

Structure and Spectra of Diatomic Molecules

CDL, spring 2005

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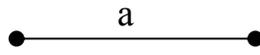
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I. Molecular Structure

1. General Properties of diatomic molecules (Based mostly on BJ)

Let a be the internuclear separation of the diatomic molecule, we can estimate the typical electronic energy, vibrational energy, and rotational energy.



(1) electronic energy

Uncertainty Principle $\Delta p \Delta x \sim \hbar$
 $\Delta p \sim \hbar / a$ $E_e = \frac{(\Delta p)^2}{2m} \cong \frac{\hbar^2}{2ma^2}$

(2) vibrational Energy

$\frac{1}{2} k a^2 \approx \frac{1}{2} M \omega^2 a^2$ is the energy needed to remove the two nuclei from the equilibrium distance to $a \rightarrow \infty$

$$= E_e = \frac{\hbar^2}{2ma^2}$$

$$\hbar^2 \omega^2 = \frac{m}{M} \frac{\hbar^2}{m^2 a^4} \hbar^2 = \frac{m}{M} E_e^2$$

$$E_v \cong \sqrt{\frac{m}{M}} E_e$$

(3) Rotational Energy

$$E_r = \frac{\hbar^2}{Ma^2} \sim \frac{m}{M} E_e$$

The mass ratio $\frac{m}{M} \approx 10^{-3}$ to 10^{-5}

Take $\frac{m}{M} = 10^{-4}$, then

$$E_e \sim 10 \text{ eV}$$

$$E_v = 0.1 \text{ eV}$$

$$E_r = 0.001 \text{ eV}$$

or in terms of time

$$T_e \sim 10^{-16} \text{ sec}$$

$$= 100 \text{ as}$$

$$T_v \sim 10^{-14} \text{ sec}$$

$$= 10 \text{ fs}$$

$$T_r = 10^{-12} \text{ sec}$$

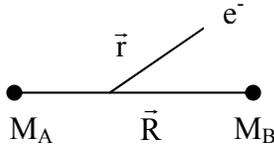
$$= 1 \text{ ps}$$

The energy scale are very different, so the wavefunctions are separable in 1st order

$$\Psi_{\text{TOT}} = \Psi_{\text{electronic}} \Psi_{\text{vibration}} \Psi_{\text{rot}}$$

This forms the physical basis of the Born-Oppenheimer approximation.

2. The Born Oppenheimer (BO) approximation for one-electron diatomic molecules.



$$\mu = \frac{M_A M_B}{M_A + M_B}$$

In the center-of-mass frame of M_A and M_B , the Schrödinger is

$$[T_N + T_e + V] \Psi(\vec{R}, \vec{r}) = E \Psi(\vec{R}, \vec{r}) \quad (1)$$

$$T_N = -\frac{\hbar^2}{2\mu} \nabla_R^2 \quad T_e = \frac{\hbar^2}{2m} \nabla_r^2 \quad V: \text{ total Coulomb Interaction}$$

Treat the electronic motion at fixed R

$$(T_e + V) \Phi_q(\vec{R}; \vec{r}) = E_q(R) \Phi_q(\vec{R}; \vec{r}) \quad (2)$$

Φ_q : electronic wave function, R is fixed in this equation.

BO expansion

$$\Psi(\vec{R}, \vec{r}) = \sum_q F_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}) \quad (3)$$

Substitute (3) into (1) and use (2), we obtain

$$\sum_q \int d\vec{r} \Phi_q^* (T_N + T_e + V - E) F_q(\vec{R}) \Phi_q = 0 \quad (4)$$

Note

$$T_N(F_q \Phi_q) = -\frac{\hbar^2}{2\mu} \left[F_q (\nabla_R^2 \Phi_q) + 2 \nabla_R F_q \cdot \nabla_R \Phi_q + \Phi_q \nabla_R^2 F_q \right] \quad (5)$$

From which

$$\left[-\frac{\hbar^2}{2\mu} \nabla_R^2 + E_s(\vec{R}) - E \right] F_s(\vec{R}) + \sum_q \langle \Phi_s | \nabla_R^2 | \Phi_q \rangle F_q + 2 \langle \Phi_s | \vec{\nabla}_R | \Phi_q \rangle \cdot \vec{\nabla}_R F_q = 0 \quad (6)$$

If the coupling terms are neglected, assuming that the change of the electronic motion with respect to R is small, then

$$\left[-\frac{\hbar^2}{2\mu} \nabla_R^2 + E_s(\vec{R}) - E \right] F_s(\vec{R}) = 0 \quad (7)$$

is to be solved for the nuclear motion.

Note

$$T_N = -\frac{\hbar^2}{2\mu} \nabla_R^2 = -\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) + \frac{\tilde{N}^2}{2\mu R^2} \quad (8)$$

where \tilde{N}^2 is the square angular momentum operator for the internuclear rotational motion.

Let

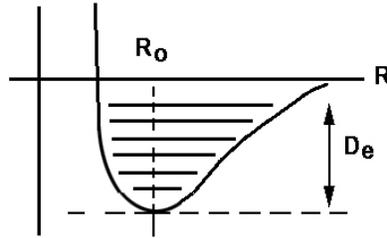
$$F_s(\vec{R}) = \frac{1}{R} F_{v,J}^s(R) Y_{JM_J}(\theta, \Phi) \quad (9)$$

where θ, Φ are spherical angles of \vec{R} with respect to the Lab-fixed axis, then

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{dR^2} \right) + \frac{\hbar^2 J(J+1)}{2\mu R^2} + E_s(R) - E_{s,v,J} \right] F_{v,J}^s(R) = 0 \quad (10)$$

The total energy $E_{s,v,J}$ is specified by the electronic state s , vibrational state v and rotational state J .

Within the BO approximation, one has to solve (2) and (10). A typical potential $E_s(R)$ for a given J .



The equilibrium distance R_0 and dissociation energy D_e are defined as above.

