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# 4.6. Molecular ~~vibronic states~~ ~~vibronic states~~ ~~vibronic states~~

Going back to 4.1, we now know how to calculate/construct the molecular electronic energies /  $\text{PE}$  surfaces  $E_e(\vec{R})$  from (4.2). Insertion into (4.6) then gives us the eigenstates of the motional state of the nuclei.

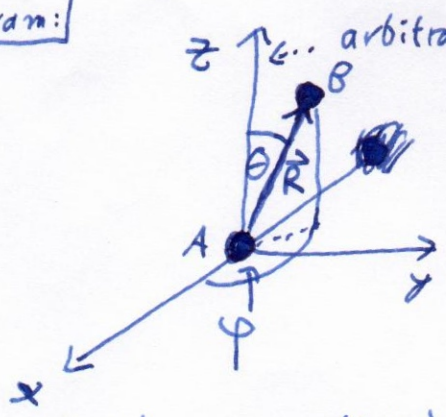
In the  $\text{BO}$ -approximation:

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_{\vec{R}}^2 + E_e(\vec{R}) \right] \hat{F}_0(\vec{R}) = E \hat{F}_s(\vec{R}) \quad (4.14)$$

For di-atomic molecule  $E_e(\vec{R}) = E_e(|\vec{R}|) \rightarrow$  mathematically ~~is~~ spherically symmetric Schrödinger equation (like e.g. Hydrogen)

Can write solution  $F_s(\vec{R}) = \frac{F_{\nu k}(R)}{R} \chi_{k m k}(\theta, \phi)$  (compare 1.18) (4.15)

Diagram:



$\dots$  arbitrary co-ordinate system, e.g. Lab fixed

We know due to spherical symmetry:

$$\chi_{k m k}(\theta, \phi) = Y_{k m k}(\theta, \phi)$$

Spherical harmonics

Insert (4.15) into (4.14) and use 3D Laplacian (all same as for Hydrogen)

Radial Schrödinger equation

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dR^2} - \frac{k(k+1)}{R^2} \right) + (E_e(R) - E_{\nu, k}) \right] F_{\nu k}(R) = 0 \quad (4.16)$$

The electronic energies  $E_e(R)$  are now "the potential"

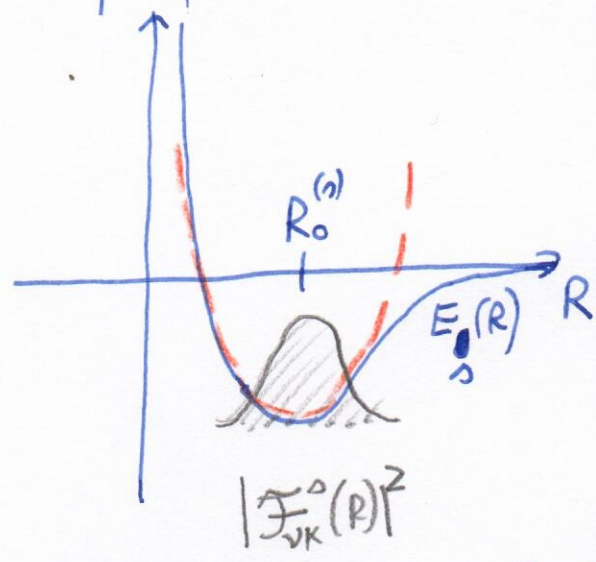
~~this takes the place of the l-terms~~

$\neq k > 0$  the molecule is rotating about the centre-point

\* represents the centrifugal force due to this.



Compare shape from section 4.3:



The binding PO-surfaces usually have one well-defined local minimum.

