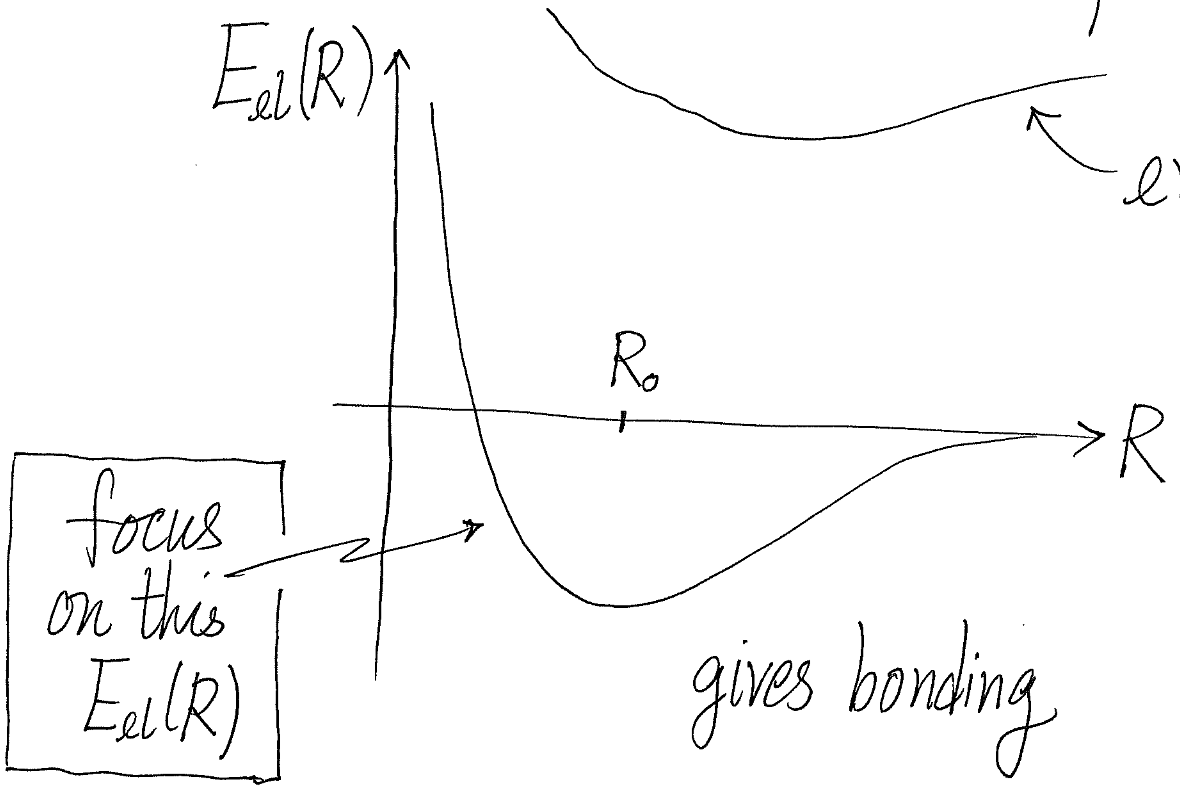
G. Including Nuclei Motions: Full Description of Molecular states

- So far, treated electronic part assuming Nuclei are fixed

$$\hat{H}_{electronic}\,\psi^{el}_{R}(\vec{r}) = E_{el}(R)\,\psi^{el}_{R}(\vec{r}) \qquad [e.g.\ H_2^+]$$

where $R = |\vec{R}_A - \vec{R}_B|$ is a parameter



even there may be higher electronic states, they are usually not important in our discussion

∵ many eV's above bonding electronic state

($kT \sim \frac{1}{40}$ eV for 300K)

