

## BO APPROXIMATION

01 MAR 2018 ①

We now apply the BO approximation in a formal manner. The starting point is the previous equation in which we drop the explicit dependences on the coordinates:

$$(\hat{T}_n + \hat{H}_e) \sum_a F_a \Phi_a = E \sum_a F_a \Phi_a$$

and we make use of the BO approximation: (recall  $T_n \equiv -\frac{\hbar^2}{2\mu} \nabla_R^2$ )

$$\nabla_R^2 F_a \Phi_a = \Phi_a \nabla_R^2 F_a$$

dependence of electronic wavefn on nuclear motion is weak

and we make use of the fact that  $\langle \Phi_a | \Phi_b \rangle = \delta_{ab}$  to get

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_R^2 + \hat{H}_e \right] \sum_a F_a \Phi_a = E \sum_a F_a \Phi_a$$

$$\Rightarrow \sum_a \Phi_a \left[ -\frac{\hbar^2}{2\mu} \nabla_R^2 F_a \right] + \sum_a F_a \hat{H}_e \Phi_a = E \sum_a F_a \Phi_a$$

$$\Rightarrow \sum_a \frac{-\hbar^2}{2\mu} \Phi_a \nabla_R^2 F_a + \sum_a E_a F_a \Phi_a = E \sum_a F_a \Phi_a$$

$$\therefore \hat{H}_e \Phi_a = E_a \Phi_a$$

(Multiply by  $\Phi_b^*$  & project out)

$$\Rightarrow \frac{-\hbar^2}{2\mu} \nabla_R^2 F_b + E_b F_b = E F_b$$

↑  
recall that this is a function of R:  $E_b(R)$

The equations thus get uncoupled.

- ▶  $F_b(R)$  is thus the nuclear wavefunction for a given electronic state  $E_b(R)$  is not a single valued energy function, but a function of the internuclear separation;  $E(R)$  thus acts as a potential energy function in the above Schrödinger equation for  $F_b(R)$
- ▶ It is evident that several solutions  $F_b(R)$  are possible for a given  $\Phi_b$
- ▶ Replacing  $\hat{V}(R; \{r_i\})$  by  $E_b(R)$  is equivalent to assuming that electronic motion is very rapid compared to nuclear motion and that the electrons respond instantaneously to a change in the nuclear configuration.

▶ The full form of the nuclear Schrödinger equation is

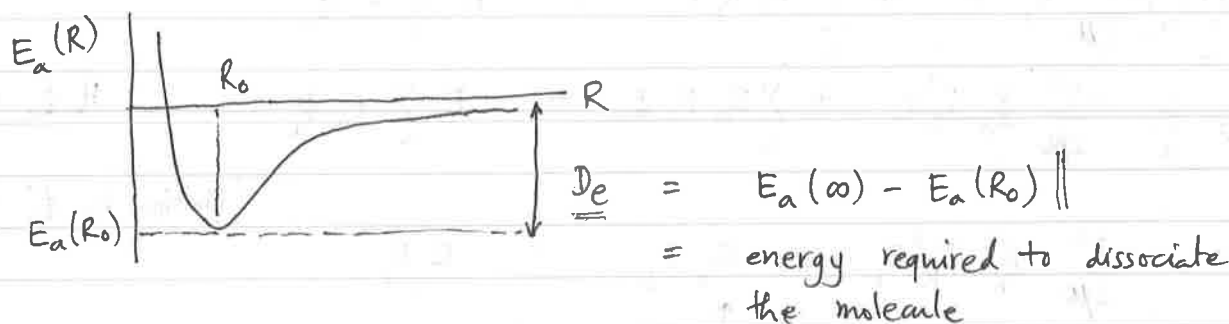
$$\left\{ \frac{-\hbar^2}{2\mu} \left[ \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} \right] - \frac{\hbar^2}{2\mu R^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] + E_a(R) \right\} F_a(R) = E F_a(R)$$

we define the nuclear angular mom op.  $\hat{K}^2 = -\hbar^2 \left[ \downarrow \right]$

Thus the BO approx allows us to decouple the electronic and nuclear wavefunctions, and

- We first solve the electronic Schrödinger equation and then use this complete basis set to write the nuclear wavefunction and finally use the difference  $\neq$  in the nuclear and electronic motion time scales to replace the potential function in the original equation by an equivalent potential energy function based on the electronic energy for a given internuclear separation,  $E(R)$ .

