

# Physics 531

## Lecture 20: Rovibration energy levels of diatomics

So far in discussing the structure of molecules, we have considered only the adiabatic energy levels of the electrons, with the nuclei fixed. Once we have calculated these Born-Oppenheimer potentials, we can study the slow motion of the nuclei.

Under the adiabatic approximation, the wave function for electrons and nuclei is

$$\Psi_0(\vec{r}_3, \vec{R}) = \chi_0(\vec{R}) \underbrace{\Phi_0(\vec{r}_3, \vec{R})}_{\substack{\text{electronic wave function} \\ \text{for fixed } \vec{R}}}$$

$\uparrow$   
 nuclear wave function

With Hamiltonian  $\hat{H} = \frac{\hat{p}_{\text{nuc}}^2}{2\mu} + \hat{H}_e(\vec{R})$

$$\hat{H}_e(\vec{R}) |\Phi_0(\vec{R})\rangle = \underbrace{V_0(\vec{R})}_{\substack{\text{Born-Oppenheimer potential} \\ \text{for fixed } \vec{R}}} |\Phi_0(\vec{R})\rangle$$

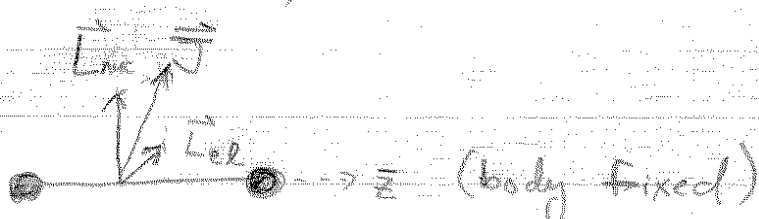
$$\Rightarrow \left[ \frac{\langle \Phi_0 | \hat{p}_{\text{nuc}}^2 | \Phi_0 \rangle}{2\mu} + V_0(\vec{R}) \right] \chi_0(\vec{R}) = E \chi_0(\vec{R})$$

$$\hat{p}_{\text{nuc}}^2 = \underbrace{-\frac{\hbar^2}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right)}_{\text{radial kinetic energy}} + \underbrace{\frac{\hat{L}_{\text{nuc}}^2}{R^2}}_{\text{angular kinetic energy}}$$

Born-Oppenheimer approx: Neglect variation of  $\Phi_0$  with  $R$

$$\Rightarrow \left( -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{\langle \Phi_0 | \hat{L}_{nuc}^2 | \Phi_0 \rangle}{2\mu R^2} + V_0(R) \right) \chi_0(R) = E \chi_0(R)$$

Now, the total angular momentum of the molecule includes the angular momentum of the nuclei, plus the angular momentum of the electrons. Neglecting spin angular momentum to start,



The electronic states are quantized with respect to a body-fixed quantization axis. Since  $\vec{L}_{nuc}$  is perpendicular to this axis  $|\vec{J}_z| = |\vec{L}_{eel,z}|$

In the absence of external fields the total angular momentum must be conserved

$$\Rightarrow \hat{J}^2 |\Psi\rangle = \hbar^2 J(J+1) |\Psi\rangle$$

Since  $J \geq |M_J|$  and  $M_J = M_{L_{eel}} = \Lambda$

Possible values of  $J$  for a given electronic state are

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

Now, since the B.O. potentials are eigenstates of

$$\hat{L}_{\alpha, z} |\Phi_0\rangle = \pm \Lambda |\Phi_0\rangle$$

$$\hat{L}_{\alpha, \pm} |\Phi_0\rangle = 0$$

$$\Rightarrow \langle \Phi_0 | \hat{L}_{\text{NUC}}^2 | \Phi_0 \rangle \chi_0 = \langle \Phi_0 | (\vec{J} - \hat{L}_{\text{el}})^2 | \Phi_0 \rangle \chi_0(\vec{R})$$

$$= \langle \Phi_0 | \vec{J}^2 + \hat{L}_{\text{el}}^2 - 2\vec{J} \cdot \hat{L}_{\text{el}} | \Phi_0 \rangle \chi_0(\vec{R})$$

$$\frac{\hbar^2}{2} [J(J+1) + \langle \Phi_0 | \hat{L}_{\text{el}, x}^2 + \hat{L}_{\text{el}, y}^2 | \Phi_0 \rangle$$

