Molecules

Introduction: (Fundamental University Physics, Part III by Alonso-Finn)

An important problem related to the structure of matter is the structure of molecules. Why do carbon atoms combine with four hydrogen atoms, forming methane, but never with three or five hydrogen atoms? Why is the CO_2 molecule linear, while H_2O is bent and NH_3 is a pyramid? Why does benzene (C_6H_6) have the form of a hexagon with all hydrogen atoms in the plane? How can hydrogen atoms join together to form the molecule H_2 but never form H_3? Why are the spectra of molecules so complex when compared with atomic spectra, ranging from the microwave up to the ultraviolet? These and many other questions could not be answered satisfactorily before the quantum theory was developed. One of the most spectacular successes of the quantum theory is the answers it provides to many of the questions physicists and chemists have been asking about molecular structure. We cannot say, however, that our view of molecular structure is a closed chapter of physics.

Let us begin our study of molecules by asking ourselves: What is a molecule?

1- The first impulse is to say that a molecule is a group of atoms bound together by some kind of interaction. But this immediately raises new questions. Do the atoms serve their individuality? How is the motion of the electrons affected when a molecule is formed? What kind of interaction gives rise to a molecule?

2- We may also adopt an opposite view by saying that a molecule is a group of nuclei surrounded by electrons in such a way that a stable arrangement is produced. This is the natural extension of the concept of an atom, which is a nucleus surrounded by electrons. Then instead of looking at the H_2 molecule as two hydrogen atoms, we may consider it as two protons and two electrons arranged according to the laws of quantum mechanics and held together by electromagnetic forces. From a structural point of view this second approach is more fundamental than the first.

However, as it is in many cases, an intermediate position is the most convenient. When two atoms form a molecule, the more tightly bound, or inner, electrons of each atom (which fill the complete shells of their respective kernels) are practically undisturbed, remaining attached to their original nuclei Only the outermost or valence, electrons in the unfilled shells are affected and they move under the resultant forces of the ions, composed of the nuclei and kernels, as well as their mutual repulsion. These valence electrons are responsible for chemical binding and for most physical properties of the molecule. This intermediate position is the model we shall adopt in this chapter; it is an excellent approximation for analyzing molecular structure.

The Hydrogen molecule ion $\left(\mathrm{H}_2^+\right)$

The simplest of all molecules is the hydrogen molecule ion H_2^+ consisting of two protons, P_1 and P_2, and one electron, see the figure 1.

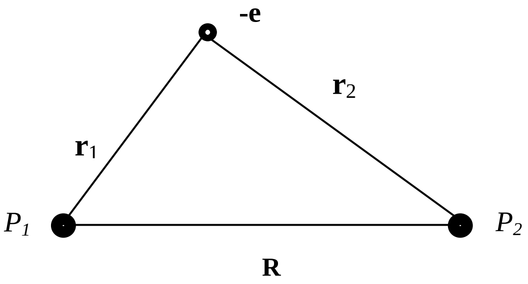


Fig. 1 A coordinate system for the Hydrogen molecule ion $\left(\mathrm{H}_2^+\right)$

Chemists write the formation of this molecule as: $H + H^+ \to H_2^+$, where H^+ is just a proton. In other words, the H_2^+ molecule is formed when a hydrogen atom captures a proton. But once the H_2^+ molecule is formed, it is no longer possible to tell which is the hydrogen atom and which is the proton. Our picture of this molecule is that shown in Figure 1: an electron moving in the electric field of two protons which are separated a distance R.

We might say that the electron does not remember which proton it initially belonged to. This lack of memory is clearly revealed by charge-exchange collisions. Suppose that the electron is initially associated with proton P_1, and proton P_2 approaches the hydrogen atom from the right from a large distance (Figure 2). In the region of closest approach the H_2^+ molecule lasts only a short time and then breaks apart. When this happens there is a certain probability that the incoming proton will take the electron with it. Thus we may write the process as

$$\mathbf{H^+ + H \to H_2^+}\begin{array}{l} \nearrow\ \mathbf{H^+ + H} \quad \textbf{(elastic collision),} \\ \\ \searrow\ \mathbf{H\ \ + H^+} \quad \textbf{(charge-exchange collision).} \end{array}$$

The relative probability of the two processes shown above can be calculated as a function of the energy of the incoming proton. The result checks well with experimental evidence.

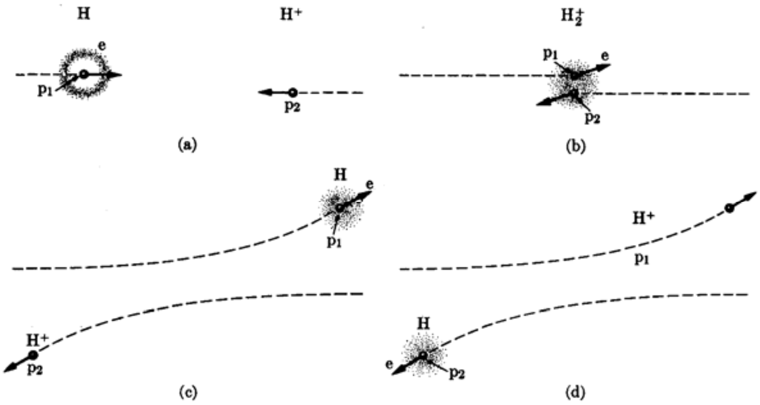


Fig. 2. Collision of a hydrogen atom (H) and a proton H^+, as seen in the CM frame of reference. (c) Elastic collision. (d) Charge-exchange collision.