3. Rotational and Vibrational Energies

Near R_0 , one can expand

$$E_s(R) = E_s(R_0) + \frac{1}{2} k (R - R_0)^2 + \dots \quad (11)$$

For small vibrations near R_0 , the rotational energy

$$E_r = \frac{\hbar^2 J(J+1)}{2\mu R_0^2} = \frac{\hbar^2}{2I_0} J(J+1) = BJ(J+1)$$

$$E_v = \hbar\omega_0(v+1/2) \quad \omega_0 = \sqrt{\frac{K}{\mu}}$$

The total energy of the diatomic molecule under this approximation

$$E_{s,v,J} = E_s(R_0) + E_v + E_r \quad (12)$$

The **Morse potential** is often used for molecular potential

$$V(R) = D_e \left[e^{-2\alpha(R-R_0)} - 2e^{-\alpha(R-R_0)} \right] \quad (13)$$

where the dissociation energy and the equilibrium distance are explicitly shown.

Typical Examples:

	$R_0(^{\circ}\text{A})$	$D_e(\text{eV})$
H_2	0.74°A	4.75eV
I_2	2.66°A	1.56eV
H_2^+	1.06	2.65eV
O_2	1.21	5.08eV
N_2	1.09	9.75eV

4. Symmetry properties of electronic wave function (nuclei fixed in space) for diatomic molecules

Clearly the internuclear axis is a symmetry axis, thus L_z has good quantum numbers (Λ).

- (i) $L_z \Rightarrow \Lambda = 0, 1, 2, 3, \dots$ (rotation along the axis)
 $\sigma, \pi, \Delta, \phi$

Thus the ϕ dependence of the electronic wavefunction is $e^{\pm i\Lambda\phi}$.

- (ii) **Reflection** (A_y) with respect to *any plane containing the internuclear axis* z , called it the y -plane.

$$[A_y, H] = 0$$

$$A_y L_z = -L_z A_y$$

A_y converts $\Lambda\hbar$ of L_z into $-\Lambda\hbar$.

Thus for $\Lambda \neq 0$ each electronic state is doubly degenerate.

(This degeneracy is removed when coupling between rotation and electronic motion is introduced, the splitting is called Λ -doubling.)

For $\Lambda = 0$, it is not degenerate. However, $A_y^2 = 1 \Rightarrow A_y = \pm 1$

Thus $\Lambda = 0$ states can have $A_y \rightarrow \pm 1$, i.e., for Σ^+ , the w.f. is symmetric with respect to a reflection against xz plane.

$$\Sigma^+ \text{ and } \Sigma^-$$

Note: Any heteronuclear diatomic molecules has the group symmetry designation $C_{\infty v}$ where the first subscript indicates that it has infinite-fold rotation with respect to its major axis.

(iii) For homonuclear diatomic molecules (parity) inversion with respect to the midpoint of the internuclear axis introduces gerade (g) and ungerade (u) states. Thus we have

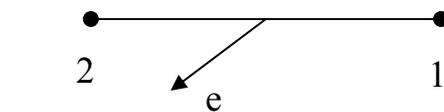
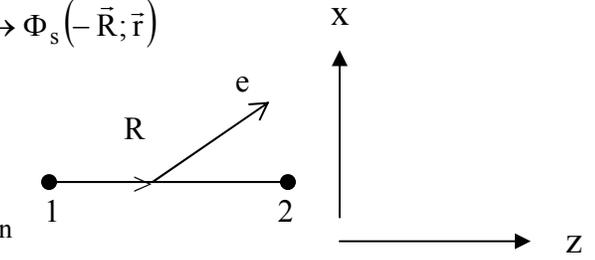
$$\sigma_g, \sigma_u, \pi_g, \pi_u, \dots \text{etc.}$$

(iv) Changing $\vec{R} \rightarrow -\vec{R}$ for homonuclear molecules (interchange of the two nuclei)

$$\Phi_s(\vec{R}; \vec{r}) \rightarrow \Phi_s(-\vec{R}; \vec{r})$$

This can be achieved by

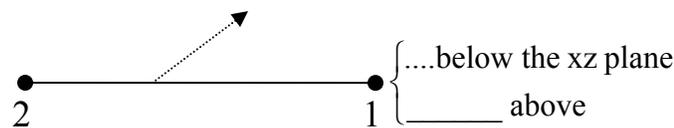
- (a) Rotation around y-axis by 180° .
This does not change the electronic wave function.
- (b) Inversion with respect to the center of the electron
This introduces (-1) for u states
- (c) Reflection with respect to the xz plane
introduces (+) or (-1) depending on A_y



Thus

$$\Phi_s(-\vec{R}; \vec{r}) = -\Phi_s(\vec{R}; \vec{r}) \text{ for } \sum_u^+, \sum_g^-$$

$$= +\Phi_s(\vec{R}; \vec{r}) \text{ for } \sum_g^+, \sum_u^-$$



(v) Spin of the electrons

If the total electron spin is S , the multiplicity is $(2S+1)$. If spin-orbit interaction is not considered, an electronic state is designated by $X^{2S+1}\Lambda$, where X stands for the ground state usually.

5. Noncrossing Rule of Potential Curves

For diatomic molecules, the potential curves depend only on R . The noncrossing rule states that two curves of the same symmetry do not cross. This is called the Wigner noncrossing rule.

(Proof): Let $E_1(R_c)$ and $E_2(R_c)$ are very close to each other

$$\text{write } H_e(R_c + \Delta R) = H_o + \left(\frac{\partial H_e}{\partial R} \right)_{R_c} \Delta R = H_o + H'$$

Let the two eigenfunctions at R_c be Φ_1^0 and Φ_2^0 , we want to obtain the eigenenergies at $R_c + \Delta R$ by diagonalizing $H_c(R_c + \Delta R)$ using Φ_1^0 and Φ_2^0 . The 2x2 matrix is

$$\begin{vmatrix} E_1 + H'_{11} & H'_{12} \\ H'_{12} & E_2 + H'_{22} \end{vmatrix} = 0 \quad H'_{ij} = \langle \Phi_i^0 | H' | \Phi_j^0 \rangle$$