$$+ \Lambda^2 - 2 \langle \Phi_0 | \vec{J} \cdot \hat{L}_{\text{el}} | \Phi_0 \rangle] \chi_0(\vec{R})$$

$$= \langle \Phi_0 | \hat{J}_z^2 | \Phi_0 \rangle = \Lambda^2$$

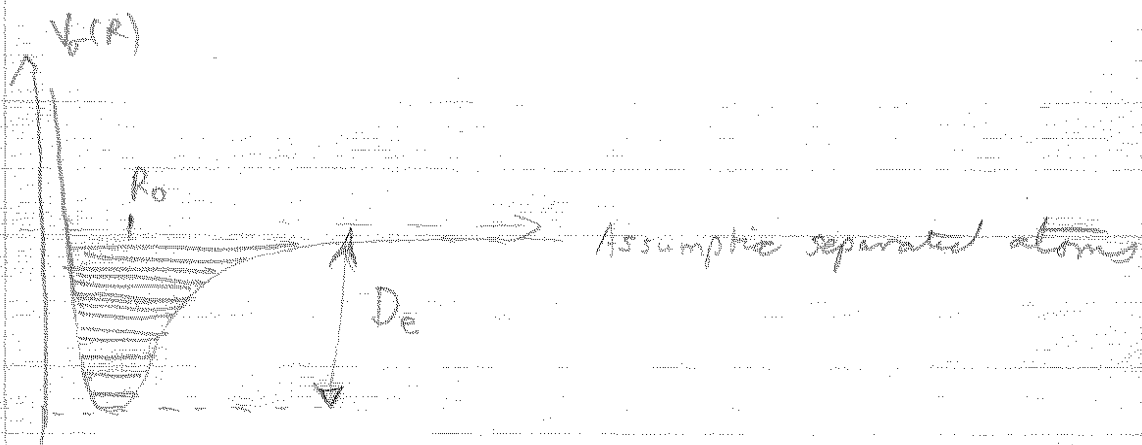
$$\Rightarrow \langle \Phi_0 | \hat{L}_{\text{NUC}}^2 | \Phi_0 \rangle \chi_0(\vec{R}) =$$

$$(J(J+1) + \langle \Phi_0 | \hat{L}_{\text{el}, x}^2 + \hat{L}_{\text{el}, y}^2 | \Phi_0 \rangle - \Lambda^2) \chi_0(\vec{R})$$

$$\therefore \frac{\hbar^2}{2\mu} \left( -\frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{J(J+1)}{R^2} + V_0(\vec{R}) \right) \chi_0(\vec{R}) = E \chi_0(\vec{R})$$

$$\text{where } V_0'(\vec{R}) = V_0(R) + \frac{\langle \Phi_0 | \hat{L}_x^2 + \hat{L}_y^2 | \Phi_0 \rangle}{2\mu R^2} - \frac{\Lambda^2}{2\mu R^2}$$

For energy levels near the minimum of the binding potential, the electronic energy is much larger than small corrections arising from the last two terms. so  $V_0'(\vec{R}) \approx V_0(R)$ .



For many situations the chemical binding potential is very deep compared to zero point energy of the motion of the nuclei. Thus, near the ground state, the potential looks very harmonic, and the atoms are near the equilibrium separation  $R_0$ .

Under the approximation  $V_0'(R) \approx V_0(R)$  we have a central potential and we can separate radial from angular motion of the nuclei

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{\hbar^2 J(J+1)}{2\mu R^2} + V_0(R) \right) F_0(R) = E F_0(R)$$

↑  
reduced radial wave func.

Expand about  $R_0$ , the point where  $\frac{dV_0}{dR} = 0$

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \quad \text{let } x = R - R_0$$

$$\hat{H}_0 = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} \mu \omega^2 x^2 + \frac{\hbar^2 J(J+1)}{2\mu R_0^2}$$

$$\hat{H}_1 = \alpha x^3 + \beta x^4 - \frac{x J(J+1)}{\mu R_0^3} + \frac{3x^2}{2} \frac{J(J+1)}{\mu R_0^4} + \dots$$

(ii) Electron spin orbit  $A\vec{L}_e \cdot \vec{S}$

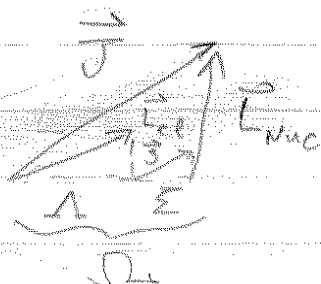
(iii) Nuclear rotation energy  $B\mathbf{J}(\mathbf{J}+1)$