Types of Molecular Orbitals (Qualitative description)

Bonding Orbitals

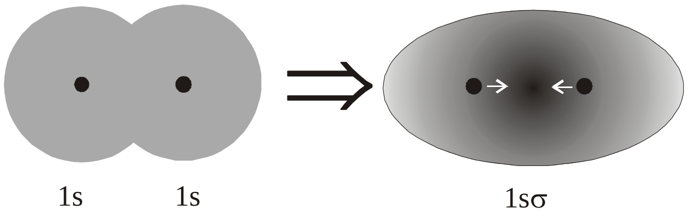
For the linear combination of only two atomic orbitals, the bonding orbital is constructed from adding the wavefunctions together.

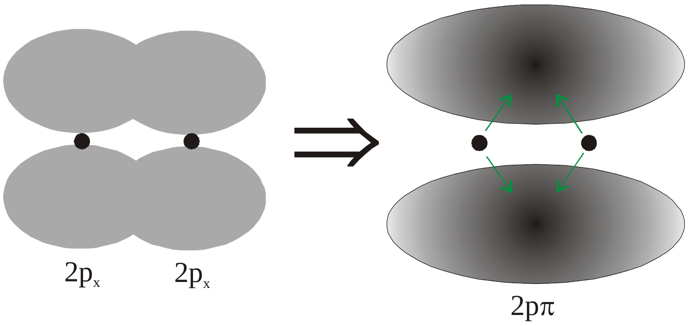
$$\psi_{MO} = \psi_{AO}(A) + \psi_{AO}(B)$$

Thus, the probability density of the bonding orbital can be written as

$$\begin{aligned} |\psi_{MO}|^2 &= |\psi_{AO}(A)|^2 + |\psi_{AO}(B)|^2 + 2\psi_{AO}(A)\psi_{AO}(B) \\ &= A^2 + B^2 + 2AB \end{aligned}$$

The term, +2AB ($S = \int AB\, d\tau$ is called **overlap integral**.), is the constructive interference of the overlap of the atomic orbitals. The interference results in an increase of electron density between the nuclei. Thus, the nuclei have greater attraction to each other, via their mutual attraction to the increased electron density.





Antibonding Orbitals

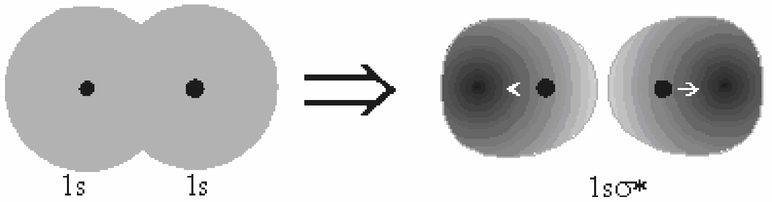
For the linear combination of only two atomic orbitals, the antibonding orbital is constructed from subtracting the wavefunctions together.

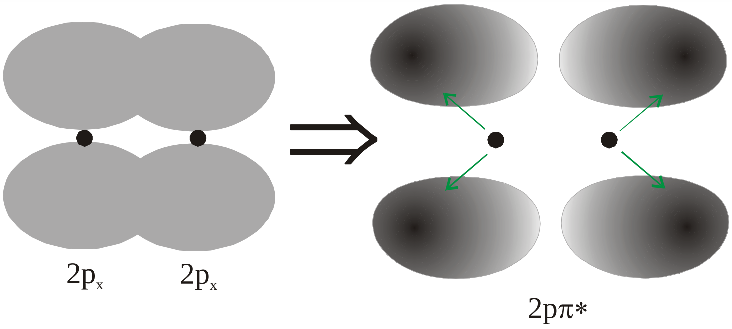
$$\psi_{MO} = \psi_{AO}(A) - \psi_{AO}(B)$$

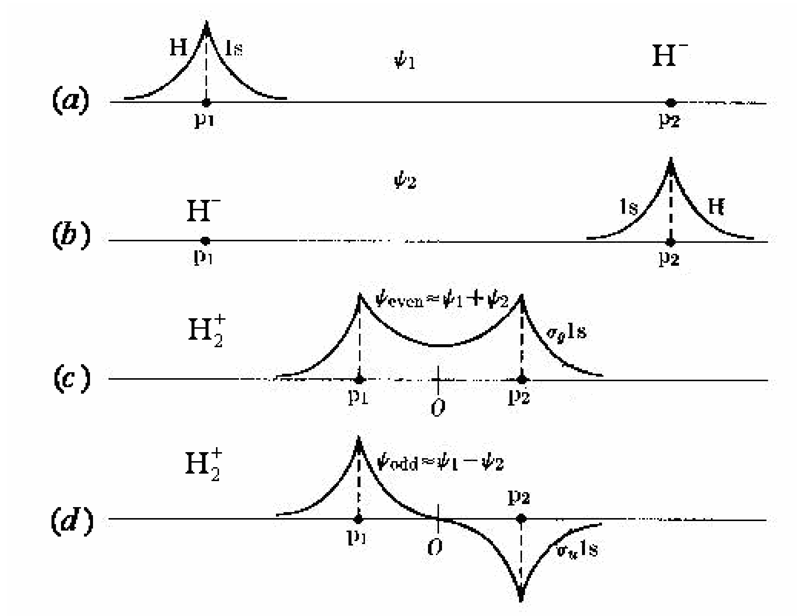
Thus, the probability density of the bonding orbital can be written as

$$\begin{aligned} |\psi_{MO}|^2 &= |\psi_{AO}(A)|^2 + |\psi_{AO}(B)|^2 - 2\psi_{AO}(A)\psi_{AO}(B) \\ &= A^2 + B^2 - 2AB \end{aligned}$$

The term, -2AB, is the destructive interference of the overlap of the atomic orbitals. The interference results in a decrease of electron density between the nuclei and increase of electron density away from the nuclei. Thus, the nuclei are drawn away from each other.







