

## 10.4: The Case of $\text{H}_2^+$

One can develop an intuitive sense of molecular orbitals and what a chemical bond is by considering the simplest molecule,  $\text{H}_2^+$ . This ion consists of two protons held together by the electrostatic force of a single electron. Clearly the two protons, two positive charges, repel each other. The protons must be held together by an attractive Coulomb force that opposes the repulsive Coulomb force. A negative charge density between the two protons would produce the required counter-acting Coulomb force needed to pull the protons together. So intuitively, to create a chemical bond between two protons or two positively charged nuclei, a high density of negative charge between them is needed. We expect the molecular orbitals that we find to reflect this intuitive notion.

The electronic Hamiltonian for  $\text{H}_2^+$  is

$$\hat{H}_{elec}(r, R) = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R} \quad (10.4.1)$$

where  $r$  gives the coordinates of the electron, and  $R$  is the distance between the two protons. Although the Schrödinger equation for  $\text{H}_2^+$  can be solved exactly because there is only one electron, we will develop approximate solutions in a manner applicable to other diatomic molecules that have more than one electron.

For the case where the protons in  $\text{H}_2^+$  are infinitely far apart, we have a hydrogen atom and an isolated proton when the electron is near one proton or the other. The electronic wavefunction would just be  $1s_A(r)$  or  $1s_B(r)$  depending upon which proton, labeled A or B, the electron is near. Here  $1s_A$  denotes a 1s hydrogen atomic orbital with proton A serving as the origin of the spherical polar coordinate system in which the position  $r$  of the electron is specified. Similarly  $1s_B(r)$  has proton B as the origin. A useful approximation for the molecular orbital when the protons are close together therefore is a linear combination of the two atomic orbitals. The general method of using

$$\psi(r) = C_A 1s_A(r) + C_B 1s_B(r) \quad (10.4.2)$$

i.e. of finding molecular orbitals as linear combinations of atomic orbitals is called the *Linear Combination of Atomic Orbitals - Molecular Orbital (LCAO-MO) Method*. In this case we have two basis functions in our basis set, the hydrogenic atomic orbitals  $1s_A$  and  $1s_B$ .

For  $\text{H}_2^+$ , the simplest molecule, the starting function is given by Equation 10.4.2. We must determine values for the coefficients,  $C_A$  and  $C_B$ . We could use the variational method to find a value for these coefficients, but for the case of  $\text{H}_2^+$  evaluating these coefficients is easy. Since the two protons are identical, the probability that the electron is near A must equal the probability that the electron is near B. These probabilities are given by  $|C_A|^2$  and  $|C_B|^2$ , respectively. Consider two possibilities that satisfy the condition  $|C_A|^2 = |C_B|^2$ ; namely,  $C_A = C_B = C_+$  and  $C_A = -C_B = C_-$ . These two cases produce two molecular orbitals:

$$\psi_+ = C_+(1s_A + 1s_B) \quad (10.4.3)$$

$$\psi_- = C_-(1s_A - 1s_B) \quad (10.4.4)$$

The probability density for finding the electron at any point in space is given by  $|\psi|^2$  and the electronic charge density is just  $e|\psi|^2$ . The important difference between  $\psi_+$  and  $\psi_-$  is that the charge density for  $\psi_+$  is enhanced between the two protons, whereas it is diminished for  $\psi_-$  as shown in Figures 10.4.1.  $\psi_-$  has a node in the middle while  $\psi_+$  corresponds to our intuitive sense of what a chemical bond must be like. The electronic charge density is enhanced in the region between the two protons. So  $\psi_+$  is called a *bonding molecular orbital*. If the electron were described by  $\psi_-$ , the low charge density between the two protons would not balance the Coulomb repulsion of the protons, so  $\psi_-$  is called an **antibonding molecular orbital**.

Now we want to evaluate  $C_+$  and  $C_-$  and then calculate the energy. The bonding and antibonding character of  $\psi_+$  and  $\psi_-$  also should be reflected in the energy. If  $\psi_+$  indeed describes a bonding orbital, then the energy of this state should be less than that of a proton and hydrogen atom that are separated. The calculation of the energy will tell us whether this simple theory predicts  $\text{H}_2^+$  to be stable or not and also how much energy is required to dissociate this molecule.