The new eigenvalue has the form

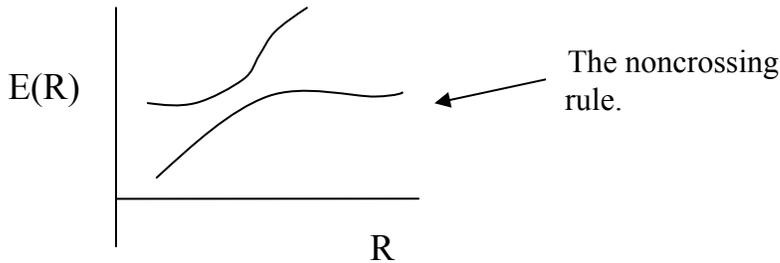
$$\chi_{\pm} = \frac{1}{2}(E_1 + E_2 + H'_{11} + H'_{22}) \pm \frac{1}{2} \sqrt{(E_1 + H'_{11} - E_2 - H'_{22})^2 + 4H'_{12}{}^2} \quad (14)$$

For χ_+ and χ_- to be equal at some $\Delta R + R_c$, we need

$$\begin{cases} E_{11} + H'_{11} - (E_2 + H'_{22}) = 0 \\ H'_{12} = 0 \end{cases} \quad (15)$$

Simultaneously. Since H_{ij} is proportional to ΔR , and in general these two equations cannot be satisfied simultaneously, thus the two curves of identical symmetry cannot cross. This is noncrossing rule.

However, if $H'_{12} = 0$ identically due to symmetry, then the two courses can cross.



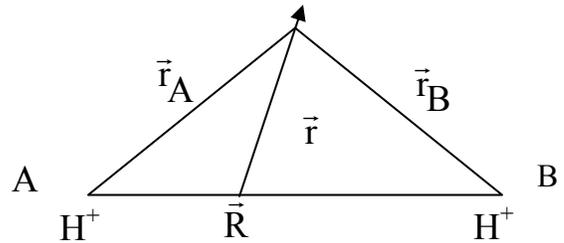
Thus potential curves of different symmetry (all the quantum numbers discussed in section 4) can cross. If they have the same symmetry they do not cross. This is the noncrossing rule. For one electron and two nuclear charges, i.e., the Coulomb problem, there is additional "dynamic" symmetry so some curves of the same symmetry (as discussed in Section 4) can cross.

6. The H_2^+ Molecule--

The electronic wavefunction can be solved exactly within the BO approximation.

6.1 The "exact" solution

The electronic Hamiltonian



$$H_e = -\frac{1}{2} \nabla_r^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

$$\vec{r}_A = \vec{r} + \vec{R}/2$$

$$\vec{r}_B = \vec{r} - \vec{R}/2$$

$$H_e \Psi_s(\mathbf{R}; \vec{r}) = E_s(\mathbf{R}) \Psi_s(\mathbf{R}; \vec{r})$$

The electronic equation is separable in elliptic coordinates

$$\begin{aligned}
\xi &= \frac{1}{R} (r_A + r_B) & 1 \leq \xi < \infty \\
\eta &= \frac{1}{R} (r_A - r_B) \\
\phi &: \text{ as in cylindrical coordinates}
\end{aligned}
\tag{16}$$

$$\Psi(\mathbf{R}; \vec{r}) = F(\xi)G(\eta)e^{im\phi} \quad m = 0, \pm 1, \pm 2, \dots$$

where

$$\begin{cases}
\frac{d}{d\xi} \left[(\xi^2 - 1) \frac{dF}{d\xi} \right] + \left[\frac{R}{2} \left(E_s - \frac{1}{R} \right) \xi^2 + 2R\xi - \frac{m^2}{\xi^2 - 1} + \mu \right] F(\xi) = 0 \\
\frac{d}{d\eta} \left[(1 - \eta^2) \frac{dG}{d\eta} \right] - \left[\frac{R}{2} \left(E_s - \frac{1}{R} \right) \eta^2 + \frac{m^2}{1 - \eta^2} + \mu \right] G(\eta) = 0
\end{cases}
\tag{17}$$

μ is a separation constant.

The above two equations can be solved numerically to obtain the energy and eigenfunctions.

⇒ See additional notes showing the potential curves of H_2^+ obtained from OneMO code.

6.2. LCAO—Linear Combination of Atomic Orbitals

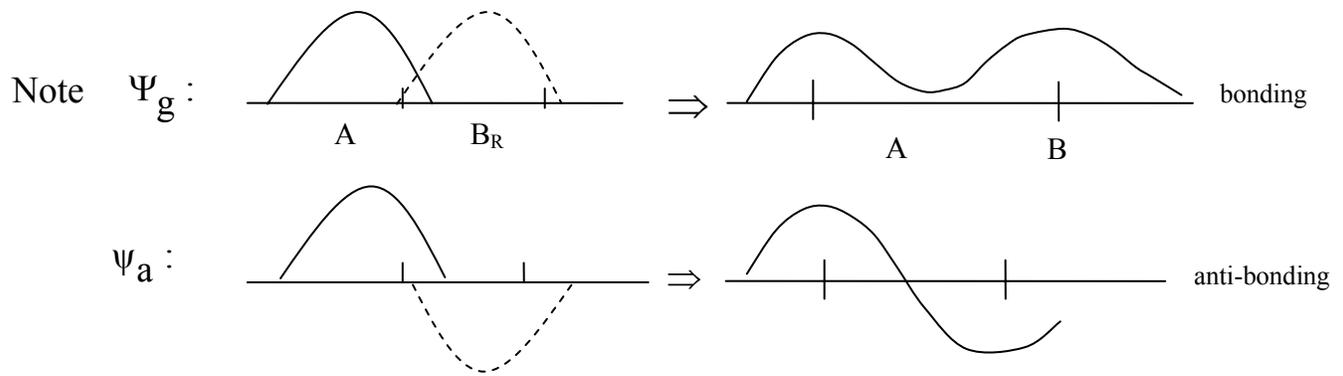
We set to obtain approximate solutions starting with atomic orbitals. Note at large R we have $\psi(\mathbf{R}; \vec{r}) = \phi_{1s}(\vec{r}_A)$ or $\psi_{1s}(\vec{r}_B)$ depending on electron is close to A or B. Since the two states are degenerate, the zeroth order solution should be

$$\begin{aligned}
\Psi_g(\mathbf{R}; \vec{r}) &= \frac{1}{\sqrt{2}} [\phi_{1s}(\vec{r}_A) + \phi_{1s}(\vec{r}_B)] \\
\Psi_u(\mathbf{R}; \vec{r}) &= \frac{1}{\sqrt{2}} [\phi_{1s}(\vec{r}_A) - \phi_{1s}(\vec{r}_B)]
\end{aligned}
\tag{18}$$

Using this model, the electronic potential is calculated from

$$E_{g,u} = \frac{\langle \Psi_{g,u} | H_e | \Psi_{g,u} \rangle}{\langle \Psi_{g,u} | \Psi_{g,u} \rangle}$$

This gives a 1st order estimate of the potential energy at large R .