Even and odd molecular orbitals in H_2^+

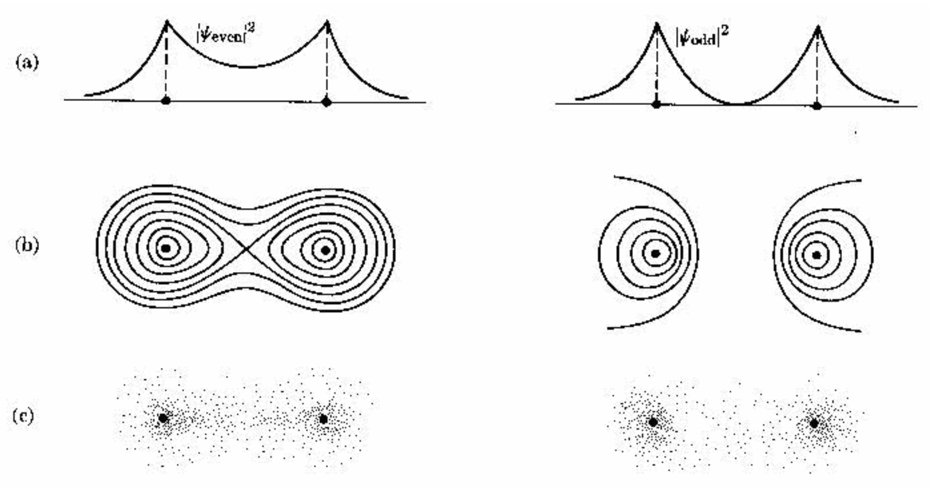


Fig. 5–5. Probability density for even and odd molecular orbitals in H_2^+. (a) Distribution along the lines joining the protons; (b) and (c) distribution in a plane containing the two protons.

Molecular-Orbital Theory

We have to explain the following statements:

1- Helium is monatomic gas.
2- Oxygen molecule has a permanent magnetic dipole moment.
3- Oxygen is paramagnetic gas.
4- Most homonuclear diatomic gases are diamagnetic.
5- He_2, Be_2 and Ne_2 are not stable molecules.
6- He_2^+ and He_2^- are exist!

Energy Level Diagrams of Diatomic Molecular Orbitals

Homonuclear Diatomic Molecules

Hydrogen Ion molecule H_2^+: This is formed by the combination of hydrogen atom containing one electron and hydrogen ion having no electron. Therefore, this ion has only one electron.

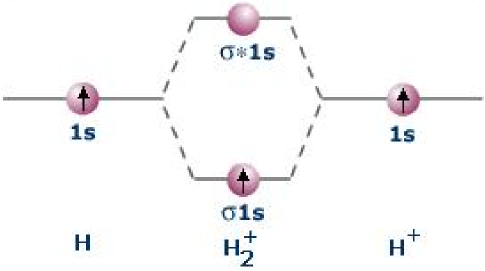


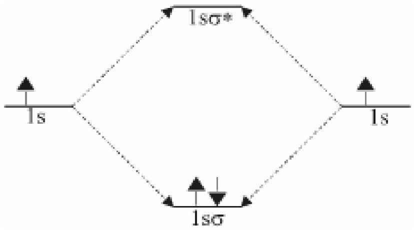
Figure: Molecular orbital energy level diagram for H_2^+ ion

The electronic configuration of the H_2^+ molecule is $\left(\sigma_g 1s\right)^1$

Bond order = ½ (# of bonding e$^-$ – # of antibonding e$^-$) = $\frac{1-0}{2} = \frac{1}{2}$.

The positive value of bond order indicates that the molecule is stable. The presence of unpaired electron in the molecule indicates that it is paramagnetic molecule. The stability of the ion as well as its paramagnetic character has been confirmed experimentally.

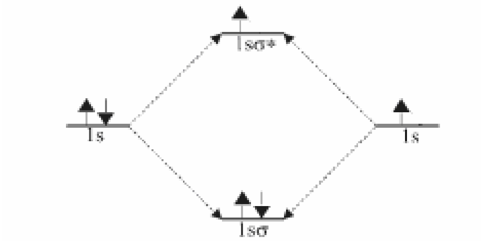
Hydrogen molecule $\left(H_2\right)$: This is formed by the combination of two-hydrogen atoms and the electronic configuration of the H_2^+ molecule is $\left(\sigma_g 1s\right)^2$.



Bond order = ½ (# of bonding e$^-$ – # of antibonding e$^-$) = $\frac{2-0}{2} = 1$.

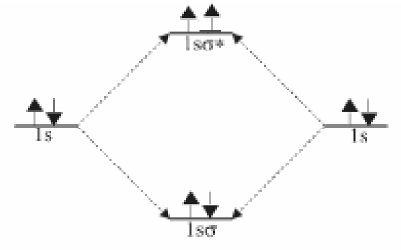
The bond length of H_2^+ ion is larger than that of H_2 molecule (bond length H_2^+ = 104 pm; H_2 = 47 pm), while its bond dissociation energy is less than that of H_2 molecule (bond dissociation energy H_2^+ = 269 KJ mol^{-1}, H_2 = 458 KJ mol^{-1}). This clearly supports the fact that bond in H_2^+ ion is, weaker than that in H_2 molecule.