• Jordan's Case (a),  $\Delta E \gg |A| \gg B$

The precession rate of  $\vec{L}$  about internuclear axis dominates. Since  $|A| \ll \Delta E$ ,  $\vec{S}$  decouple from  $\vec{L}_e$   $\Rightarrow$  Product state, with quantization of along internuclear axis

We denote  $|M_{L_{tot}}| = \Lambda$   $M_S = \Sigma$

$$M_{J_{tot}} = \pm \Lambda + \Sigma = \Omega$$



Possible values of  $\Omega$

example:  $3\Pi$

$$\Rightarrow \Lambda = 1 \quad S = 1$$

$$\Rightarrow \Omega = 0, 1, 2$$

denote  ${}^3\Pi_0, {}^3\Pi_1, {}^3\Pi_2$

The  $B=0$  energy  $E_0^{total}(R) = E_0(R) + E_{LS}$

$$E_{LS} = A \langle \Phi_0 | \vec{L} \cdot \vec{S} | \Phi_0 \rangle = A \Lambda \Sigma$$

Split up into  $2S+1$  multiplet

Rotational energy depends on  $\Omega$  as well as  $J$

## Spin and Fine-Structure: Hund's Rules

So far we have not included the electron spin angular momentum in the discussion of the energy levels beyond the exchange symmetry. The spin of the electrons does contribute to the total angular momentum, and thus to the energy of molecule. In addition there is spin-orbit interaction which contributes to the total energy. There are three angular momenta:

- Electron orbital angular momentum:  $\vec{L}_{ee}$
- Nuclear orbital angular momentum:  $\vec{L}_{nuc}$   
(rotation of the molecule)
- Spin angular momentum of electrons:  $\vec{S}$

Now these are coupled together to form the total angular momentum  $\vec{J}$  will depend on which forces dominate.

### Relevant Forces

- (i) Electrostatic energy: Because of the strong fields along the internuclear axis, the electrons angular momentum will tend to precess around the internuclear axis

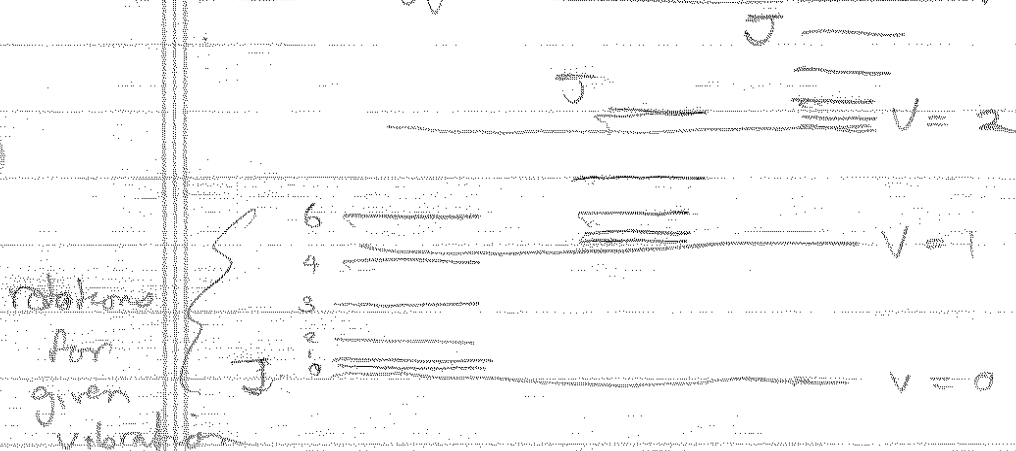


Rate set by  $\Delta E$   
of electronic energy levels

The zeroth order Hamiltonian describe simple harmonic radial motion plus the angular motion of a rigid rotator.