But the whole problem is

$$\Big[\underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}}_{\text{ignored so far}} + \overbrace{\underset{\uparrow}{\hat{H}_{el}(R)}\Big]\psi^{el}_R(\vec{r})}^{\nearrow \text{ treated as electronic part, gives } E_{el}(R)\,\psi^{el}_R(\vec{r})}\;\psi_N(\vec{R}) = E^{(molecule)}_{total}\,\psi^{el}_R(\vec{r})\,\psi_N(\vec{R}) \qquad (33)$$

taken as a number (parameter)
[pretended R NOT to be an operator]

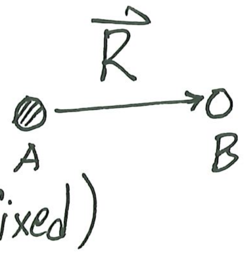
×

Consider nuclei motion

- put back $-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}$
- See $\vec{R}$ as an operator again, conjugate to $\vec{P} = \frac{\hbar}{i}\vec{\nabla}_{\vec{R}}$

$\Rightarrow$ do QM on nuclei motion

diatomic $\vec{R}$ ↗ relative coordinate



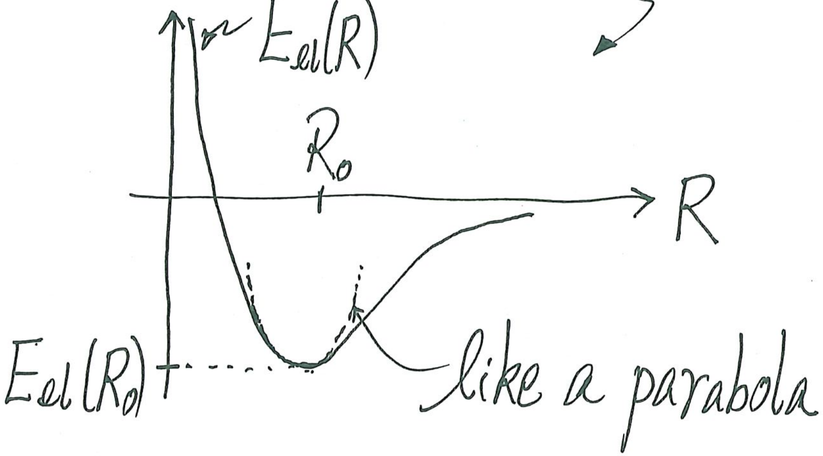
Putting back k.e. term of nuclei relative motion

$$\Big[\underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}}_{\text{ignored in Step 1}} + \underbrace{\hat{H}_{el}(R)}\Big]\underbrace{\psi^{el}_{R}(\vec{r})}\,\psi_N(\vec{R}) = E^{(molecule)}_{total}\,\psi^{el}_{R}(\vec{r})\,\overbrace{\psi_N(\vec{R})}^{\text{Wavefunction of Nuclei motion}}$$

LCAO (electronic part) gives $E_{el}(R)\,\psi^{el}_{R}(\vec{r})$

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}} + E_{el}(R)\right]\psi_N(\vec{R})\,\psi^{el}_{R}(\vec{r}) = E^{(molecule)}_{total}\,\psi_N(\vec{R})\,\psi^{el}_{R}(\vec{r})$$

[See $\vec{R}$ as operator conjugated to $\vec{P} = \frac{\hbar}{i}\nabla_{\vec{R}}$]

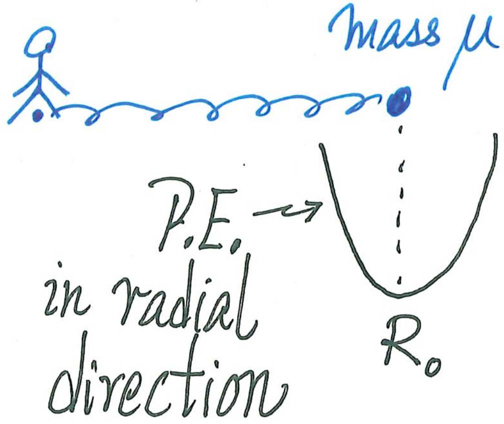


$$E_{el}(R) \approx \underbrace{E_{el}(R_0)}_{\text{a constant}} + \underbrace{\frac{1}{2}\left.\frac{d^2E_{el}(R)}{dR^2}\right|_{R=R_0}}_{\text{spring constant } k \text{ [provided by the electrons]}} \cdot (R-R_0)^2$$