Helium Ion molecule $\left(He_2^+\right)$: This is formed by the combination of helium atom containing two electrons and helium ion having one electron. Therefore, this ion has only three electrons. The electronic configuration of the $\left(He_2^+\right)$ molecule is $\left(\sigma_g 1s\right)^2 \left(\sigma_u^* 1s\right)^1$.



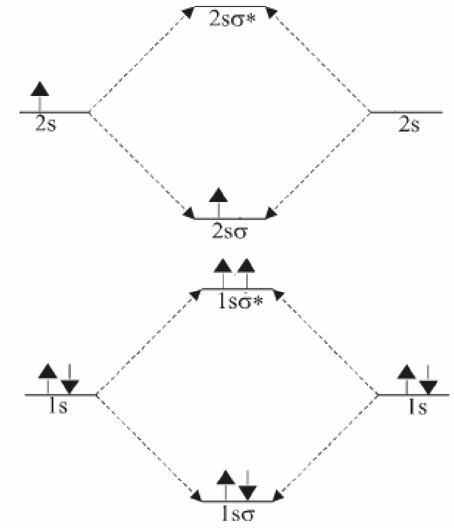
The bond order for the helium ion molecule is $\frac{2-1}{2}=1$, i.e., He_2^+ does exist.

Helium molecule $\left(\mathrm{He}_2\right)$: has four electrons, two in the bonding state $\sigma_g 1\mathrm{s}$ land two in the antibonding state $\sigma_u^* 1\mathrm{s}$; that is, $\left(\sigma_g 1\mathrm{s}\right)^2\left(\sigma_u^* 1\mathrm{s}\right)^2$

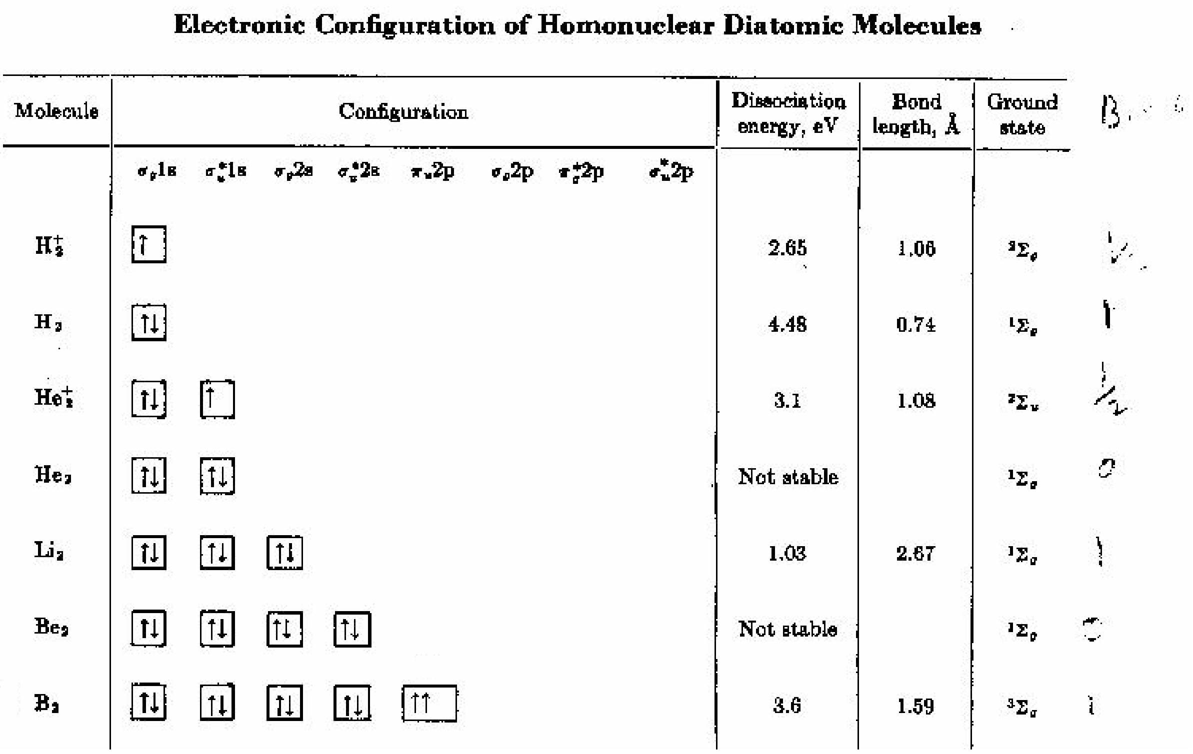


The bond order for the helium molecule is $\frac{2-2}{2}=0$, i.e. **no stable configuration is produced**, so He_2 does not exist. ***This explains why helium is a monatomic gas***. However, an excited molecule may be formed if one of the electrons of the $\left(\sigma_u^* 1\mathrm{s}\right)^2$ is excited to the bonding state $\left(\sigma_g 2\mathrm{s}\right)$, resulting in $\left(\sigma_g 1\mathrm{s}\right)^2\left(\sigma_u^* 1\mathrm{s}\right)^1\left(\sigma_g 2\mathrm{s}\right)^1$.

Helium negative Ion molecule He_2^-: has five electrons, two in the bonding state $\sigma_g 1\mathrm{s}$, two in the antibonding state $\sigma_u^* 1\mathrm{s}$; and one in the state $\sigma_g 2\mathrm{s}$; that is $\left(\sigma_g 1\mathrm{s}\right)^2\left(\sigma_u^* 1\mathrm{s}\right)^2\left(\sigma_g 2\mathrm{s}\right)^1$



The bond order for the helium ion molecule is $\frac{3-2}{2}=\frac{1}{2}$, i.e., He_2^- does exist.