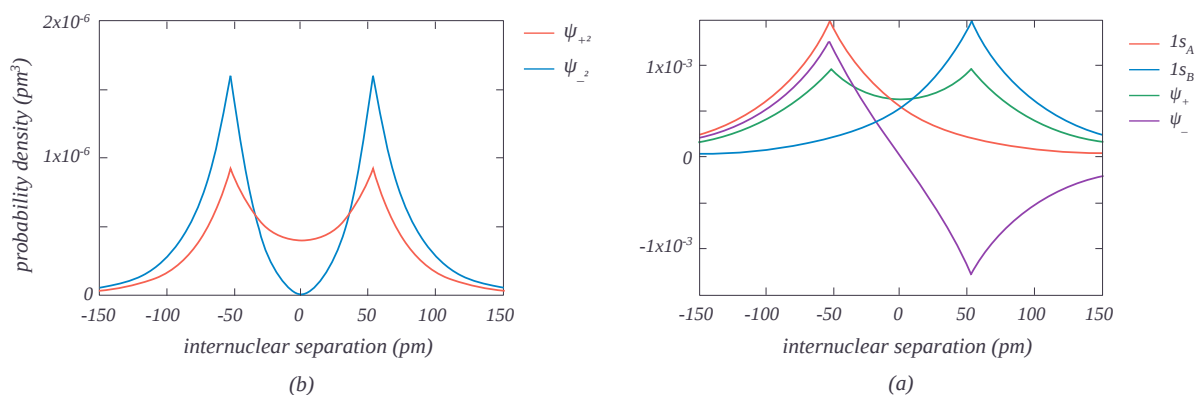


Figure 10.4.1: a) The 1s basis functions and bonding and antibonding molecular orbitals plotted along the internuclear axis, which is defined as the z-axis, for  $\text{H}_2^+$ . The protons are located at  $\pm 53 \text{ pm}$ , which corresponds to the experimental bond length. b) The electron probability density for the bonding and antibonding molecular orbitals

#### Exercise 10.4.1

From the information in Figure 10.4.1 for  $\text{H}_2^+$ , calculate the difference in the electronic charge density ( $\text{C/pm}^3$ ) at a point halfway between the two nuclei for an electron in the bonding molecular orbital compared to one in the antibonding molecular orbital.

The constants  $C_+$  and  $C_-$  are evaluated from the normalization condition. Bracket notation,  $\langle | \rangle$ , is used in Equation 10.4.5 to represent integration over all the coordinates of the electron for both functions  $\psi_+$  and  $\psi_-$ . The right bracket represents a function, the left bracket represents the complex conjugate of the function, and the two together mean integrate over all the coordinates.

$$\int \psi_{\pm}^* \psi_{\pm} d\tau = \langle \psi_{\pm} | \psi_{\pm} \rangle = 1 \quad (10.4.5)$$

$$\langle C_{\pm} [1s_A \pm 1s_B] | C_{\pm} [1s_A \pm 1s_B] \rangle = 1 \quad (10.4.6)$$

$$|C_{\pm}|^2 [(1s_A | 1s_A) + (1s_B | 1s_B) \pm (1s_B | 1s_A) \pm (1s_A | 1s_B)] = 1 \quad (10.4.7)$$

Since the atomic orbitals are normalized, the first two integrals are just 1. The last two integrals are called *overlap integrals* and are symbolized by  $S$  and  $S^*$ , respectively, since one is the complex conjugate of the other.

#### Exercise 10.4.2

Show that for two arbitrary functions  $\langle \varphi_B | \varphi_A \rangle$  is the complex conjugate of  $\langle \varphi_A | \varphi_B \rangle$  and that these two integrals are equal if the functions are real.

The overlap integrals are telling us to take the value of  $1s_B$  at a point multiply by the value of  $1s_A$  at that point and sum (integrate) such a product over all of space. If the functions don't overlap, i.e. if one is zero when the other one isn't and vice versa, these integrals then will be zero. It also is possible in general for such integrals to be zero even if the functions overlap because of the cancellation of positive and negative contributions, as was discussed in Section 4.4.

If the overlap integral is zero, for whatever reason, the functions are said to be *orthogonal*. Notice that the overlap integral ranges from 0 to 1 as the separation between the protons varies from  $R = \infty$  to  $R = 0$ . Clearly when the protons are infinite distance apart, there is no overlap, and when  $R = 0$  both functions are centered on one nucleus and  $\langle 1s_A | 1s_B \rangle$  becomes identical to  $\langle 1s_A | 1s_B \rangle$ , which is normalized to 1, because then  $1s_A = 1s_B$ .