As R is decreased, the nodal structure stays the same, $\psi(R; \vec{r})$ is called a molecular orbital.

6.3 Correlation Diagram for H_2^+

The molecular orbitals and the potential energy curves depend on R . We know the two limits, $R \rightarrow \infty$, the **separate atom limit** and $R \rightarrow 0$, the **united atom limit**

We want to construct rules to connect potential curves, see separate notes (Note-3 below)

7. The elementary angular momenta of a diatomic molecule

Elementary angular momenta: $\left\{ \begin{array}{l} \text{orbital} \\ \text{spin of electrons} \end{array} \right\}$ of nuclei A and B

$\left\{ \begin{array}{l} \text{orbital (relative motion)} \\ \text{spin} \end{array} \right\}$

Let us neglect spin interaction first

$$\vec{K} = \vec{N} + \vec{L} \quad (19)$$

↑
↑

nuclear rotation
total e^- orbital angular momentum

$$\vec{N} = \vec{R} \times \vec{P}$$

Since \uparrow
momentum of A and B

$$\vec{R} \cdot \vec{N} = 0$$

Thus

$$K_z = \vec{K} \cdot \hat{R} = \vec{L} \cdot \hat{R} = L_z \quad (20)$$

For an isolated molecule, the total wave function is eigenfunction of K^2 and K_z

$$\begin{cases} K^2 \Psi_s = K(K+1)\hbar^2 \Psi_s \\ K_z \psi_s = M \hbar \psi_s \end{cases} \quad (21)$$

when $\Psi_s = F_s(\vec{R})\Phi_s(\vec{R}; \vec{r})$ as given in the B.O. approximation.

$$\text{We also know } L_z \psi_s = \pm \hbar \Lambda \psi_s \quad (22)$$

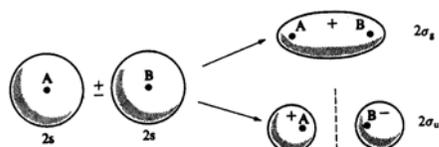
From (20),

$$K_z = \pm \Lambda \hbar$$

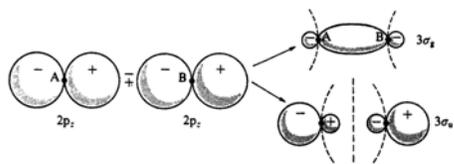
$$K = \Lambda, \Lambda + 1, \Lambda + 2, \dots$$

8. All that you need to know about molecular orbitals of diatomic molecules

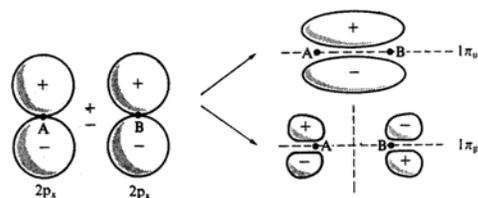
The molecular orbitals are central to the understanding of the electronic structure of molecules. They are the equivalent of atomic orbitals for atoms. We will focus only on diatomics here. The orbital energies, as well as the orbital wavefunctions, depend on the internuclear separation R . The molecular orbitals can be "constructed" from the linear combination of atomic orbitals. This set of drawings shows how the MO's of a homonuclear molecule are constructed from the + and - combination of two AO's from the two centers. The dashed lines are the nodal surfaces.



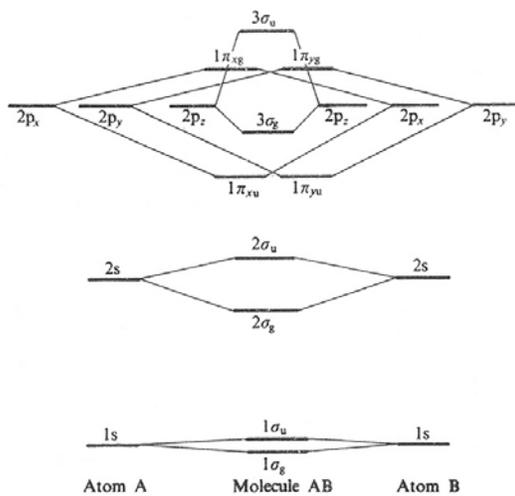
F1. g&u states from two 2s AO's.



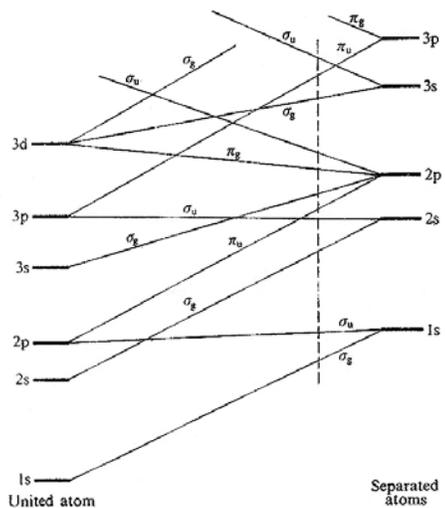
F2. from two 2p_z orbitals.