Electronic Configuration of Homonuclear Diatomic Molecules

Molecule	Configuration								Dissociation energy, eV	Bond length, Å	Ground state	B. O.
	$\sigma_g 1s$	$\sigma_u^* 1s$	$\sigma_g 2s$	$\sigma_u^* 2s$	$\pi_u 2p$	$\sigma_g 2p$	$\pi_g^* 2p$	$\sigma_u^* 2p$				
H_2^+	↑								2.65	1.06	$^2\Sigma_g$	½
H_2	↑↓								4.48	0.74	$^1\Sigma_g$	1
He_2^+	↑↓	↑							3.1	1.08	$^2\Sigma_u$	½
He_2	↑↓	↑↓							Not stable		$^1\Sigma_g$	0
Li_2	↑↓	↑↓	↑↓						1.03	2.67	$^1\Sigma_g$	1
Be_2	↑↓	↑↓	↑↓	↑↓					Not stable		$^1\Sigma_g$	0
B_2	↑↓	↑↓	↑↓	↑↓	↑↑				3.6	1.59	$^3\Sigma_g$	1

The above Table shows the electronic configuration of the homonuclear diatomic molecules up to Ne_2. The table also indicates the binding energy and the bond length of the ground state of these molecules. Some interesting features can be seen in his table. In general, molecular binding results when two electrons with opposite spins concentrate in the region between the two combining atoms; that is, they occupy bonding molecular orbitals. This, however, is not a strict rule, since Li_2 has only three electrons, and in B_2 and O_2, the last pair of electrons are in π-orbitals and their spins are parallel instead of opposed. This characteristic of B_2 and O_2 is due to the fact that π-orbitals can accommodate up to four electrons, two with spin up and two with spin down, while these molecules have only two electrons in that energy level. From the atomic case we recall that the repulsion among the electrons favors the most antisymmetric space wave function. This requires the most symmetric spin wave function according to the exclusion principle, which means in this case that the two electrons have their spins parallel. Since the resultant spin of O_2 is one, the oxygen molecule has a. permanent magnetic dipole moment, thereby explaining why Oxygen is a paramagnetic gas, while most homonuclear diatomic gases are diamagnetic. We may also expect that the stability of the molecule will depend on the relative number on the relative bonding and antibonding pairs of electrons. For example, we have indicated that He_2 has the same number of bonding and antibonding pairs of electrons and is not stable. The same happens to Be_2 therefore both molecules are unstable. On the other hand, the stability of .N_2, O_2, F_2 and N_2 (as measured by the dissociation energy) decreases because the difference between bonding and antibonding pairs for these molecules is a 2, 1, and 0, respectively.

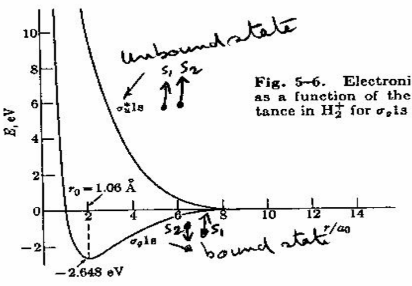


Fig. 5–6. Electronic potential energy as a function of the internuclear distance in H_2^+ for σ_g1s and σ_u^*1s states.

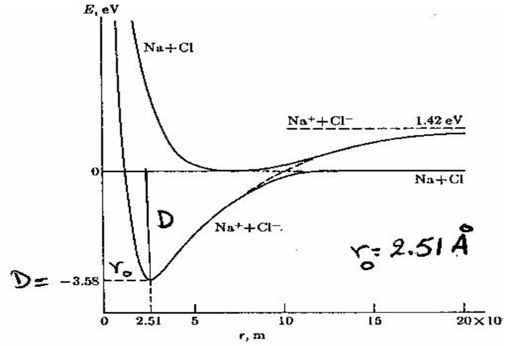


Fig. 5–14. Potential energy curves for NaCl and Na^+Cl

r_0 ≡ equilibrium distance (at which the energy will be minimum
D = dissociation energy of a molecule (energy needed to separate a molecule in its lowest energy state into its components)

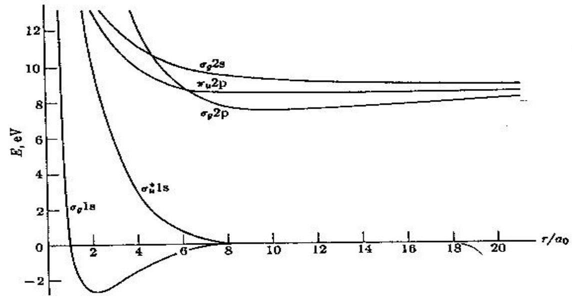


Fig. 5–7. Electron potential energies in H_2^+ for the ground state and some excited states.

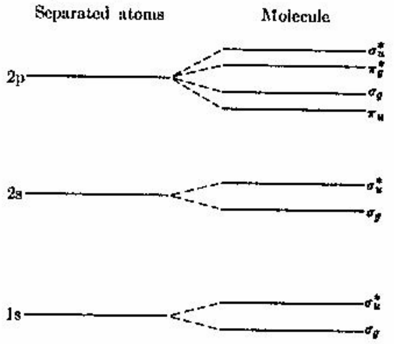
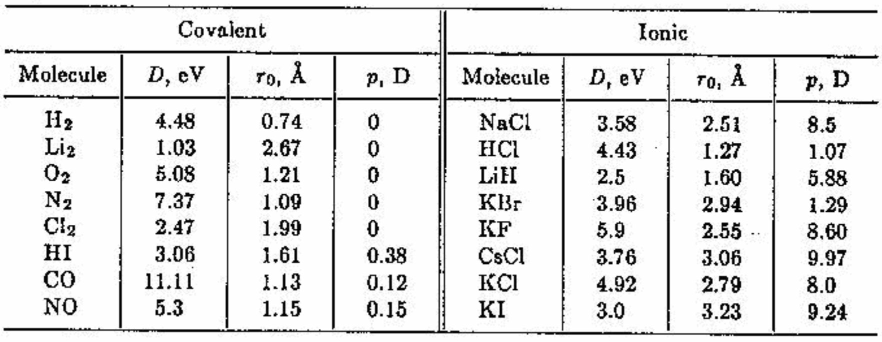


Fig. 5–11. Electronic energy levels in homonuclear diatomic molecules.