With these considerations and using the fact that  $1s$  wavefunctions are real so

$$\langle 1s_A | 1s_B \rangle = \langle 1s_B | 1s_A \rangle = S \quad (10.4.8)$$

Equation 10.4.7 becomes

$$|C_{\pm}|^2 (2 \pm 2S) = 1 \quad (10.4.9)$$

The solution to Equation 10.4.9 is given by

$$C_{\pm} = [2(1 \pm S)]^{-1/2} \quad (10.4.10)$$

The energy is calculated from the expectation value integral,

$$E_{\pm} = \langle \psi_{\pm} | \hat{H}_{elec} | \psi_{\pm} \rangle \quad (10.4.11)$$

which expands to give

$$E_{\pm} = \frac{1}{2(1 \pm S)} [\langle 1s_A | \hat{H}_{elec} | 1s_A \rangle + \langle 1s_B | \hat{H}_{elec} | 1s_B \rangle \pm \langle 1s_A | \hat{H}_{elec} | 1s_B \rangle \pm \langle 1s_B | \hat{H}_{elec} | 1s_A \rangle] \quad (10.4.12)$$

### Exercise 10.4.3

Show that Equation 10.4.11 expands to give Equation 10.4.12

The four integrals in Equation 10.4.12 can be represented by  $H_{AA}$ ,  $H_{BB}$ ,  $H_{AB}$ , and  $H_{BA}$ , respectively. Notice that A and B appear equivalently in the Hamiltonian operator, Equation 10.4.1. This equivalence means that integrals involving  $1s_A$  must be the same as corresponding integrals involving  $1s_B$ , i.e.

$$H_{AA} = H_{BB} \quad (10.4.13)$$

and since the wavefunctions are real,

$$H_{AB} = H_{BA} \quad (10.4.14)$$

giving

$$E_{\pm} = \frac{1}{1 \pm S} (H_{AA} \pm H_{AB}) \quad (10.4.15)$$

Now examine the details of  $H_{AA}$  after inserting Equation 10.4.1 for the Hamiltonian operator.

$$H_{AA} = \left\langle 1s_A \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_A \right\rangle + \frac{e^2}{4\pi\epsilon_0 R} \langle 1s_A | 1s_A \rangle - \left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle \quad (10.4.16)$$

The first term is just the integral for the energy of the hydrogen atom,  $E_H$ . The second integral is equal to 1 by normalization; the prefactor is just the Coulomb repulsion of the two protons. The last integral, including the minus sign, is represented by  $J$  and is called the **Coulomb integral**. Physically  $J$  is the potential energy of interaction of the electron located around proton A with proton B. It is negative because it is an attractive interaction. It is the average interaction energy of an electron described by the  $1s_A$  function with proton B.

Now consider  $H_{AB}$ .

$$H_{AB} = \left\langle 1s_A \left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_B} \right| 1s_B \right\rangle + \frac{e^2}{4\pi\epsilon_0 R} \langle 1s_A | 1s_B \rangle - \left\langle 1s_A \left| \frac{e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle \quad (10.4.17)$$

In the first integral we have the hydrogen atom Hamiltonian and the H atom function  $1s_B$ . The function  $1s_B$  is an eigenfunction of the operator with eigenvalue  $E_H$ . Since  $E_H$  is a constant it factors out of the integral, which then becomes the overlap integral,  $S$ . The first integral therefore reduces to  $E_H S$ . The second term is just the Coulomb energy of the two protons times the overlap integral. The third term, including the minus sign, is given the symbol  $K$  and is called the **exchange integral**. It is called an exchange integral because the electron is described by the  $1s_A$  orbital on one side and by the  $1s_B$  orbital on the other side of the operator. The electron changes or exchanges position in the molecule. In a Coulomb integral the electron always is in the same orbital; whereas, in an exchange integral, the electron is in one orbital on one side of the operator and in a different orbital on the other side.

Using the expressions for  $H_{AA}$  and  $H_{AB}$  and substituting into Equation 10.4.15 produces:

$$E_{\pm} = \frac{1}{1 \pm S} \left[ \left( E_H + \frac{e^2}{4\pi\epsilon_0 R} \right) (1 \pm S) + J \pm K \right] \quad (10.4.18)$$

$$= \underbrace{E_H}_{\text{H Atom Energy}} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R}}_{\text{Proton-Proton repulsion}} + \underbrace{\frac{J \pm K}{1 \pm S}}_{\text{Bonding Energy}} \quad (10.4.19)$$