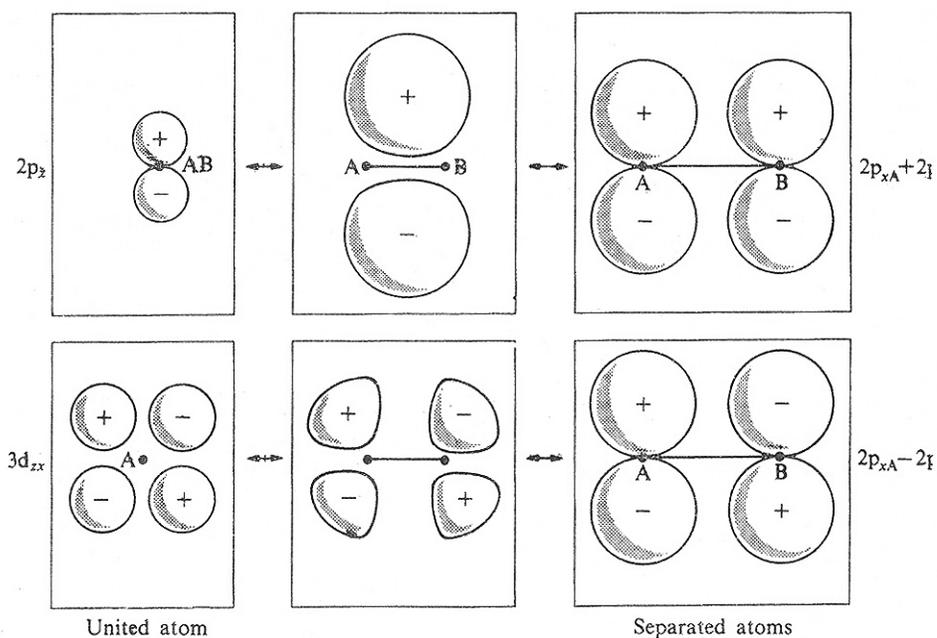
F3. from two 2p_x orbitals.



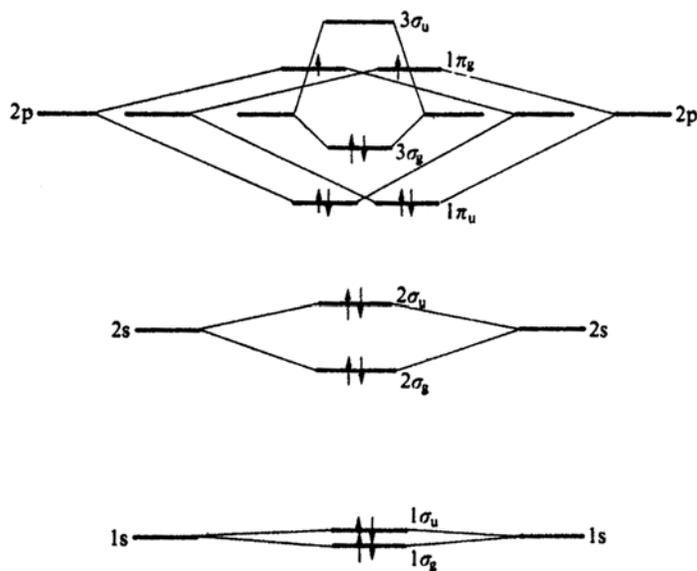
F4. alternative way: bringing two AO's to form MO's.



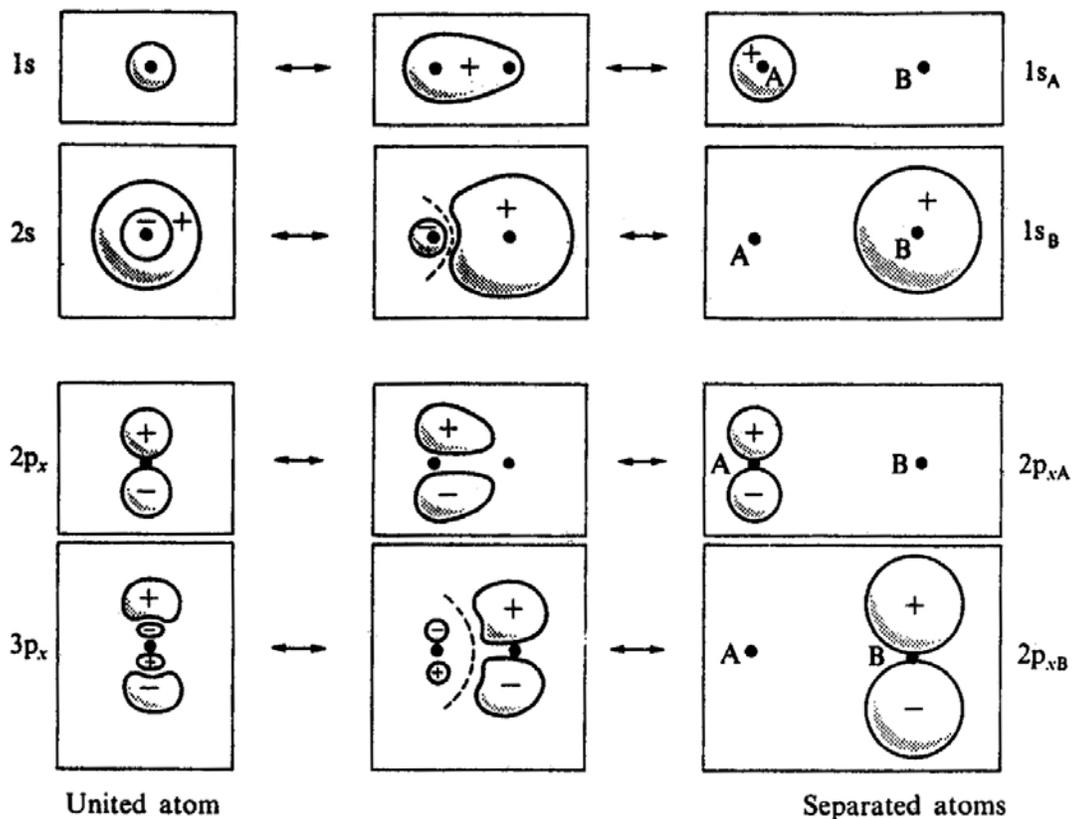
F5. This is the correlation diagram for homonuclear molecules.



F6. This figure illustrates how the molecular orbitals evolves from the SA limit to the UA limit. Note that the inversion symmetry and the nodal plane along the AB axis is preserved as R is changed.



F7. This shows how O_2 has two unpaired orbitals, resulting in triplet state.



F8. This shows how the SA limit is evolved into the UA limit. Note that this is for heteronuclear molecules where $Z_A > Z_B$.