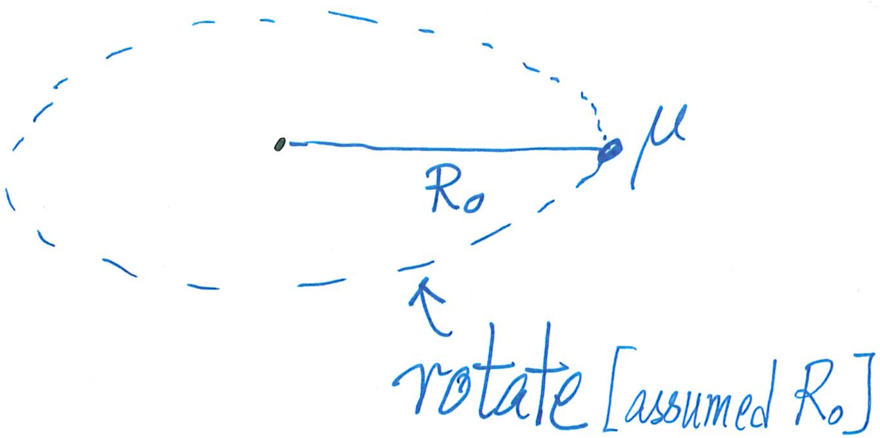
for $R \approx R_0$

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}} + \frac{1}{2}k\,(R-R_0)^2\right]\psi_N^{\nu}(\vec{R}) = \left(E^{(\text{molecule})}_{\text{total}} - E_{el}(R_0)\right)\psi_N^{\nu}(\vec{R}) \qquad (34)$$

- TISE for nuclei relative motion (3D problem)
- $U(R)$ only [not (R_x, R_y, R_z) or (R, Θ, Φ), just R; <u>spherically symmetric</u>]
- $\hat{\vec{P}}$, $\hat{\vec{R}}$ restored their operator roles (ignored in Step 1)
- Pictorially



vibrate



rotate [assumed R_0]

$\omega = \sqrt{\frac{k}{\mu}}$ is <u>normal mode frequency</u>

$$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}$$

Nuclei Wavefunction ↗

$$\psi_N(\vec{R}) = \underbrace{\phi_n(R-R_0)}_{\substack{\text{(known)}\ \text{harmonic oscillator} \\ \text{wavefunction centered at } R_0}} \cdot \underbrace{Y_{\ell m}(\Theta,\Phi)}_{\substack{\text{rotation (rigid rotor problem)} \\ \text{"partice-on-a-sphere"}}} \qquad (35)$$

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2_{\vec{R}} + \frac{1}{2}k(R-R_0)^2\right]\psi_N(\vec{R}) = \left[\left(n+\frac{1}{2}\right)\hbar\underbrace{\sqrt{\frac{k}{\mu}}}_{\omega} + \frac{\ell(\ell+1)\hbar^2}{2\mu R_0^2}\right]\psi_N(\vec{R}) \qquad (36)$$

(Done!)

- Made use of solutions to standard QM problems
- Need Eq. (35) to understand transitions between a molecular state (e.g. n, ℓ) to another molecular state (e.g. n', ℓ') (c.f. selection rules)

$$\longrightarrow \underbrace{\int \psi^*_{\text{final}}\, \overset{\text{electric dipole moment of } \underline{\text{molecule}}}{\vec{\mu}}\, \psi_{\text{initial}}\, d\tau}_{}$$

(molecular states)

$$\boxed{E_{\text{total}}^{(\text{molecule})} = E_{el}(R_0) + \left(n+\frac{1}{2}\right)\hbar\omega + \frac{l(l+1)\hbar^2}{2I}} \qquad (37) \text{ (see Eq. (34))}$$