For most diatomics the vibrational frequency  $\omega$  is in the near infrared,  $\frac{\omega}{2\pi c} \sim 10^3 \text{ cm}^{-1}$  whereas the rotation energy corresponds to photons in the microwave,  $\frac{\omega}{2\pi c} \sim 1 \text{ cm}^{-1} - 10 \text{ cm}^{-1}$

The energy level spectrum (say  $A=0$ )



### Corrections

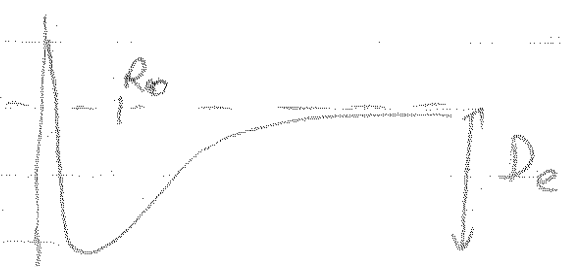
- Anharmonicity: Near the ground state, the 'anharmonic' corrections  $\hat{H}_1 = \alpha \hat{x}^3 + \beta \hat{x}^4$  to first order, shift  $\beta \langle v | \hat{x}^4 | v \rangle \sim \beta x_0^4$
- Non-rigid rotator (centrifugal distortion):

The molecule stretches due to vibrational motion and this will effect the moment of inertia.

## Morse potential:

In order to obtain estimates of the molecular motion one uses an analytic empirical model, good near the minimum due to Morse

$$V_M(R) = D_e [e^{-\alpha(R-R_0)} - 1]^2 - D_e$$



$\alpha$  is determined by the curvature near  $R_0$

$$\Rightarrow D_e \alpha^2 = \frac{1}{2} \mu \omega^2$$

One can solve for the energy levels exactly:

$$\text{the vibrational energy } h\nu_0 \left[ \left( v + \frac{1}{2} \right) - \beta \left( v + \frac{1}{2} \right)^2 \right]$$

$$\text{where } \beta = \frac{h\nu_0}{4D_e} \text{ (anharmonic correction)}$$

The effect of vibration on rotational splitting is known as the "centrifugal distortion". We can use the Morse potential to estimate that. Write

$$V_{\text{eff}}(R) = V_M(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2}$$

There is thus a new equilibrium point  $R_1$ , due to centrifugal barrier  $\left. \frac{dV_{\text{eff}}}{dR} \right|_{R_1} = 0$



$$\Rightarrow R_1 \approx R_0 \left( 1 + \frac{\hbar^2 J(J+1)}{2\mu R_0^2 \left( \frac{1}{2} \mu \omega_0 R^2 \right)} \right)$$

$$V_{\text{eff}}(R) = V_0 + \frac{1}{2} k (R - R_1)^2 + \underbrace{c_1 (R - R_1)^3 + c_2 (R - R_1)^4}_{\text{Perturbations}}$$

→ Energy levels of nuclear motion  
in a Born Oppenheimer potential

$$E_{v,J} \approx -D_e + \hbar \omega_0 \left[ \left( v + \frac{1}{2} \right) - \beta \left( v + \frac{1}{2} \right)^2 \right] + \underbrace{\left( \frac{\hbar^2}{2\mu R_0^2} - a \left( v + \frac{1}{2} \right) \right)}_{\equiv B_v} J(J+1) - b J^2(J+1)^2$$

where  $a = \frac{3}{2} \left( \frac{\hbar^2}{2\mu R_0^2} \right) \left( \frac{\Delta X_{\text{zero}}}{R_0} \right)^2 \left( R_0 - \frac{1}{2} \right)$

$$b = \frac{\hbar^4}{2\mu^3 \omega_0^2 R_0^6} = \hbar \omega_0 \left( \frac{\Delta X_{\text{zero}}}{R_0} \right)^6$$

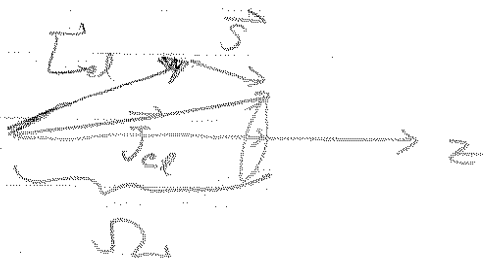
The constant  $B_v$  describes the vibrational dependent moment of inertia

• Hund's Case (b)  $|A| \gg B \gg |A|$

The spin-orbit is negligible here compared to rotational energy, good  $Q$ -number  $\Lambda, S_{\text{rot}}, \Omega$

• Hund's Case (c)  $|A| \gg |A| \gg B$

Here spin-orbit dominates. The total electron angular momentum is then coupled to internuclear axis



The good  $q$ -number is the coupled  $J_{e,z} = \Omega$

Denote molecular states by the value of  $\Omega$ , numerically,

ex:  $\Omega=0$ , homonuclear, parity even, reflection odd =  $O_g^-$