Figure 10.14 of BJ Show the correlation diagram for homonuclear diatomic molecules.

Figure 10.15 of BJ show the correlation diagram for heteronuclear diatomic molecules for $Z_A > Z_B$.

9. The H_2 Molecules

From the gerade and ungerade molecular orbitals (for each electron) one can construct total antisymmetric two-electron wavefunctions for the two electrons in H_2 at each internuclear distance R ,

$$\begin{aligned}
 \sum_g^+ \Phi_A(1,2) &= \Phi_g(1) \Phi_g(2) \chi_{0,0} \\
 \sum_g^+ \Phi_B(1,2) &= \Phi_u(1) \Phi_u(2) \chi_{0,0} \\
 \sum_u^+ \Phi_C(1,2) &= \frac{1}{\sqrt{2}} (\Phi_g \Phi_u + \Phi_u \Phi_g) \chi_{1,0} \\
 \sum_u^+ \Phi_D(1,2) &= \frac{1}{\sqrt{2}} (\Phi_g \Phi_u - \Phi_u \Phi_g) \chi_{1,M_s}
 \end{aligned} \tag{23}$$

where the symmetry designation of each state is given on the left. Here $\Phi_A(1,2)$ is the ground state, $\Phi_D(1,2)$ is the first excited state

Express $\Phi_{g,u} = \frac{1}{\sqrt{2}}(\phi_A + \phi_B)$ as the gerade and ungerade combination of atomic orbitals

Then $\Phi_A(1,2) = \Phi_A^{\text{cov}} + \Phi_B^{\text{ion}}$

Where

$$\begin{aligned}\Phi_A^{\text{cov}} &= \frac{1}{2} [\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)] \chi_{0,0} \\ \Phi_A^{\text{ion}} &= \frac{1}{2} [\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)] \chi_{0,0}\end{aligned}\tag{24}$$

are the **covalent and ionic** wavefunctions.

Note that Φ_A^{cov} dissociates, into H+H, while Φ_A^{ion} dissociates into H^+H^- and H^-H^+ . Thus at finite R, the ground state of H_2 can be expressed as the linear combination of covalent and ionic orbitals. Clearly Φ_A does not dissociate correctly to H+H at large R. This deficiency prevails for all molecules, i.e., for large internuclear separation, the molecular orbitals do not dissociate correctly.

10. The Hartree-Fock Method

The concept of self-consistent field (SCF) can be extended to molecules. Start with the spin-orbital for each electron, one can construct the Slater determinant. Vary the orbitals until the minimum total energy is obtained. At each R, the energies of the occupied orbitals are obtained. The molecular orbitals are calculated over the whole range of R. Unfortunately, such information is not readily available.

As in atoms, one can improve HF method by introducing configuration interaction. There are computational packages called Gaussian, GAMESS and others for users. Similarly the density function theory has been extended to molecules.

Once the molecular orbitals are calculated, the electronic configurations for the ground state of a diatomic molecule can be "filled" up from the lowest orbital and up. Here is an example, taken from the literature. Unfortunately, the relative energy order of the molecular orbitals do depend on the internuclear separation, and on the method used to do the calculation. For some molecules, the Hartree-Fock approximation is not accurate enough and configuration mixing is needed. In such cases, the concept of orbital becomes less accurate.

TABLE 4.3
Electron configurations in ground states of homonuclear diatomic molecules

	Electron configuration†	No. of valence electrons		Bond number	Dissociation‡ energy (eV)	Spectroscopic ground state
		Bonding	Antibonding			
H ₂ ⁺	1σ _g	1		½	2.793	2Σ _g ⁺
H ₂	1σ _g ²	2		1	4.748	1Σ _g ⁺
He ₂ ⁺	1σ _g ² 1σ _u	2	1	½	2.6	2Σ _u ⁺
He ₂	1σ _g ² 1σ _u ² (=KK)	2	2	0		1Σ _g ⁺
Li ₂	KK2σ _g ²	2	0	1	1.14	1Σ _g ⁺
Be ₂	KK2σ _g ² 2σ _u ²	2	2	0		1Σ _g ⁺
B ₂	KK2σ _g ² 2σ _u ² 1π _u ²	4	2	1	3.0	3Σ _g ⁻
C ₂	KK2σ _g ² 2σ _u ² 1π _u ⁴	6	2	2	6.36	1Σ _g ⁺
N ₂ ⁺	KK2σ _g ² 2σ _u ² 3σ _g 1π _u ⁴	7	2	2½	8.86	2Σ _g ⁺
N ₂	KK2σ _g ² 2σ _u ² 3σ _g ² 1π _u ⁴	8	2	3	9.90	1Σ _g ⁺
O ₂ ⁺	KK2σ _g ² 2σ _u ² 3σ _g ² 1π _u ⁴ 1π _g	8	3	2½	6.77	2Π _g
O ₂	KK2σ _g ² 2σ _u ² 3σ _g ² 1π _u ⁴ 1π _g ²	8	4	2	5.21	3Σ _g ⁻
F ₂ ⁺	KK2σ _g ² 2σ _u ² 3σ _g ² 1π _u ⁴ 1π _g ³	8	5	1½		2Π _g
F ₂	KK2σ _g ² 2σ _u ² 3σ _g ² 1π _u ⁴ 1π _g ⁴	8	6	1	1.34	1Σ _g ⁺

† The order of the orbitals does not necessarily correspond to increasing energy (see text).

‡ Best values currently available, but some uncertainties remain.

F9. Here the KK means the filled orbitals of 1s σ_{g,u}. Those from 2s are called 2σ, and those from 2p_x are called 3σ. 1π is constructed from 2p_x.

Normally the energy order is

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 1\pi_u < 3\sigma_g < 1\pi_g < 3\sigma_u$$

However, you can see the order of 1π_u and 3σ_g can switch for some molecules, see C₂ as compared to N₂ through F₂. Here the numbers of bonding electrons and antibonding electrons are given as well. The bond number is the difference of these two numbers divided by 2.

We now know that for N₂ listed in the table above is wrong. They should be ...1π_u⁴3σ_g² for the ground state. See RMP32, 245 (1960). The Hatree-Fock model for F₂ is very poor-- it does not predict a bound potential for the ground state.