The difference in energies of the two states  $\Delta E_{\pm}$  is then:

$$\Delta E_{\pm} = E_{\pm} - E_H \quad (10.4.20)$$

$$= \frac{e^2}{4\pi\epsilon_0 R} + \frac{J \pm K}{1 \pm S} \quad (10.4.21)$$

Equation 10.4.19 tells us that the energy of the  $\text{H}_2^+$  molecule is the energy of a hydrogen atom plus the repulsive energy of two protons plus some additional electrostatic interactions of the electron with the protons. These additional interactions are given by

$$\frac{J \pm K}{1 \pm S} \quad (10.4.22)$$

If the protons are infinitely far apart then only  $E_H$  is nonzero. To get a chemical bond and a stable  $\text{H}_2^+$  molecule,  $\Delta E_{\pm}$  (Equation 10.4.20) must be less than zero and have a minimum, i.e.

$$\frac{J \pm K}{1 \pm S} \quad (10.4.23)$$

must be sufficiently negative to overcome the positive repulsive energy of the two protons

$$\frac{e^2}{4\pi\epsilon_0 R} \quad (10.4.24)$$

for some value of  $R$ . For large  $R$  these terms are zero, and for small  $R$ , the Coulomb repulsion of the protons rises to infinity.

#### Exercise 10.4.4

Show that Equation 10.4.1 follows from Equation 10.4.15

We will examine more closely how the Coulomb repulsion term and the integrals  $J$ ,  $K$ , and  $S$  depend on the separation of the protons, but first we want to discuss the physical significance of  $J$ , the Coulomb integral, and  $K$ , the exchange integral.

Both  $J$  and  $K$  have been defined as

$$J = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_B} \right| 1s_A \right\rangle = - \int \varphi_{1s_A}^*(r) \varphi_{1s_A}(r) \frac{e^2}{4\pi\epsilon_0 r_B} d\tau \quad (10.4.25)$$

$$K = \left\langle 1s_A \left| \frac{-e^2}{4\pi\epsilon_0 r_A} \right| 1s_B \right\rangle = - \int \varphi_{1s_A}^*(r) \varphi_{1s_B}(r) \frac{e^2}{4\pi\epsilon_0 r_A} d\tau \quad (10.4.26)$$

Note that both integrals are negative since all quantities in the integrand are positive. In the Coulomb integral,  $e\varphi_{1s_A}^*(r)\varphi_{1s_A}(r)$  is the charge density of the electron around proton A, since  $\mathbf{r}$  represents the coordinates of the electron relative to proton A. Since  $r_B$  is the distance of this electron to proton B, the Coulomb integral gives the potential energy of the charge density around proton A interacting with proton B.  $J$  can be interpreted as an average potential energy of this interaction because  $e\varphi_{1s_A}^*(r)\varphi_{1s_A}(r)$  is the probability density for the electron at point  $\mathbf{r}$ , and  $\frac{e^2}{4\pi\epsilon_0 r_B}$  is the potential energy of the electron at that point due to the interaction with proton B. Essentially,  $J$  accounts for the attraction of proton B to the electron density of hydrogen atom A. As the two protons get further apart, this integral goes to zero because all values for  $r_B$  become very large and all values for  $1/r_B$  become very small.

In the exchange integral,  $K$ , the product of the two functions is nonzero only in the regions of space where the two functions overlap. If one function is zero or very small at some point then the product will be zero or small. The exchange integral also approaches zero as internuclear distances increase because the both the overlap and the  $1/r$  values become zero. The product  $e\varphi_{1s_A}^*(r)\varphi_{1s_B}(r)$  is called the *overlap charge density*. Since the overlap charge density is significant in the region of space between

the two nuclei, it makes an important contribution to the chemical bond. The exchange integral,  $K$ , is the potential energy due to the interaction of the overlap charge density with one of the protons. While  $J$  accounts for the attraction of proton B to the electron density of hydrogen atom A,  $K$  accounts for the added attraction of the proton due the build-up of electron charge density between the two protons.

#### Exercise 10.4.5

Write a paragraph describing in your own words the physical significance of the Coulomb and exchange integrals for  $H_2^+$ .

Figure 10.4.2 shows graphs of the terms contributing to the energy of  $H_2^+$ . In this figure you can see that as the internuclear distance  $R$  approaches zero, the Coulomb repulsion of the two protons goes from near zero to a large positive number, the overlap integral goes for zero to one, and  $J$  and  $K$  become increasingly negative.