For stable molecules (bound states) the  $E(R)$  function looks typically like this



- Multiple solutions to the nuclear Schrödinger equations give multiple energy eigenvalues corresponding to vibrational ( $R$  part of the equation) and to rotational ( $\theta, \phi$  part) of the nuclear motion.
- For diatomic molecules there is a cylindrical symmetry so the motion does not depend on  $\phi$ . Thus rotational motion corresponds to changes in  $\theta$ .
- However as seen at the beginning, the energies corresponding to the nuclear motion are much smaller than the electronic energies.

ROTATIONAL MOTION

The equation

$$-\frac{\hbar^2}{2\mu} \nabla_R^2 F_a(\vec{R}) + E_a(R) F_a(\vec{R}) = E F_a(\vec{R})$$

is a variable-separable equation for the equivalent reduced mass  $\mu$  since  $E(R)$  acts like a central potential acting on  $\mu$ , referred to the CoM.

Separating the radial and angular part, and solving for the angular part alone gives the equation

$$\left\| \frac{\hbar^2}{2\mu R_0^2} F_{a,J}(R_0; \theta) = E_J F_{a,J}(R_0; \theta) \right.$$

where  $E_J$  is the separation constant, which has the value  $J(J+1)\hbar^2/2I$  where  $J$  are integers and the angular wavefunctions are spherical harmonics;  $I = \mu R_0^2$ , the moment of inertia about an axis  $\perp$  to the internuclear line segment passing through the CoM.

Scale of  $E_J$ :

$$I \sim \mu a_0^2 \quad \therefore E_J \sim \hbar^2 / \mu a_0^2 \quad \text{while } E_{\text{electronic}} \sim \hbar^2 / m_e a_0^2$$

$$\Rightarrow E_{\text{rotational}} \sim \frac{M}{m_e} \frac{m_e}{\mu} E_{\text{electronic}}$$

So once again the BO approx - neglecting the  $F_a \nabla_R^2 \Phi_a$  term relative to  $\Phi_a \nabla_R^2 F_a$ , is validated

The rotational energy levels are usually written as

$$E_J = B J(J+1); \quad \text{where } B = h / 8\pi c I \quad \text{in units of } \text{cm}^{-1}$$

Transitions between level  $J$  &  $J'$  are allowed if  $\langle J' | \vec{p} | J \rangle$ , i.e. the dipole matrix element is non-zero.

These are non-zero IFF  $\Delta J = J' - J = \pm 1$  and  $\Delta M = M' - M = 0, \pm 1$  and  $\vec{p}$  has to be non-zero

Homonuclear diatomics have no (pure) rotational spectrum.

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## VIBRATIONAL MOTION (IN BOUND STATES)

The molecular potential energy function  $E_a(R)$  can be expanded around the mean (equilibrium) position:

$$E_a(R) = \underbrace{E_a(R_0)}_{\text{constant}} + \frac{1}{2} (R-R_0)^2 \underbrace{\frac{\partial^2 E_a(R)}{\partial R^2}}_{\text{harmonic approximation term}} + \dots \uparrow \text{neglected}$$

The approximate harmonic potential would correspond to an oscillator with an eigenfrequency  $\omega_0 = \left[ \frac{1}{\mu} \frac{\partial^2 E_a}{\partial R^2} \Big|_{R=R_0} \right]^{1/2}$

and energy levels  $E_a(R_0) + (n + \frac{1}{2}) \hbar \omega_0 \equiv E$ , the molecular energy.