Some examples of potential curves.

11. Heitler-London or Valence bond method

In (24), we show that molecular wavefunctions constructed from MO's can be expressed as linear combination of covalent and ionic wavefunctions. In (24) if we treat the atomic wavefunctions in (24) variationally then we can calculate the molecular wavefunctions as function of R. This is the Heitler-London method or the valence-bond method.

To get accurate result, as can be expected from (23), in general one needs to add the ionic wavefunctions.

Such method has been used for small molecules but it is difficult to extend to larger molecules.

12. bonding, antibonding, π -bonds, hybrid orbitals, ionic bonding

MO's formed from the two atoms can form **bonding** (e.g., σ_g) or **antibonding** (e.g., σ_u) orbitals. Additional examples can be found in the table on page 4.

When the MO's are formed from the π orbitals, then form **π -bonds**. Since these bonds tend to be nearly orthogonal to the internuclear axis, they tend to be weaker.

For heteronuclear molecules, such as LiH, we need to consider **hybridization**. The point is that the energy levels of 2s and 2p states of Li are quite close. In the presence of another atom, the 2s and 2p₀ state can mix to form a hybrid orbital, similar to the Stark effect. The molecular orbital is then formed by the mixture from 1s of H with hybrid orbital of Li. Fig. 10.17 of BJ illustrates this point well.

Note that the electron cloud for heteronuclear molecule is not symmetric with respect to the midpoint of the molecule such that each molecule has permanent electron dipole moment along the direction of the molecular axis.

Molecules like NaCl has ionic bonding. The molecule dissociates into Na⁺+ Cl⁻ asymptotically. Thus even at finite R, it still exhibits ionic behavior. Thus for NaCl the internuclear potential can take the form

$$E_s(R) = E_0 - \frac{1}{R} + Ae^{-cR}$$

13. The rotation and vibration of diatomic molecules (recap of section 7)

First we consider the case that there is no spins from the electrons and the nuclei. The total orbital angular momentum $\mathbf{K}=\mathbf{L}+\mathbf{N}$ where \mathbf{L} is for the electrons and \mathbf{N} for the nuclei. Since $\mathbf{N}=\mathbf{R}\times\mathbf{P}$ it is perpendicular to \mathbf{R} and $\mathbf{K}_z=\mathbf{L}_z$ where z is along \mathbf{R} . The eigenvalues of K_z are the same as the eigenvalues of L_z , which are $\pm \Lambda\hbar$. Thus the values of K are $\Lambda, \Lambda + 1, \Lambda + 2, \dots$

A few remarks--details see BJp514--521

The rotational wavefunctions are given by the familiar spherical harmonics if $\Lambda = 0$. Otherwise you need to use the wavefunctions from Appendix 11 of BJ.

For each rotational quantum number K , solve (10.94) of BJ to get the vibrational energies for each electronic state s .

If we assume that the molecule is fixed at the equilibrium distance then the rotational energy is given by $BK(K+1)$ where $B = \hbar^2 / 2I_0$ is the rotational constant. If the molecule is allowed to vibrate, and for the lower states, one can approximate the potential curves by a harmonic potential, then the vibrational energy is given by $\hbar\omega(v + 1/2)$. The vibrational period and the rotational constant, together with the equilibrium distance R_0 and the dissociation energy D_e are important properties of each diatomic molecule in the ground state. For higher rotational and vibrational states the centrifugal distortion is large and corrections to the simple model discussed here have to be addressed.

14. Including electron spin--Hund's case (i-v) or a-e.

When the spin S of the electrons is included, the angular momentum algebra becomes rather complicated. Basically the total $\mathbf{J} = \mathbf{L} + \mathbf{N} + \mathbf{S}$. Depending on the relative magnitude of the electrostatic interactions between the electrons, the spin-orbit interaction and the spin-rotation interaction, which is the coupling of the spin to the internuclear axis, different coupling schemes to get the total \mathbf{J} are needed. You need to understand this subject if you do high-precision spectroscopy or cold molecules. Fortunately we can skip this part since we will be dealing with high-energy or high-power light sources only in this course. Recall that we have encountered similar coupling schemes in atoms.

For Hund case (a), the electronic states (due to different molecular orbitals) are separated first, then the spin-orbital interaction comes in to split each curve into fine structure components. Thus the "good" quantum number is the $\Omega = \Lambda + \Sigma$, where Λ is the projection of the electronic orbital angular momentum, and Σ is the projection of spin angular momentum, along the internuclear axis. Thus an electronic state is designated as

$$^{2S+1}\Lambda_{\Omega}$$

Again, for $\Lambda = 0$, you need + or - for the superscript. For homonuclear molecules you need gerade or ungerade.

15. Nuclear spin symmetry and rotational levels

The total wavefunction of a molecule can be written as

$$\Psi_{total} = \Psi_{electron}(\vec{R}, \vec{r}) \Psi_{rotation} \Psi_{nuclearspin}$$

For homonuclear molecules, if the two nuclei are bosons of spin I , the total wavefunction should be symmetric under the exchange of the two nuclei. Among the $(2I+1)^2$ degeneracy of the nuclear spin, $(2I+1)(I+1)$ are symmetric and $(2I+1)I$ are antisymmetric. The symmetry property of the rotational wavefunctions is that they are symmetric for even J and antisymmetric for odd J . For the electronic wavefunction, the interchange of the two nuclei amounts to change \mathbf{R} to $-\mathbf{R}$. This change is even for Σ_g^+ and

Σ_u^- and odd for Σ_u^+ and Σ_g^- (see Section 4. iv) . Thus for $^{16}\text{O}_2$ which has a $^3\Sigma_g^-$ ground state and $I=0$, even J will go with antisymmetric nuclear spin states with weight 0 and odd J will go with symmetric nuclear spin state with weight 1. Thus all the even J rotational states are missing.

For H_2 , similar argument shows that even J has weight of 1 and odd J has weight of 3.