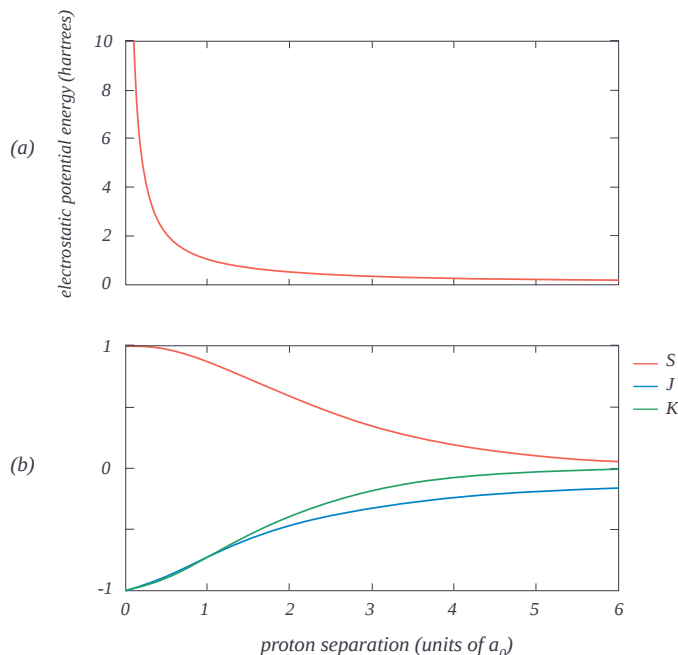


Figure 10.4.2 a) The electrostatic energy (in hartrees, 27.2 eV) of two protons separated by a distance  $R$  in units of the Bohr radius (52.92 pm). b) The overlap, Coulomb, and exchange integrals at different proton separations. The units for  $J$  and  $K$  are hartrees;  $S$  has no units.

Figure 10.4.3 shows the energy of  $H_2^+$  relative to the energy of a separated hydrogen atom and a proton as given by Equation 10.4.19. For the electron in the antibonding orbital, the energy of the molecule,  $E_H(R)$ , always is greater than the energy of the separated atom and proton.

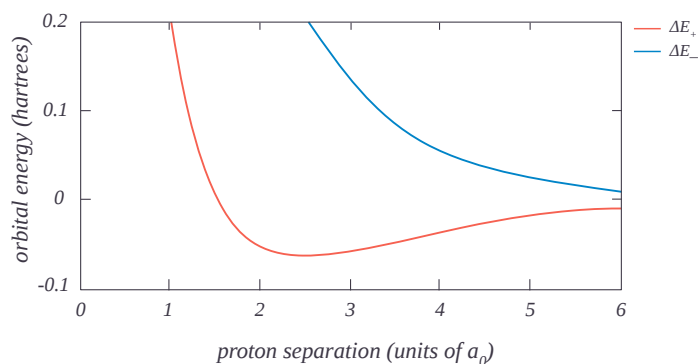


Figure 10.4.3: Energy of the  $H_2^+$  bonding molecular orbital  $\Delta E_+$  and the antibonding molecular orbital  $\Delta E_-$ , relative to the energy of a separated hydrogen atom and proton.

For the electron in the bonding orbital, you can see that the big effect for the energy of the bonding orbital,  $E_+(R)$ , is the balance between the repulsion of the two protons  $\frac{e^2}{4\pi\epsilon_0 R}$  and  $J$  and  $K$ , which are both negative.  $J$  and  $K$  manage to compensate for the repulsion of the two protons until their separation is less than 100 pm (i.e the energy is negative up until this point), and a minimum in the energy is produced at 134 pm. This minimum represents the formation of a chemical bond. The effect of  $S$  is small. It only causes the denominator in Equation 10.4.19 to increase from 1 to 2 as  $R$  approaches 0.

For the antibonding orbital,  $-K$  is a positive quantity and essentially cancels  $J$  so there is not sufficient compensation for the Coulomb repulsion of the protons. The effect of the  $-K$  in the expression, Equation 10.4.19 for  $E_-$  is to account for the absence of overlap charge density and the enhanced repulsion because the charge density between the protons for  $\psi_-$  is even lower than that given by the atomic orbitals.

This picture of bonding in  $H_2^+$  is very simple but gives reasonable results when compared to an exact calculation. The equilibrium bond distance is 134 pm compared to 106 pm (exact), and a dissociation energy is 1.8 eV compared to 2.8 eV (exact).

#### Exercise 10.4.6

Write the final expressions for the energy of  $\psi_+$  and  $\psi_-$ , explain what these expressions mean, and explain why one describes the chemical bond in  $H_2^+$  and the other does not.

#### Exercise 10.4.7

Figure 10.4.2 shows that  $S = 1$  and  $J = K = 1$  hartree when  $R = 0$ . Explain why  $S$  equals 1 and  $J$  and  $K$  equal -1 hartree when  $R = 0$ .

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