to improve these results? We get one clue if we expand the spatial part of our antisymmetrized wavefunction to obtain

$$\psi_{spatial} = 1s_A(1)\,1s_A(2) + 1s_A(1)\,1s_B(2) + 1s_A(2)\,1s_B(1) + 1s_B(1)\,1s_B(2).$$

The first and last terms correspond to electron configurations where both of the hydrogen molecule electrons are sitting on one atom while the other has none. In other words these two terms represent ionic bonding between an H^+ and an H^-. The other two terms represent configurations where each atom has one electron and represent the covalent part of the wavefunction. This predicts that when the bond is broken and the hydrogen atoms are completely separated, that fully half of the time we'll end up with H^+ and H^-, a so called heterolytic cleavage. This is highly unlikely, since the separation of charge makes this a much higher energy reaction than breaking the bond to form 2 neutral H atoms, a homolytic cleavage.

Since this wavefunction overemphasizes the ionic terms, a simple correction would be to use this wavefunction as a trial function for a variational calculation and make the variational parameters the % of covalent and ionic character of the bond. In other words, our trial function becomes

$$\psi = c_1(R)\, \psi_{\text{covalent}} + c_2(R)\, \psi_{\text{ionic}},$$

where $$\psi_{\text{covalent}} = 1s_A(1)\, 1s_B(2) + 1s_A(2)\, 1s_B(1)$$

and $$\psi_{\text{ionic}} = 1s_A(1)\, 1s_A(2) + 1s_B(1)\, 1s_B(2).$$

When we apply the variation method to this trial function we get values of c_1 and c_2 which are substantially different from our 50:50 division, and the values of $r_e = 74.9$ pm and $D_0 = 386$ kJ mol^{-1} are much closer to the experimental values.

The most common starting point in molecular orbital theory calculations uses the Hartree-Fock method. In general, **the trial functions represent the one electron orbitals as linear combinations of atomic orbitals**. **The more orbitals that are used in the calculation, the better the results generally are**. In other words, our first guess is that the molecular orbitals for the ground state are made up of the two 1s orbitals. Our second guess would be to include a 2s orbital, our third guess a second 2s and our fourth guess a 2p orbital as well. The results of the calculation for each choice of orbitals are compared until they match to within a predetermined limit. Essentially what we are doing by adding more orbitals is expanding the molecule's wavefunction as a linear combination of a complete set of orthonormal functions. Remember that if we use the whole set of orthonormal functions the wavefunction can be written exactly, but if we use less than the complete set, we're only generating an approximate wavefunction. When we start by using only one orbital, we're using only a very little bit of the complete orthonormal set. Each orbital we add brings us closer to the exact solution.

These results will have the limitation that they still do not include electron correlation, which we mentioned when we discussed the helium atom. The general recipe for dealing with electron correlation is to include electron configurations in which one or more of the electrons is in an excited state configuration. For reasons I don't completely understand, this seems to account for most of the effects of electron correlation.

We can use the same LCAO procedure to calculate the molecular orbitals for other homonuclear diatomic molecules. However, in order to accommodate the larger number of electrons in these atoms, we will need to generate more than the two molecular orbitals we generated for H_2. The procedure will be to combine an atomic orbital from one of our atoms with an atomic orbital from the other atom to generate two molecular orbitals, a bonding and an antibonding orbital. There are, however, two rules that we need to follow in creating these molecular orbitals. First, **in order for orbitals to combine they must be of comparable energy**. For example, in homonuclear diatomic molecules, a 1s orbital will not combine with a 3p orbital, because the energies are so different, but only with another 1s orbital. Second, **we need to be concerned with the phase of each lobe of the orbital**. This phase is a property of all atomic orbitals. For s orbitals the phase is arbitrary. It comes into play most importantly for orbitals with one or more angular nodes. For example, the two lobes of a p orbital are commonly labeled with a + or a -, and always have opposite labels. The four lobes of a d orbital will always have alternating phase. The significance of the phase is that **in order for two atomic orbitals to create a bonding orbital, the lobes that overlap must have the same phase**. Remember that when we are creating a constructive interference between two waves, we must add the waves so that they are in phase, i.e. so that the crests of the waves line up. When we require that two atomic orbitals add with identical phases to construct a bonding orbital, we are ensuring that a constructive interference of the wavefunction is formed.