II. Radiative Transitions in Diatomic molecules

16. summary of electric dipole selection rules:

The electric dipole transition matrix element is given by

$$\begin{aligned} \vec{\mu} &= \left\langle \Phi^{s'}(R, \vec{r}) F^{v'}(R) H_{KM'}(\theta, \phi) \left| \sum_i Z_i \vec{R}_i - \sum_j \vec{r}_j \right| \Phi^s(R, \vec{r}) F^v(R) H_{KM}(\theta, \phi) \right\rangle_{R,r} \quad (1) \\ &= \left\langle F^{v'}(R) H_{KM'}(\theta, \phi) \left| \vec{D}(\vec{R}) \right| F^v(R) H_{KM}(\theta, \phi) \right\rangle_R \end{aligned}$$

where

$$\vec{D}(R) = \left\langle \Phi^{s'}(R, \vec{r}) \left| \sum_i Z_i \vec{R}_i - \sum_j \vec{r}_j \right| \Phi^s(R, \vec{r}) \right\rangle_r \quad (2)$$

is the **electronic dipole** moment at internuclear distance R.

If $s' = s$. For homonuclear molecules, $\vec{D}(R) = 0$. (the electronic wf has well-defined parity at each R, and the integral in eq 2 vanishes.)

For heteronuclear diatomic molecules, $\vec{D}(R) = D_z(R)$ (axial symmetry of the electron density).

If $s' \neq s$, one can write (1) further (by expressing the operator as a tensor operator) as

$$\vec{\mu} = \left\langle F^{v'}(R) \left| D(R) \right| F^v(R) \right\rangle \left\langle H_{KM'}(\theta, \phi) \left| Y_{1q} \right| H_{KM}(\theta, \phi) \right\rangle \quad (3)$$

The 2nd term in (3) gives the selection rule $\Delta N = \Delta K = \pm 1$ if $\Lambda = 0$
 $\Delta N = \pm 1, 0$ if $\Lambda \neq 0$

The 1st term of (3) gives $\Delta v = \pm 1$ under harmonic approximation.

For electronic transitions, $s' \neq s$.

If $D(R)$ is assumed to be independent of R, then

$$\vec{\mu} \sim \left\langle F_{s'}^{v'}(R) \left| F_s^v(R) \right\rangle = f_{v'v}.$$

This is called the **Frank-Condon principle**.

Magnetic selection rules for electronic transitions.

From (2), $\Lambda' = q + \Lambda$
where Λ', Λ are projection of orbital angular momentum along the internuclear axis, and q is the polarization of the light with respect to the internuclear axis. Clearly, $\Sigma^+ \rightarrow \Sigma^+$ and $\Sigma^- \rightarrow \Sigma^-$. For homonuclear molecules, $g \rightarrow u$ and $u \rightarrow g$.

17. Rotational transitions of diatomic molecules

We first consider transitions where the electronic state remain the same.

For homonuclear molecules, there is no permanent dipole moment so there is no rotational transitions.

For heteronuclear molecules, the nonzero dipole moment gives rotational spectra. The selection rules clearly are

$$\begin{aligned} \Delta K &= \pm 1 & \text{for } \Lambda = 0 \\ \Delta K &= \pm 1, 0 & \text{for } \Lambda \neq 0 \end{aligned}$$

For diatomic molecules the dipole moment is directed along the internuclear axis thus there is an additional constraint: $\Delta \Lambda = 0$.

From the rotational spectra, one can get the rotational constant and thus the equilibrium distance R_0 .

18. Vibrational-rotational spectra of diatomic molecules-- the R, P, and Q branches

If the transition matrix element

$$[1] \quad \bar{D}_{v'v} = \int_0^\infty \psi_{v'}^*(R - R_0) \bar{D}(R) \psi_v(R - R_0) dR$$

is not zero then we can have transitions between different vibrational levels. If one expand $D(R)$ near the equilibrium distance R_0 , then the dipole matrix element is proportional to

$$[2] \quad I_{v'v} = \int_0^\infty \psi_{v'}^*(R - R_0) (R - R_0) \psi_v(R - R_0) dR$$

Assume that the vibrational wavefunctions are approximated by the harmonic oscillator wavefunctions, then the change of v is to $v+1$ or $v-1$.

Since the one-unit of angular momentum of photon will be taken by the rotation, vibrational transition is accompanied by rotational transitions. Thus the transition from (v, K) to (v', K') is governed by

$$\text{R-branch} \quad hv^R = E(v+1, K+1) - E(v, K) = 2B(K+1) + hv_0$$

$$\text{P-branch} \quad hv^P = E(v+1, K-1) - E(v, K) = -2B(K+1) + hv_0$$

for $\Lambda = 0$.

For $\Lambda \neq 0$, one also has the Q-branch corresponding to $(v+1, K)$ to (v, K) transitions. This case is allowed since the one unit of angular momentum can be taken by the electron. Within the harmonic oscillator approximation the whole Q branch collapses to hv_0 .

When better approximations are used, the separation between different levels within the branch would deviate from the constant and the Q-branch spreads out too.

19. Raleigh and Raman scattering

When the dipole transition operator is considered to 2nd order, we can have two-photon type transitions. The first photon can be absorbed to reach some virtual excited electronic states and then it is re-emitted later. Another way to see this is that the transition goes through the induced dipole moment.

If the final state is identical to the initial state, the process is called **Raleigh scattering**. If the final state is not the same as the initial state, then we have the **Raman scattering**.

Raman scattering can be used to study the rotational levels of homonuclear molecules. The selection rule is $\Delta K = 0, \pm 2$. The rotational spectra are separated into Stokes lines ($\nu' > \nu$) or AntiStokes lines ($\nu' < \nu$). Since the rovibrational level spacings for molecules are quite small, Raleigh and Raman scattering are quite important.

20. Electronic transitions and Franck-Condon principle

see pp553-554 of BJ

The electronic transitions occur very fast essentially at the constant internuclear distance of the initial state. See Fig 11.8 of BJ. The transition amplitude is proportional to the overlap integral between the vibrational states of the two electronic states.

The precise selection rule for dipole transitions depends on the coupling scheme of the molecule. For Hund's case (a) or (i), which is valid for small molecules, the selection rules are $\Delta \Lambda = 0, \pm 1$ and no spin change. For Σ states, + goes to +, - goes to -. For homonuclear molecules, g goes to u and vice versa.