Key Result [allowed energies for a molecule]

$$= E_{el}(R_0) + \underbrace{E_n^{vib} + E_l^{rot}}_{E^N} \qquad (38)$$

$E_{el}(R_0)$: which electronic state (lowest here)

E_n^{vib}: which vibrational level

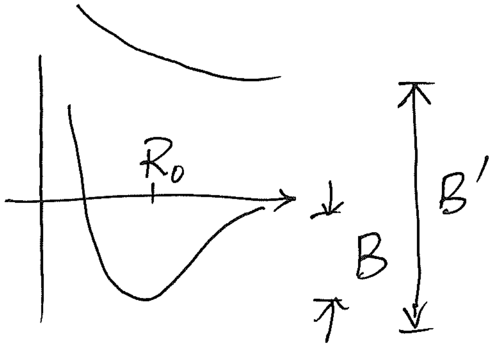
E_l^{rot}: which rotational level (degeneracy behind m)

E^N ← due to nuclei motion [new! no such terms for atoms]

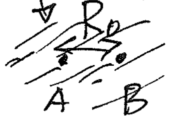
- A full specification of a molecular energy level requires:
  - which electronic state [c.f. HK or Kowloon or NT in mailing]
  - which vibrational level n [c.f. District]
  - which rotational level l [c.f. Street]

Typical Energy Scales

(i) Binding due to electrons



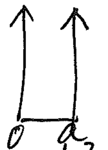
electron confined



in region characterized by R_0

m = electron mass

estimated by confinement energy $\sim \dfrac{\hbar^2}{m\underset{\substack{\uparrow\\(1\text{-}2\,\text{Å})}}{R_0^2}}$ (c.f.



$\sim \dfrac{\hbar^2}{ma^2}$ or

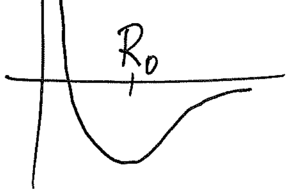
H-atom $\dfrac{\hbar^2}{ma_B^2}$)

$\sim$ a few eV [UV range]

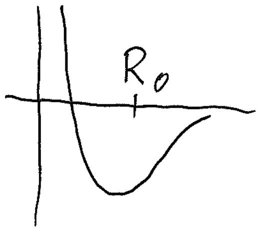
$\therefore$ $\boxed{\text{B or B' are several eV range}}$

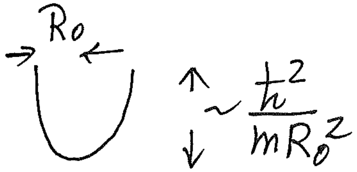
Only UV (or higher frequency) light can probe electronic transitions

IR and microwave experiments involve only



(ii) Vibrational energy scale





spring constant
↓
$$kR_0^2 \sim \frac{\hbar^2}{mR_0}$$

But $k = \mu\omega^2$ (μ = reduced mass [nucleus M_A, M_B])

↑ thousands times of m ($\mu \gg m$)

$$\mu\omega^2R_0^2 \sim \frac{\hbar^2}{mR_0^2} \Rightarrow \omega = \sqrt{\frac{\hbar^2}{\mu m R_0^4}} = \sqrt{\frac{1}{\mu m}} \cdot \frac{\hbar}{R_0^2}$$

$\hbar\omega$ = typical vibrational energy scale

$$= \sqrt{\frac{1}{\mu m}} \cdot \frac{\hbar^2}{R_0^2} = \sqrt{\frac{m}{\mu}} \cdot \left(\frac{\hbar^2}{mR_0^2}\right) = \underbrace{\sqrt{\frac{m}{\mu}}}_{\sim 10^{-2} \text{ OR } 1\%} \cdot \overbrace{[\text{several eV}]}^{E_{\text{electronic}}}$$

$$\therefore \boxed{E^{vib} \sim 0.01\,\text{eV} - 0.1\,\text{eV} \quad (\text{IR})}$$