TABLE 5–2 **Dissociation Energies *D*, Bond Lengths r_0, and Electric Dipole Moments *p* of Some Diatomic Molecules***



Covalent				Ionic			
Molecule	*D*, eV	r_0, Å	*p*, D	Molecule	*D*, eV	r_0, Å	*p*, D
H_2	4.48	0.74	0	NaCl	3.58	2.51	8.5
Li_2	1.03	2.67	0	HCl	4.43	1.27	1.07
O_2	5.08	1.21	0	LiH	2.5	1.60	5.88
N_2	7.37	1.09	0	KBr	3.96	2.94	1.29
Cl_2	2.47	1.99	0	KF	5.9	2.55	8.60
HI	3.06	1.61	0.38	CsCl	3.76	3.06	9.97
CO	11.11	1.13	0.12	KCl	4.92	2.79	8.0
NO	5.3	1.15	0.15	KI	3.0	3.23	9.24

* The molecules are grouped according to the dominant character of the bond. Electric dipole moments are expressed in *debyes* (D). One D is 3.3×10^{-30} m C.

Ionic molecule ≡ polar moleculer ≡ hetropolar (dissimilar)

Covalent bond ≡ homopolar bond

Example: work out the lowest energy states of the Hydrogen molecule ion$\left(\mathrm{H}_2^+\right)$. Use the trial linear combination of atomic orbital (LCAO) functions in the form:

$$\varphi = a_1\psi_1 + a_2\psi_2\,; \tag{1}$$

Where

$$\psi_i = \frac{1}{\sqrt{\pi}} e^{-r_i}$$

And neglect the motion of the nucleus (This called Born-Oppenheimer approximation). Write your comments in the states. [Hint: Write the electronic Hamiltonian $\hat{H}$, solve the secular determinant using the abbreviations H_{ij}, S_{ij}, where i and j take the values 1 and 2. and then calculate the integrals using the elliptical coordinate system.

Answer: The Hamiltonian is given by (**neglect the K.E. operator for the protons**):

$$\hat{H} = \hat{H}_{el} + \frac{1}{R} = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}, \qquad \hat{H}_{el} = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_1} - \frac{1}{r_2}\ , \tag{2}$$

Define the integrals:

$$H_{ij} = <\psi_i\,|\hat{H}\,|\psi_j> = H_{ji}\,;$$

and the overlap integrals:

$$\mathrm{S}_{ij} = <\psi_i\,|\psi_j> = \frac{1}{\pi}\int e^{-pr_1}\, e^{-qr_2}\, d\tau_1 d\tau_2 = \mathrm{S}_{ji}$$

Then the secular determinant will be:

$$\begin{vmatrix} (H_{11}-E\,) & (H_{12}-E\mathrm{S}) \\ (H_{21}-E\mathrm{S}) & (H_{22}-E\,) \end{vmatrix} = 0 \tag{3}$$

which we used the abbreviations (See the appendix for full calculation):

$$H_{11} = <\psi_1|\hat{H}\,|\psi_1> = H_{22};$$

$$H_{12} = <\psi_1|\hat{H}\,|\psi_2> = H_{21};$$

$$S_{11} = <\psi_1|\psi_1> = S_{22} = 1;$$

$$\mathrm{S}_{12} = <\psi_1|\psi_2> = \mathrm{S}_{21} = S$$

From (3), one finds:

$$H_{11} - E = \pm\left(H_{12} - E\ \mathrm{S}\right) \tag{4}$$

And we get the roots of the lowest energy states:

$$E_+ = \frac{H_{11}+H_{12}}{1+\mathrm{S}}, \qquad E_- = \frac{H_{11}-H_{12}}{1-\mathrm{S}} \tag{5}$$

To calculate the eigenfunctions, we use the equation:

$$a_1(H_{11}-E\,) + a_2(H_{12}-\mathrm{S}E\,) = 0 \tag{6}$$

that gives (for the root E_+) $a_2 = a_1 = c_1$ and:

$$\varphi_+ = c_1(\psi_1 + \psi_2)$$

And for the root E_-, we have $a_2 = -a_1 = c_2$ and:

$$\varphi_- = c_2(\psi_1 - \psi_2)$$

H.W.

a- Use $<\varphi_+|\varphi_+>=1$ to proof $c_1=\dfrac{1}{\sqrt{2+2\mathrm{S}}}$

b- Use $<\varphi_-|\varphi_->=1$ to proof $c_2=\dfrac{1}{\sqrt{2-2\mathrm{S}}}$

Summary:

$$E_+=\frac{H_{11}+H_{12}}{1+\mathrm{S}},\quad \varphi_+=\frac{\psi_1+\psi_2}{\sqrt{2+2\mathrm{S}}}\qquad \text{[bonding orbital, symmetrical (gerade)]}$$

$$E_-=\frac{H_{11}-H_{12}}{1-\mathrm{S}},\quad \varphi_-=\frac{\psi_1-\psi_2}{\sqrt{2-2\mathrm{S}}}\qquad \text{(antibonding orbital)}$$