Let’s clarify these ideas by looking at some of the molecular orbitals that are important in homonuclear diatomic molecules. We've already considered the combination of two 1s orbitals, but let’s consider it quickly again, this time focusing on the angular portion of the molecular orbital. We have two different combinations of these s orbitals, the sum and the difference. The sum yields the bonding $s\sigma_g$ orbital, while the difference yields the antibonding $s\sigma_u$ orbital.

The other combination that we will consider here is the combination of two p orbitals. There are three different ways we could imagine two p orbitals combining. One is end to end, with the lobes with the same phase overlapping. Again, we combine them in two different ways, the sum and the difference. The sum is a bonding orbital called a $p\sigma_g$ orbital, while the difference is antibonding and is called a $p\sigma_u$ orbital. A second possibility would be to combine two p orbitals oriented at 90° to each other. However, in this case no molecular orbital will form, because the positive phase on one p orbital is overlapping with both the positive and negative phases of the other p orbital and the net interaction is 0. The third possibility is for the p orbitals to overlap side by side, with positive and negative lobes aligned. Again two molecular orbitals result, however, in this case the bonding orbital has ungerade symmetry and is a $p\pi_u$ orbital while the antibonding orbital has gerade symmetry and is a $p\pi_g$ orbital.

Notice that in naming these molecular orbitals, the σ and π orbitals seem to follow the same pattern of s, p, and d for the orbitals on atoms. This is no accident. These σ and π designations represent different orbital angular momenta of electrons in these molecular orbitals. They particularly represent the angular momentum along the bond axis. These angular momentum states are represented by the quantum number λ, which can have values of 0, 1, 2, ... The angular momentum along the bond axis associated with these states is equal to

$$L_z = \pm\lambda\hbar$$

A molecular orbital with λ = 0 is called a σ orbital, one with λ = 1 is called a π orbital, one with λ = 2 is called a δ orbital, λ = 3 yields a ϕ orbital and so on.

To generate molecular electronic configurations from these molecular orbitals, we combine our new orbitals with the Pauli exclusion principle, limiting the number of electrons per orbital to two, and filling the orbitals from the lowest energy to the highest. The relative energies of these molecular orbitals vary as we move across the periodic table, and usually need to be calculated. However, for the first two rows of the periodic table the

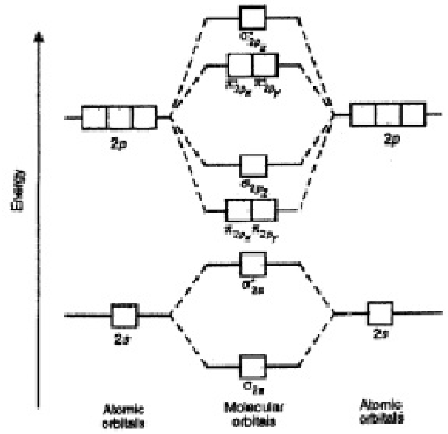


Fig. a Molecular orbital energy level diagram for diatomic homonuclear molecules of first and second period (except O_2, F_2 etc.)

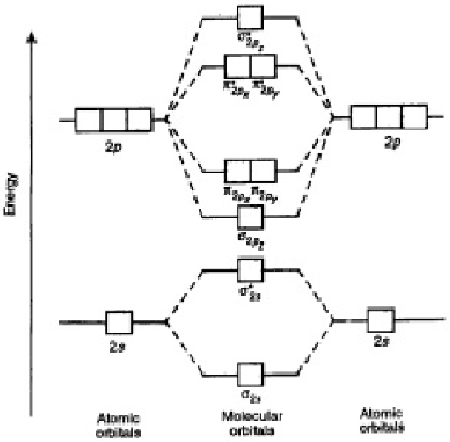


Fig. b. Molecular orbital energy level diagram for homonuclear diatomic molecules of O_2 and other heavier elements

two energy level diagrams above apply, one for $Z \leq 7$ and the other for $Z > 7$.