We can expand  $E_s(R)$  around this minimum (red line)

$$E_s(R) = E_s(R_0) + \frac{1}{2} K_s (R - R_0)^2$$

$$K_s = \left. \frac{d^2 E_s(R)}{dR^2} \right|_{R=R_0^{(n)}}$$

from now write  $R_0^{(n)} = R_0$

• Since usually also  $|F_{v,k}^0(R)|^2$  is non-zero only close to this minimum, we can also write  $+ \frac{\hbar^2}{2\mu} \frac{k(k+1)}{R^2} \rightarrow \frac{\hbar^2}{2\mu} \frac{k(k+1)}{R_0^2}$  in (4.16)

We call this the rotational energy  $E_{rot} = \frac{\hbar^2}{2\mu R_0^2} k(k+1)$  (4.17)

$I = \mu R_0^2 = \text{moment of inertia}$   $= \frac{\hbar^2}{2I} k(k+1)$

We can now rewrite (4.16) as harmonic oscillator TISE

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} K_s (R - R_0)^2 - E_v \right] F_{v,k}^0(R) = 0 \quad (4.18)$$

where we used

total energy

$$E_{s,v,k} = E_s(R_0) + E_v + E_{rot,k} \quad (4.19)$$

$E_{s,v,k}$ : electronic state label  
 $E_s(R_0)$ : equilibrium position  
 $E_v$ : vibrational energy  
 $E_{rot,k}$ : rotational quantum number

Vibrational energies as usual

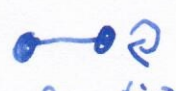
$$E_{vib,v} = \hbar \omega_0 \left( v + \frac{1}{2} \right) \quad v = 0, 1, 2, \dots \quad (4.18)$$

$$\omega_0 = \left( \frac{K_s}{\mu} \right)^{\frac{1}{2}}$$

• Deviations from (4.18) due to anharmonicity of  $E_s(R)$  at larger  $v$

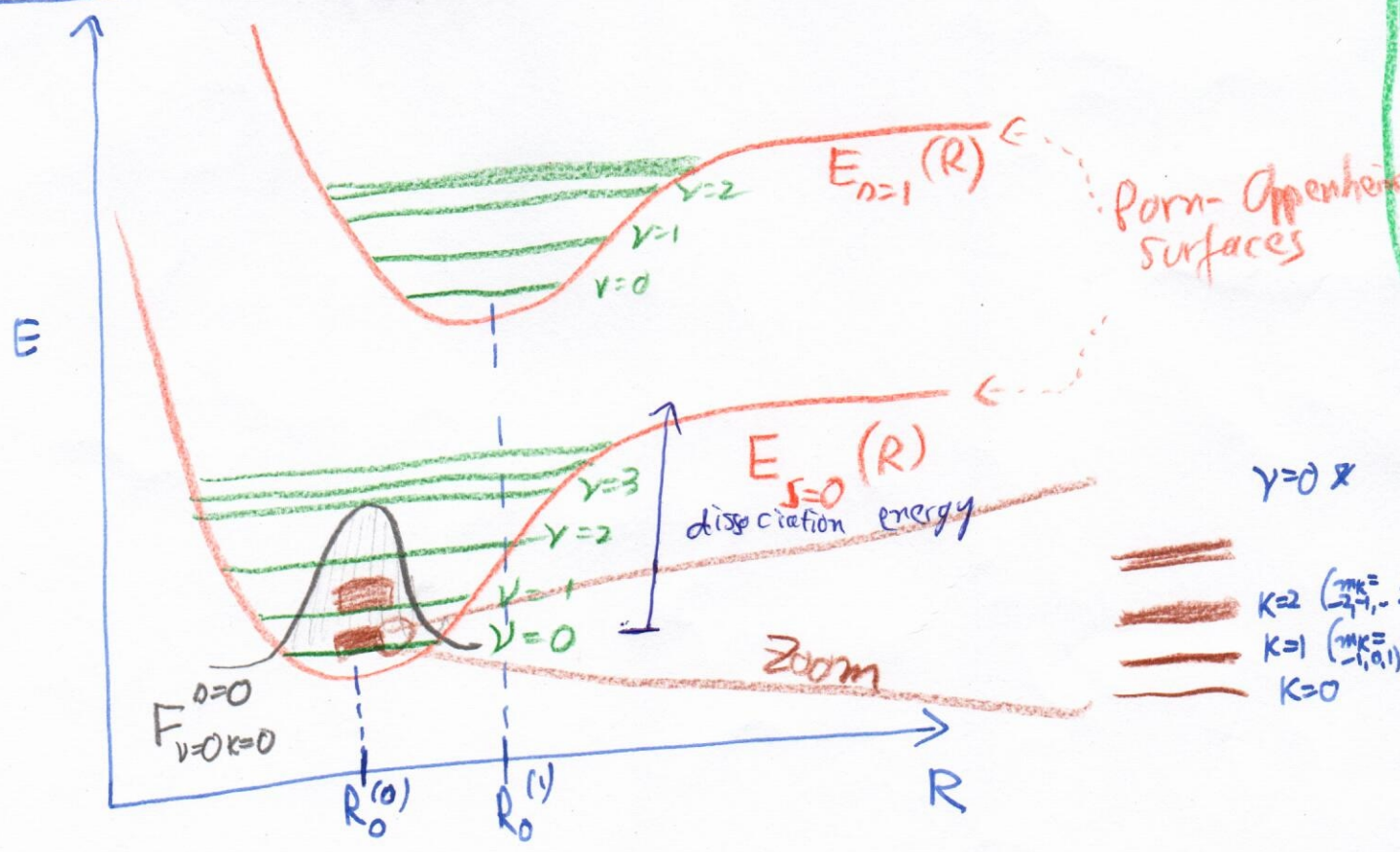
•  $\frac{F_{v,k}^0(R)}{R} \chi_{kMk}(\theta, \phi)$  is called a ro-vibronic state.