Mathematical preliminarily

Use the H-wave equation:

$$\left(-\frac{1}{2}\nabla_i^2-\frac{1}{r_i}\right)\psi_i(r)=-\frac{1}{2}\psi_i(r),\qquad i=1,2$$

then

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

where J is the Coulomb (direct) integral:

$$J=<\psi_1|-\frac{1}{r_2}+\frac{1}{R}|\psi_1>$$

and

$$H_{12}=-\frac{\mathrm{S}}{2}+K$$

where K is the exchange integral:

$$K=<\psi_1|-\frac{1}{r_1}+\frac{1}{R}|\psi_2>$$

Then

$$E_\pm=\frac{H_{11}\pm H_{12}}{1\pm\mathrm{S}}=E_H+\frac{J\pm K}{1\pm\mathrm{S}};$$

$$\Delta E_\pm=E_\pm-E_H=\frac{J\pm K}{1\pm\mathrm{S}}$$

H.W. Use the Elliptic coordinate system to proof the following integrals:

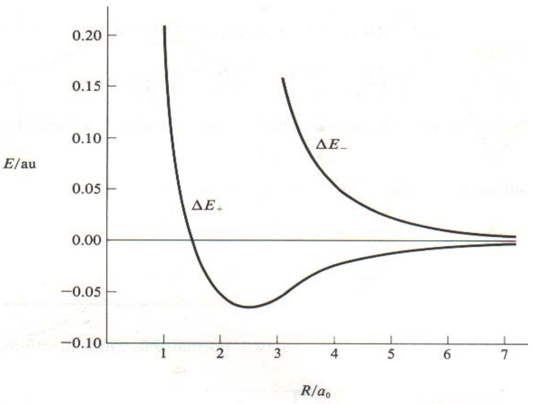
$$\mathrm{S}=(1+R+\frac{R^2}{3})\,e^{-R};\quad J=(1+\frac{1}{R})\,e^{-2R};\quad K=\frac{\mathrm{S}}{R}-(1+R)\,e^{-R}$$

Finally

$$E_\pm=E_{1s}+\frac{1}{R}\,\frac{(1+R)e^{-2R}\pm(1-\frac{2}{3}R^2)e^{-R}}{1\pm(1+R+\frac{1}{3}R^2)e^{-R}}$$

H.W. Plot and discuss the following figure:

Comments:



e 9-6. The energy as a function of internuclear separation for the H_2^+ molecular ion

1- E_+ corresponding to the symmetrical (gerade) and exhibit a minimum at R_o with the value $2.49\text{ a.u.} = 1.32\ \overset{\circ}{\text{A}}$

2- The dissociation energy will be $D_e = E_{1s} - E_+(R_o) = 0.065\text{ a.u.} = 1.77\text{ eV}$

3- As $R \to \infty$, one finds $S = J = K = 0$ and $E_\pm = E(1s)$ for hydrogen atom.

4- As $R \to 0$, one finds $S = 1,\quad J \approx 1,\quad K \approx 1$ and $E_+ = 3E(1s)\quad E_- = 0$ for hydrogen atom. It is about to be He-like ion with $E_+ = Z^2 = 4E(1s)$. In order to get a good approximation for small R, we should include many atomic orbitals for each atom, or use a variational parameter.

In figure 9-6, the energy ΔE_+ describes a stable molecular species whose dissociation energy is 0.065 au = 1.77 eV and whose equilibrium bond length is 2.49 au = 0.132 nm, compared to the experimental values of 0.102 au = 2.78 eV and 2.00 au = 0.106 nm, respectively. If we simply use is orbitals with the exponent as a variational parameter, then we obtain a dissociation energy of 0.083 au = 2.25 eV and a bond length of 2.00 au = 0.106 nm.

Although we could obtain increasingly better values of the energy and bond length of H_2^+, we are primarily interested in the corresponding wave functions.

The energy increase of the antibonding orbital is slightly higher than the energy decrease of the bonding orbital. $\text{E}_\pm \propto \dfrac{1}{1 \pm \text{S}}$ (S is the overlap integral)

Example: Let $\text{S} = \dfrac{1}{4}$, then $\text{E}_+ \propto \dfrac{1}{1+\text{S}} = \dfrac{1}{1+\dfrac{1}{4}} = \dfrac{1}{\dfrac{5}{4}} = \dfrac{4}{5}$ $\text{E}_- \propto \dfrac{1}{1-\text{S}} = \dfrac{1}{1-\dfrac{1}{4}} = \dfrac{1}{\dfrac{3}{4}} = \dfrac{4}{3}$