To make an estimate of the vibrational energy  $\hbar \omega_0$ , we note that  $E_a(R_0)$  is of the order  $(\hbar^2/a_0^2 m_e)$  ( $\because p \sim \hbar/a_0$ )

so  $\partial^2 E / \partial R^2$  is of order  $(\hbar^2/a_0^4 m_e)$

$$\Rightarrow \frac{1}{\mu} \frac{\partial^2 E}{\partial R^2} \text{ is of order } \frac{\hbar^2}{a_0^4 m_e \mu}$$

$$\Rightarrow \hbar \omega \text{ is of order } \frac{\hbar^2}{a_0^2 \sqrt{m_e \mu}}$$

$$\Rightarrow E_{\text{vibr}} \simeq [m_e / \mu]^{1/2} E_{\text{elec}} \simeq 1\%$$

## JUSTIFICATION OF BO APPROXIMATION

$$\langle p_{\text{nuclear}}^2 \rangle \sim 2\mu \langle E_{\text{vibr}} \rangle = \sqrt{\frac{\mu}{m_e}} \frac{\hbar^2}{a_0^2}$$

$$\Rightarrow \nabla_R^2 F_a \sim \sqrt{\frac{\mu}{m_e}} \frac{1}{a_0^2} F_a$$

On the other hand  $\nabla_R^2 \Phi_a \sim (1/a_0^2) \Phi_a$  which is again  $\sim 100$  times

$$\Rightarrow \Phi_a \nabla_R^2 F_a = \sqrt{\frac{\mu}{m_e}} \times F_a \nabla_R^2 \Phi_a$$

LHS is thus  $\sim 100$  times ~~smaller~~ <sup>larger</sup> than  $F_a \nabla_R^2 \Phi_a$   
 so neglecting  $F_a \nabla_R^2 \Phi_a$  relative to  $\Phi_a \nabla_R^2 F_a$  is justified.

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### BETTER APPROXIMATION TO $E_a(R)$

The harmonic approximation to  $E_a(R)$  is rather drastic. Even if we include a few higher order terms, the approximation to the actual  $E_a(R)$  is seen to be quite poor. Moreover, a SHO has  $\infty$  levels, which contradicts reality. P M Morse ( ) proposed an empirical potential

$$E_a^{\text{MORSE}}(R) = E_a^{(0)} [1 - \exp(-a(R-R_e))]^2$$

$$\text{where } a = \left[ \frac{\mu}{2E^{(0)}} \right]^{1/2}$$

and  $E^{(0)}$  is the Dissociation energy ( $D_e$  in previous figure)

This potential gives vibrational energy values of the form

$$E_{\text{vib}} = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 \quad \text{where } \omega_e = a \left( \frac{\hbar D_e}{\pi c \mu} \right)^{1/2}$$

$$\omega_e x_e = \frac{\hbar a^2}{4\pi c \mu}$$

### TRANSITIONS BETWEEN VIBRATIONAL LEVELS

Let  $S(R)$  be the vibrational part of the nuclear wavefunction. Then the (approximate) eigenstates, the SHO wavefunction will be denumerated by the vibrational quantum number  $v$  and the energy levels will be

$$E_v = \left( v + \frac{1}{2} \right) \hbar \omega \quad \text{where } \omega = \left[ \frac{1}{\mu} \left. \frac{\partial^2 E_a(R)}{\partial R^2} \right|_{R=R_0} \right]^{1/2}$$

As a hybrid model we may take  $E_a^{\text{MORSE}}(R)$  instead of  $E_a(R)$ . In that case  $\partial E_a^{\text{MORSE}} / \partial R = 0$  at  $R=R_e$  and  $\partial^2 E_a^{\text{MORSE}} / \partial R^2$  at  $R=R_e$  is  $2a^2 E^{(0)}$

Transition occur between states that have non-zero coupling through the dipole operator, ie when  $\langle v' | \vec{p} | v \rangle \neq 0$

For homonuclear diatomics  $\vec{p} = 0$  so pure vibrational transitions cannot occur in such molecules.