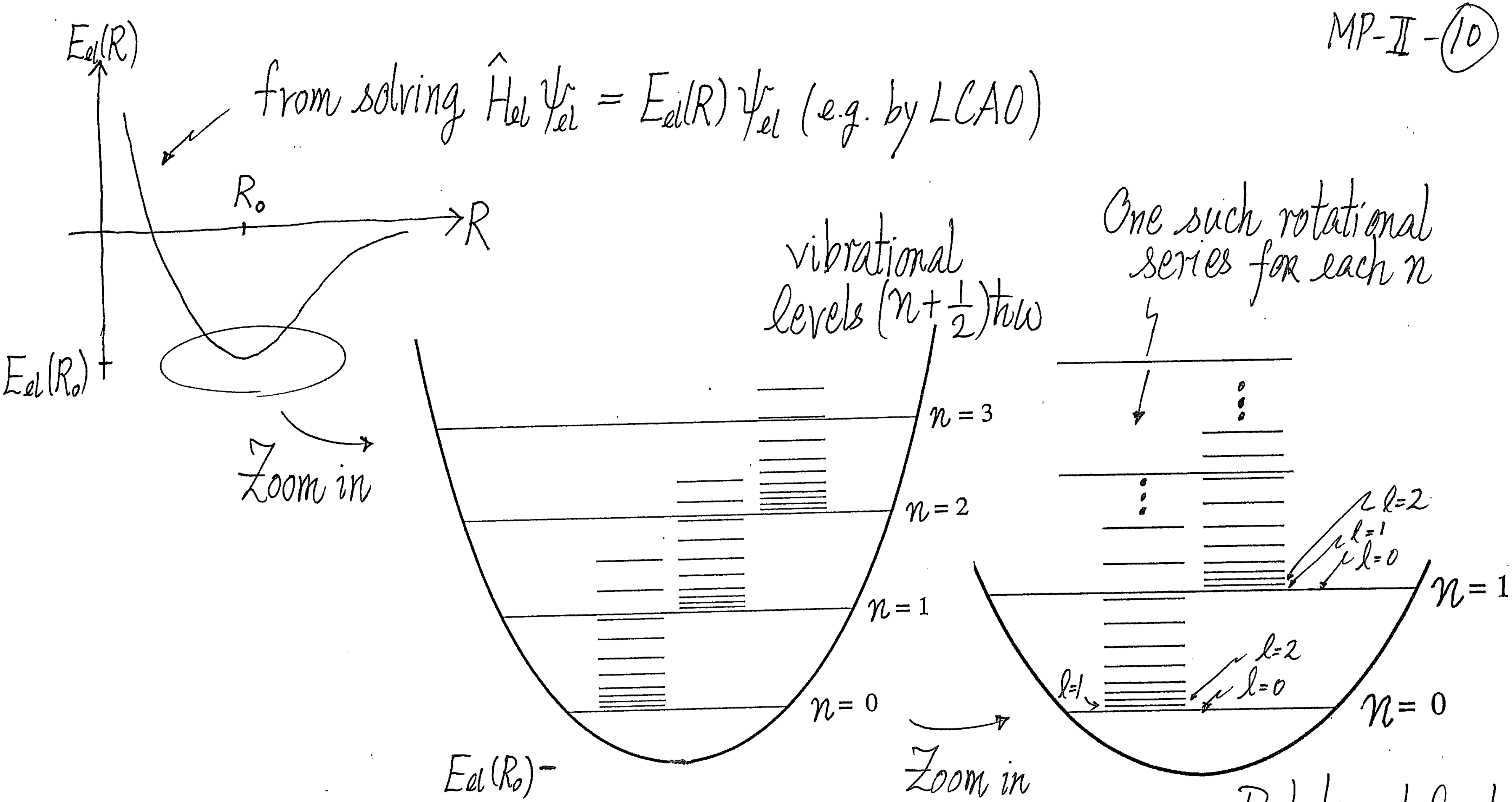
(iii) Rotational energy scale

$$E^{rot} \sim \frac{L^2}{2I} \sim \frac{\hbar^2}{2\mu R_0^2} \sim \underbrace{\underbrace{\left(\frac{m}{\mu}\right)}_{10^{-4}}}_{(1\% \cdot 1\%)} \cdot \left(\frac{\hbar^2}{mR_0^2}\right) \sim \underbrace{10^{-3} - 10^{-4}\,\mathrm{eV}}_{\text{microwave}}$$