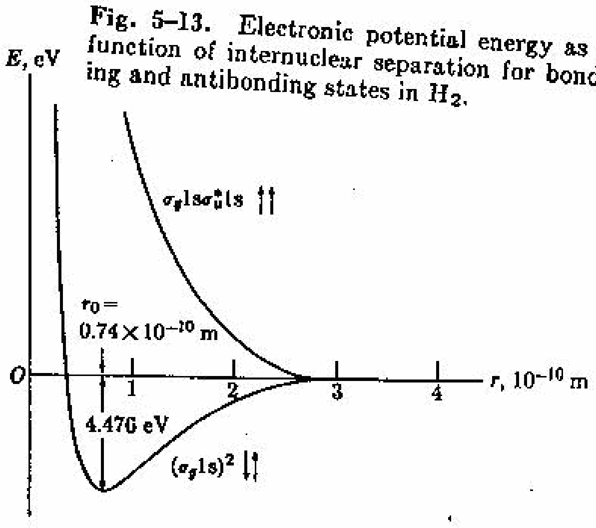


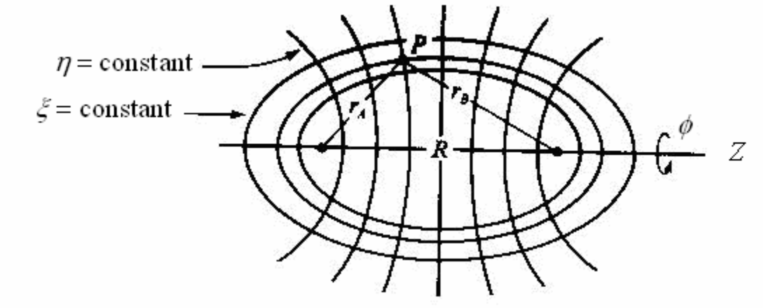
Fig. 5–13. Electronic potential energy as a function of internuclear separation for bonding and antibonding states in H_2.

Evaluation of two-center integrals

The overlap integral and other integrals that arise in two-center problems like H_2, such as:

$$\Im = \int \frac{e^{-pr_A}\ e^{-qr_B}}{r_A\ r_B} d\ \tau, \qquad d\ \tau = d\tau_A d\tau_B \tag{1}$$

are called two-center integrals. Two-center integrals are most easily evaluated by using a coordinate system called **confocal elliptic** coordinates.



Elliptic coordinates

In this coordinate system (See Figure), there are two fixed points, separated by a distance R. A point P is given by the three coordinates:

$$\begin{aligned} \xi &= \frac{(r_A + r_B)}{R}, \qquad & 1 \le \xi \le \infty \\ \eta &= \frac{(r_A - r_B)}{R}, \qquad & -1 \le \eta \le +1 \end{aligned} \tag{2}$$

and the azimuthal angle ϕ, $0 \le \phi \le 2\pi$, which is the angle that the (r_A, r_B, R) triangle makes about the interfocal axis (take it z-axis). Note: $r_A = \frac{R}{2}(\xi + \eta)$ and $r_B = \frac{R}{2}(\xi - \eta)$, $\xi^2 - \eta^2 = \frac{4r_A r_B}{R^2} \Rightarrow 4r_A r_B = R^2(\xi^2 - \eta^2)/4$. The volume integral is given by:

$$d\ \tau_A d\ \tau_B = \frac{R^3}{8}(\xi^2 - \eta^2) d\xi d\eta d\phi \tag{3}$$

so that:

$$\Im = \frac{R}{2} \int_1^\infty d\xi \int_{-1}^{1} d\eta \int_0^{2\pi} d\phi e^{-a\xi - b\eta} \tag{4}$$

where

$$a = \frac{R}{2}(p+q), \qquad b = \frac{R}{2}(p-q), \tag{5}$$

The integral [4] is now elementary and is given by:

$$\Im = \frac{\pi R}{ab} e^{-a}\left(e^{b} - e^{-b}\right) = \frac{4\pi}{R}\frac{1}{p^2 - q^2}\left(e^{-qR} - e^{-pR}\right) \tag{6}$$

The other relevant integrals are obtained by differentiating the above result with respect to p and q. That is,

$$K = \int \frac{e^{-pr_A} e^{-qr_B}}{r_A} d\mathbf{r} = -\frac{\partial}{\partial q}\mathcal{J}$$
$$= \frac{4\pi}{R}\left[\frac{R}{p^2-q^2}e^{-qR} + \frac{2q}{(p^2-q^2)^2}\left(e^{-pR}-e^{-qR}\right)\right] \qquad [7]$$

And

$$S_{AB} = \int \frac{e^{-pr_A}\, e^{-qr_B}}{r_A} d\,\tau = -\frac{\partial}{\partial p}K$$
$$= \frac{8\pi}{R(p^2-q^2)^2}\left[R\left(pe^{-qR}+qe^{-pR}\right) + \frac{4pq}{p^2-q^2}\left(e^{-pR}-e^{-qR}\right)\right] \qquad [8]$$

In the particular case $p = q$, we have

$$\Im = \int \frac{e^{-pr_A}\, e^{-pr_B}}{r_A\, r_B} d\,\tau_A d\,\tau_B = \frac{2\pi}{p}e^{-pR} \qquad [9]$$

$$K = \int \frac{e^{-pr_A}\, e^{-pr_B}}{r_A} d\,\tau_A d\,\tau_B = \int \frac{e^{-pr_A}\, e^{-pr_B}}{r_B} d\,\tau_A d\,\tau_B = \frac{\pi}{p^2}(1+pR)e^{-pR} \qquad [10]$$

and

$$S_{AB} = \int e^{-pr_A}\, e^{-pr_B}\, d\,\tau_A d\,\tau_B = \frac{\pi}{p^3}(1+pR+\frac{1}{3}p^2R^2)e^{-pR} \qquad [11]$$

One more useful integral:

$$I = \int \frac{e^{-2r_A}}{r_B} d\,\tau_A d\,\tau_B = \frac{1}{R}\left[1-e^{-2R}(1+R)\right] \qquad [12]$$

H.W. Plot the following: For $q = p = 1$, we have: $\Im = 2\pi e^{-R}$, $K = \pi(1+R)e^{-R}$, $S_{AB} = \pi(1+pR+\frac{1}{3}R^2)e^{-R}$, $I = \frac{1}{R}\left[1-e^{-2R}(1+R)\right]$