In other molecules  $\vec{p}$  is a function of  $R$ , and we may write

$$\vec{p}(R) = \vec{p}_0(R_0) + \frac{\partial \vec{p}}{\partial R} (R - R_0)$$

$$\text{Then } \langle v' | \vec{p} | v \rangle = \frac{i \hbar}{2\mu \omega} \left[ \sqrt{v+1} \delta_{v', v+1} - \sqrt{v} \delta_{v', v-1} \right]$$

COUPLING OF ROT & VIB MOTION

We took  $E(R) = \frac{J(J+1) \hbar^2}{2I}$  for rotational motion  
(barring a constant) where  $I = \mu R_0^2$

and  $E(R) = \left(n + \frac{1}{2}\right) \hbar \omega_0$  for vibrational motion,  
(barring a constant) where  $\omega_0^2 = \frac{1}{\mu} \left[ \frac{\partial^2 E_a}{\partial R^2} \right]_{R=R_0}$

however these two motion are not strictly independent. In the simplest argument against independence, the approximation  $I = \mu R_0^2$  should be replaced by  $I = \mu R^2$  where  $R$  is now given by the instantaneous value owing to vibrational motion.

Thus, we should take

$$E(R) = E_a(R_0) + \left(n + \frac{1}{2}\right) \hbar \omega_0 + \frac{1}{2\mu R^2} J(J+1) \hbar^2$$

$\uparrow$  electronic energy  $\hat{H}_{ee}(\Phi_e)$        $\uparrow$  vibrational       $\uparrow$  centrifugal distortion,  $R \rightarrow R_0$

CENTRIFUGAL DISTORTION

$$F_{\text{centr}} = \mu \omega^2 R_0 = J / \mu R_0^3 \rightarrow J / \mu R^3$$

The  $F_{\text{harmonic}} = -\mu \omega^2 (R - R_0)$

$$E_{\text{rot, with cent. dist}} = \frac{1}{2} \mu \omega^2 (R - R_0)^2 + \frac{J}{2\mu R^2} \left\{ \int E = -\int F_{\text{cent}} dR \right\}$$

$$= \frac{J^2}{2\mu R_0^2} - \frac{J^4}{2\mu^3 R_0 \omega^2}$$

We write this as  $E_{\text{rot, with cent. dist}} = B_v J(J+1) - D_v [J(J+1)]^2$

where  $B_v = \frac{\hbar^2}{8\pi^2 \mu c} \left\langle v \left| \frac{1}{R^2} \right| v \right\rangle$

$$D_v = \frac{\hbar^4}{32\pi^2 \mu^3 \omega^2 c} \left\langle v \left| \frac{1}{R^4} \right| v \right\rangle$$

## ELECTRONIC WAVEFUNCTION OF THE $H_2^+$ MOLECULAR ION

We consider ~~three~~ <sup>two</sup> methods to obtain the wavefunction

- (1) An approximate method based on Linear Combinations of Atomic Orbitals or LCAO method, which can be generalised to other molecules
- (2) A semi-exact method involving separation of variables that is specific to  $H_2^+$ .

The LCAO method begins with the assumption that the electron can be in either of the separated atoms (ions); ~~so~~ so that when the atoms (ions) are combined, the net wavefunction will be a linear combination of the two atomic wavefunctions. Since the two nuclei are identical, this means that the molecular orbital has the form with the required symmetry

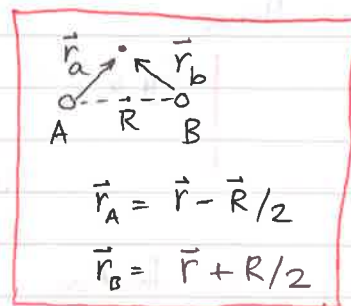
$$\Phi(R) = \frac{1}{\sqrt{2}} (\phi(r_a) \pm \phi(r_b))$$

where  $\phi(r)$  is a hydrogenic ground-state wavefunction.