• Harmonic approximation (4.18) for vibrational energies breaks down for larger  $v$ , because potential  $E_s(R)$  ceases to be harmonic for larger  $(R-R_0)$

• Di-atomic molecules can also rotate around the inter-nuclear axis : this is represented within the electronic wave function  $\Phi(\vec{R}, \vec{r}_1, \vec{r}_2, \dots)$  as nonzero  $L$  (see section 4.4)

• ~~When~~ Rotations usually weakly couple to vibrations; Fast rotation increases centrifugal potential  $\sim \frac{K(K+1)}{R^2}$  and can thus cause vibrations. This effect drops out if we replace  $R \rightarrow R_0$  in (4.16). If we include it  $F_v^0(R) \rightarrow F_{vK}^0(R)$

Example @ 4.6: Energy-levels of diatomic molecule:



# 4.7. Molecular Spectra

- For the same arguments as used in section 3 in the case of atoms, transitions between different molecular states (label  $a = \{n, v, k, m_k\}$ ) are governed by the
 

$\frac{\partial \psi_a(\vec{R})}{\partial R_{km}} (\theta, \phi)$

  
 $\hookrightarrow$  State:  $\psi_a = \Phi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) F_a(\vec{R})$

Molecular dipole-moment operator:

$$\hat{\vec{D}} = e \left( \sum_i z_i \vec{R}_i - \sum_j \vec{r}_j \right) \quad (4.19)$$

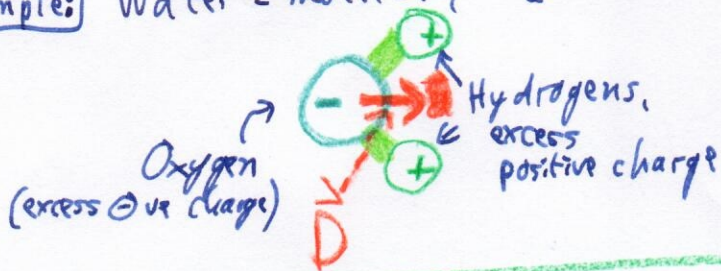
positions of nuclei
positions of electrons

Unlike the case for atoms, where always  $\langle \phi_n | -e\vec{r} | \phi_n \rangle = 0$  (same  $n$ )

molecules can have a permanent electric dipole moment

$$\vec{D}_{aa} = \langle \psi_a | \hat{\vec{D}} | \psi_a \rangle \neq 0 \quad (4.20)$$

Examples: Water-molecule,  $H_2O$ :