$$\boxed{\begin{aligned} &E_{el} \sim \text{few to tens eV} \\ &E^{vib} \sim 10^{-2} \cdot E_{el} \sim 0.01 - 0.1\,\mathrm{eV} \\ &E^{rot} \sim 10^{-4} \cdot E_{el} \sim 10^{-2} \cdot E^{vib} \sim 10^{-4} - 10^{-3}\,\mathrm{eV} \end{aligned}} \qquad (39)$$

Very different energy scales

$$\text{c.f.} \quad \boxed{\text{Room temperature } 300\mathrm{K} \rightarrow \frac{1}{40}\,\mathrm{eV} \sim 0.024\,\mathrm{eV}} \qquad (40)$$

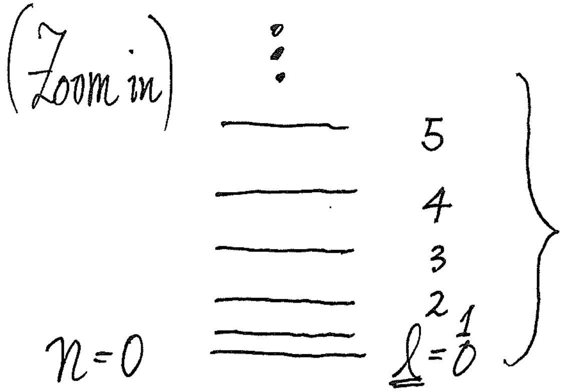


An energy diagram showing the rotational levels associated with each vibrational state in diatomic molecule.

Rotational levels
$$\frac{l(l+1)\hbar^2}{2I}$$
[each l, $(2l+1)$ values of m]
degeneracy

Picture of Key Result Eq. (37) after considering energy scales of E^{vib} and E^{rot}

- A gas of molecules at room temperature ($T \sim 300K$) [$kT \sim \frac{1}{40}$ eV]
  - Almost all of them in $n=0$ vibrational state
    [compare $\hbar\omega$ with kT, and thermal physics]
  - Molecules are <u>thermally excited</u> to occupy <u>rotational levels</u> (spread in different values of ℓ, but $n=0$) belonging to $n=0$ vibrational state



molecules occupy different values of ℓ according to thermal physics (Boltzmann factor)

Key Points:

- Rotational, Vibrational, and electronic transitions have very different characteristic energies
- Spectroscopy in different parts of EM spectrum

Regions of the Electromagnetic Spectrum and the Corresponding Molecular Processes [in units other than eV]

Region	*Frequency/Hz*	*Wavelength/m*	*Wave number/cm^{-1}*	*Energy/J·molecule^{-1}*	*Molecular process*
Microwave	10^{9}–10^{11}	3×10^{-1}–3×10^{-3}	0.033–3.3	6.6×10^{-25}–6.6×10^{-23}	Rotation of polyatomic molecules
Far infrared	10^{11}–10^{13}	3×10^{-3}–3×10^{-5}	3.3–330	6.6×10^{-23}–6.6×10^{-21}	Rotation of small molecules
Infrared	10^{13}–10^{14}	3×10^{-5}–3×10^{-6}	330–3300	6.6×10^{-21}–6.6×10^{-20}	Vibration of flexible bonds
Visible and ultraviolet	10^{14}–10^{16}	3×10^{-6}–3×10^{-8}	3300–3.3×10^{5}	6.6×10^{-20}–6.6×10^{-18}	Electronic transitions

physical sense

physical sense