that is there are two possible states

$$- \Phi_g(R, r) = \frac{1}{\sqrt{2}} [\phi(r_a) + \phi(r_b)]$$

$$- \Phi_u(R, r) = \frac{1}{\sqrt{2}} [\phi(r_a) - \phi(r_b)]$$



The  $\Phi_g$  state is symmetric under reflection through the CoM and the  $\Phi_u$  state is antisymmetric under the same operation.

Since  $\phi(r_a)$  and  $\phi(r_b)$  are both 1s states, the projection of the angular momentum on the R axis is zero, so  $\Phi_g$  and  $\Phi_u$  represent the  $\sigma_g$  and  $\sigma_u$  molecular terms.

The energy eigenvalue of these molecular wavefunctions is given by

$$E = \frac{\int \Phi^* \hat{H}_{el} \Phi d\tau}{\int \Phi^* \Phi d\tau} \quad \text{where} \quad \hat{H}_{el} = -\frac{1}{2} \nabla_r^2 - \frac{1}{|\vec{r} - \vec{r}_A|} - \frac{1}{|\vec{r} - \vec{r}_B|} + \frac{1}{r_{AB}}$$

$\vec{r}_{AB} \equiv R \hat{z}$

The numerator is evaluated as

$$\begin{aligned} \int \Phi^* \hat{H}_{el} \Phi d\tau &= \frac{1}{2} \int \phi(r_a) \hat{H}_{el} \phi(r_a) d\tau_a + \frac{1}{2} \int \phi(r_b) \hat{H}_{el} \phi(r_b) d\tau_b \\ &\quad \pm \frac{1}{2} \int \phi(r_a) \hat{H}_{el} \phi(r_b) d\tau_a \pm \frac{1}{2} \int \phi(r_b) \hat{H}_{el} \phi(r_a) d\tau_b \\ &= \int \phi(r_a) \hat{H}_{el} \phi(r_a) d\tau_a \pm \int \phi(r_a) \hat{H}_{el} \phi(r_b) d\tau_a \\ &= \underline{H_{AA} \pm H_{AB}} \end{aligned}$$

$$\underline{H_{AA}} = E_0 + \frac{1}{R} (1+R) e^{-2R}$$

$$\underline{H_{AB}} = \left[ E_0 + \frac{1}{R} \right] s(R) - (1+R) e^{-R}$$

NOTE  
 $\int d\tau_a = \int d\tau_b = \int d\tau$ .  
 since  $\bar{R}$  is fixed.

where  $\underline{s(R)} = \int \phi(r_a) \phi(r_b) d\tau \rightarrow$  called the overlap integral.

The denominator is

$$\frac{1}{2} \int [|\phi(r_a)|^2 + |\phi(r_b)|^2 \pm 2\phi(r_a)\phi(r_b)] d\tau$$

$$= \underline{1 + s(R)}$$

Hence

$$E_{g,u} = \frac{E_0 + \frac{1}{R} (1+R) e^{-2R} \pm (1-2R^2/3) e^{-R}}{1 \pm (1+R+R^2/3) e^{-R}}$$

$\uparrow$   
 $(\equiv -0.5)$

The function  $E_g - E_0$  has a minimum ( $< 0$ ) for  $R = 2.5$

The function  $E_u - E_0$  has no minimum and is always +ve



- For homonuclear diatomic molecules another symmetry arises. due to the presence of a centre of symmetry. (which coincides with the centre of mass)

Both, the hamiltonian  $\hat{H}_e$  and  $\hat{L}_z$  are invariant under a reflection of coordinates, about this point. That is, if  $\vec{r} \rightarrow -\vec{r}$ ,  $\hat{H}_e$  and  $\hat{L}_z$  remain unaltered.