Dipole-moment of Water:

$$|\vec{D}| = 1.85 \text{ D [D=Debye]}$$

$$1 \text{ Debye} \approx 0.2 \text{ e} \cdot \text{\AA}$$

It will also be useful to consider the dipole-moment in electronic state  $n$  for nuclear configuration  $\vec{R}$ :

$$\vec{D}_s(\vec{R}) = \langle \Phi_n | \hat{\vec{D}} | \Phi_n \rangle = \int d^3r_i \Phi_n^*(\vec{r}_1, \vec{r}_2, \dots) \hat{\vec{D}} \Phi_n(\vec{r}_1, \vec{r}_2, \dots) \quad (4.21)$$

still depends on  $\vec{R}$

For the same reasons as in atoms, transitions between ~~molecular~~ molecular states due to absorption or emission of elm-radiation (which give rise to spectra) are governed by transition matrix elements:

$$\vec{D}_{ba} = \langle \psi_b | \hat{\vec{D}} | \psi_a \rangle \quad (4.22)$$

# 4.7.1. Rotational transitions

Consider a transition without change of electronic or vibrational state, i.e.  $a = \{s, v, k, m_k\}$  Assume  $v=0$  (i.e. vibrational ground state)  
 $\rightarrow b = \{s, v, k', m_{k'}\}$

For simplicity assume di-atomic molecule, but n.n. homonuclear, e.g. CO  $\text{O}=\text{C}$   $[0,1,2,2,0]$

Also move to a ket notation for the total state

$$\Psi_a(\vec{R}, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \Phi_s(\vec{R}, \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \frac{\mathcal{F}_{v,0}^s(R)}{R} \mathcal{X}_{k, m_k}(\theta, \varphi)$$

$$\downarrow$$

$$|\Psi_a\rangle = |s, v, k, m_k\rangle = |s\rangle |v, k, m_k\rangle$$

↑ electrons      ↑ nuclei

We now see  $\vec{D}_{ba} = \langle \Psi_b | \vec{D} | \Psi_a \rangle = \langle v, k', m_{k'} | \langle s | \vec{D} | s \rangle | v, k, m_k \rangle$   
 $= \vec{D}_s(\vec{R})$   
using Eq. (4.21)

$$= \int \mathcal{X}_{k', m_{k'}}^*(\theta, \varphi) \left( \int_0^\infty dR |\mathcal{F}_{v,0}^s(R)|^2 \vec{D}_s(R) \right) \mathcal{X}_{k, m_k}(\theta, \varphi) d\Omega$$

$\approx \vec{D}_s(\vec{R}_0)$  Dipole moment at equilibrium configuration

(4.23) (explain w. picture)

$\Rightarrow$  only molecules with permanent dipole moment can have purely rotational transition at  $\vec{R}_0$

The remaining integration in (4.23) over  $d\Omega$  gives as for hydrogen atom

Rotational selection rules:

$$(\Delta L = 0)$$

$$\Delta K = \pm 1$$

$$\Delta m_k = 0, \pm 1$$

$$(4.24)$$

• photon absorption implies angular momentum change by  $\pm 1$  through angular momentum conservation.

From Eq. (4.17) we find that photon energies of matching a rotational transition are

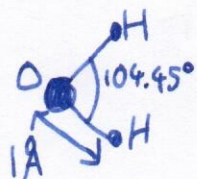
$$\Delta E = E_{rot}(K+1) - E_{rot}(K) = \frac{\hbar^2}{MR_0^2} (K+1) = \frac{\hbar^2}{2I} (K+1) \quad (4.2)$$

↑ di-atomic      ↑ more general

### Examp @: Microwave-Oven:

These operate typically at  $\sim \nu_m = 2.4 \text{ GHz} \rightarrow \lambda = 12 \text{ cm}$

Consider a water-molecule: As seen on p.75 it has  $|\vec{D}|_{\text{on}} \neq 0$  and can thus undergo purely rotational transitions



Moment(s) of Inertia

$$I \approx 2 \cdot 10^{-47} \text{ kg m}^2$$

$$\Rightarrow \Delta E = \frac{\hbar^2}{2I} K(K+1) = E_0$$

$$\lambda = \frac{hc}{E_0} = 0.7 \text{ mm} \quad \nu = \frac{E_0}{h} = 420 \text{ GHz}$$

Since rotations are the lowest energy excitations  $\nu_m$  is closest to these & oven excites rotations.