- Under the same transformation two wavefunctions  $\Phi_\Lambda$  may either flip or not flip their sign. <sup>represent what?</sup> Wavefunctions that flip the sign, are called ungerade states, while the ones that do not, represent gerade states. (u and g states)

- Thus, the <sup>electronic</sup> state of molecule is, in addition to its energy, classified on the basis of  $\Lambda$ , and their parity. For the case  $\Lambda=0$ , another symmetry comes in, the  $\pm$  sign under reflection

- Thus  $\Sigma$  states can be  $\Sigma_g^+$   $\Sigma_u^+$   $\Sigma_g^-$   $\Sigma_u^-$

while  $\Pi$  and  $\Delta$  states can be  $\Pi_g$  or  $\Pi_u$  and  $\Delta_g$  or  $\Delta_u$ .

- In addition to this an electron state is classified by the spin multiplicity for ~~spin~~ total spin  $S$  the multiplicity is  $2S+1$ . This number is shown as a pre-superscript, e.g. a state with  $S=1$ ,  $\Lambda=1$  and of even parity will be shown as a  ${}^3\Pi_g$  state.

- Barring  $\$$  a few exceptions it is found that the ground state of molecules is usually a  ${}^1\Sigma_g^+$  state, and for homonuclear diatomics it is  $\$$   ${}^1\Sigma_g^+$ .

## SYMMETRIES OF A MOLECULE

A diatomic molecule has an axis of cylindrical symmetry, the internuclear axis and if this axis is taken as the z-axis, the

- $\hat{L}_z$  operator commutes with the Hamiltonian (azimuthal symmetry) (in the body-fixed coordinates)
- However  $\hat{L}_x$ ,  $\hat{L}_y$ ,  $\hat{L}^2$  do not commute with  $\hat{H}_{el}$  - the <sup>electronic</sup> Hamiltonian is not invariant under rotation about this axis.

Hence, the electronic eigenfunctions  $\Phi_a$  are simultaneous eigenfunctions of  $\hat{L}_z$  and  $\hat{H}_e$ :

$$\left\{ \begin{array}{l} \hat{L}_z \Phi_a = \Lambda_a \Phi_a \quad \Lambda = 0, 1, 2, \dots \\ \Sigma, \Pi, \Delta, \dots \text{ states} \end{array} \right.$$

- The electronic Hamiltonian is invariant under reflection in a plane containing the z-axis (eg. XZ or YZ plane). In the XZ plane reflection implies  $y \rightarrow -y$  and refl. in the YZ plane implies  $x \rightarrow -x$

If the reflection operator is  $\hat{A}$ , then the above implies  $[\hat{A}, \hat{H}_e] = 0$  and the reflection operator flips the sign of  $L_z$ , so  $\hat{A} \hat{L}_z = -\hat{L}_z \hat{A}$

- This implies, that if  $\hat{A} \Phi \rightarrow \Phi'$  where <sup>then</sup>  $\Phi'$  and  $\Phi$  differ only in the sign of the eigenvalue of  $L_z$  for this eigenfunction. [as long as  $\Lambda \neq 0$ ]

- Thus  $\Lambda \neq 0$  states are doubly degenerate, states with  $\pm \Lambda$  have the same energy.

- If  $\Lambda = 0$ , however, then the ~~two~~ states are <sup>unaffected by reflection</sup> non-degenerate, that is  $\Sigma$  states have no degeneracy, but <sup>there can be two types of</sup> ~~the two~~ wavefunctions ~~are~~ different.

- The difference between the wavefunction of the original and reflected cases can only be in the form of a constant multiplier. for  $\Sigma$  states.

Since double reflection is a unity (identity) operation, this constant can only be  $\pm 1$  for all  $\Sigma$  states. We thus distinguish between two kinds of  $\Sigma$  states.

- States for which a reflection (in a plane containing the z-axis) changes the sign are called  $\Sigma^+$  states, those for which the sign changes are called  $\Sigma^-$  states.