Why aren't we going onto rotation resonance? [Food opaque resonator design]

### 4.7.2 RO-vibrational transitions

Next consider the slightly more general transition

$$a = \{s, \nu, k, m_k\} \rightarrow b = \{s, \nu', k', m_{k'}\}, \quad \nu \neq \nu'$$

where also the vibrational state can change

$$\text{As before we can write } \vec{D}_{ba} = \langle \psi_b | \vec{D} | \psi_a \rangle = \langle \nu' k' m_{k'} | \vec{D}_s(\vec{R}) | \nu k m_k \rangle$$

Let us expand the dipole moment around the equilibrium position.

$$\vec{D}_s(\vec{R}) \approx \vec{D}_s(\vec{R}_0) + \underbrace{\left( \frac{\partial \vec{D}_s(\vec{R})}{\partial \vec{R}} \right)}_{\substack{\text{Fix this for 3D} \\ \text{with } \nu' \nu}} (\vec{R} - \vec{R}_0) + \dots \quad (4.26)$$

Insertion into "(4.23)" gives

$$\vec{D}_{ba} = \int d\Omega e^{i(\theta, \varphi)} \left( \int_0^\infty F_{\nu' k'}^*(R) \left( \vec{D}_s(\vec{R}_0) + \frac{\partial \vec{D}_s(\vec{R})}{\partial \vec{R}} (\vec{R} - \vec{R}_0) \right) F_{\nu k}(R) dR \right) d\Omega$$

Only since  $F_{\nu' k'} F_{\nu k}$  orthonormal (=0 here)

If  $\vec{D}_s$  constant (indep of  $\vec{R}$ ) this and all h.o.t. vanish. (4.27)

$\Rightarrow$  only molecules where the dipole-moment changes as a function of  $\vec{R}$  (as "a function of vibrations") can have purely ro-vibrational transitions (without electronic state change  $s=s'$ )

If  $\frac{\partial}{\partial R} \vec{D}_S(R)$  non zero, integration over  $R$  and angles gives

ro-vibrational selection rules (harmonic vibrations)

$$(L > 0) \quad \Delta v = \pm 1 \quad \Delta K = \pm 1 \quad \Delta m_K = 0, \pm 1 \quad (4.28)$$

To see  $\Delta v = \pm 1$  use oscillator states for  $F_v(R)$  and use  $2x H_v(x) = 2v H_{v-1}(x) + H_{v+1}(x)$  [ $H_v(x)$  Hermite polynomial]

We still need a change of rotational state  $\Delta K = \pm 1$  for angular momentum conservation (vibration does not directly affect angular momentum)

Deviations from (4.28) happen due to  
 - higher than linear (in  $(R-R_0)$ ) terms in (4.27)  
 - Anharmonicity of  $E_S(R)$ , see comment below (4.18)

These then weakly allow  $\Delta v = \pm 2, \Delta v = \pm 3$  etc.

All up, photon energies matching ro-vibrational transitions are:

$$\Delta E = \underbrace{h\nu_0}_{\text{see 4.18}} + \frac{h^2}{2I}(K+1) \quad \Delta K = +1 \quad \text{R-branch} \quad (4.29)$$

$$- \frac{h^2}{2I}K \quad \Delta K = -1 \quad \text{P-branch}$$

Example: Greenhouse effect

Earth likes to shed excess energy through IR radiation around  $\lambda \approx 4-100 \mu\text{m}$

Atmosphere is mostly  $O_2, N_2$ . ~~There~~  $N_2, O_2$   $\lambda = \frac{c}{\nu_0} = 6 \mu\text{m}$   $\lambda = \frac{c}{\nu_0} = 3 \mu\text{m}$   $\uparrow$  dangerously close

These would scatter IR radiation and thus retain heat, but cannot, since  $\vec{D}_{an}(\vec{R}) = 0$  for a homonuclear molecule due to symmetry.

However:  $CO_2$  or  $CH_4$  can have  $\frac{\partial}{\partial R} \vec{D}_S(R) \neq 0$

(carbon dioxide) (methane) (even though  $D_S(R_0) = 0$ )

$\Rightarrow$  these are greenhouse gases that scatter IR radiation.

