D. Born-Oppenheimer Approximation

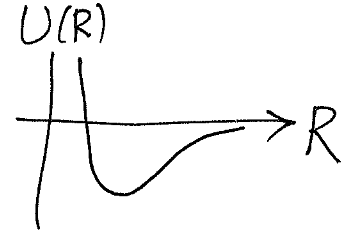
[Max Born] [J. Robert Oppenheimer]

- Made approximations to justify separation (decoupling) of $\Psi_{molecule}$ into electronic part and nuclear part

nuclei fixed with separation R

$$\Psi_{molecule}(\vec{R};\vec{r}_1,\dots,\vec{r}_N) \approx \psi_N(\vec{R})\cdot\psi_{el}(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N;\vec{R}) \qquad (7)$$

- Why is it a good approximation?
- How bonding comes out from solving ψ_{el}?
- How vibrational and rotational motions come out from $\psi_N(\vec{R})$?



Key idea

- $\underset{\substack{\uparrow \\ \text{electron}}}{m} \ll \overset{\substack{\text{nucleus} \\ \swarrow}}{\mu}$ $\qquad \frac{m}{\mu} \sim 10^{-3} \text{ to } 10^{-5} \ll 1$

time scale of nucleus motion >> time scale of electrons' motion
[slow] [fast]

⇒ for electrons, in their time scale, they "see" a potential energy function due to the nuclei as if the nuclei are fixed with a separation R

⇒ Solve Schrödinger Equation for electrons only with nuclei separated by R (with R being a parameter, not an operator any more) (8)

Meaning:

nuclei k.e. (for electronic problem, ignore for now)

$$\hat{H}_{total} \approx \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}\right)$$

$\vec{R}_A, \vec{R}_B$ are regarded fixed $\quad R = |\vec{R}_A - \vec{R}_B|$

involves electrons $\{\hat{\vec{p}}_i, \hat{\vec{r}}_i\}$ only →

$$\boxed{\begin{aligned} &+\left(\sum_{i=1}^{N}\frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_i}\right) - \sum_{i=1}^{N}\left(\frac{Z_A e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{R}_A|} + \frac{Z_B e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{R}_B|}\right) + \underbrace{\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}}_{\text{a number for fixed } R} \\ &\qquad + \sum_{i<j}\frac{e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{r}_j|}\end{aligned}}$$

$$= \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}\right) + \boxed{\hat{H}_{electronic}(\hat{\vec{p}}_1,\ldots,\hat{\vec{p}}_N;\vec{r}_1,\ldots,\vec{r}_N;R)} \qquad (9)$$

consider this only after solving $\hat{H}_{el}$ Schrödinger problem

involves only electronic variables (with R being a constant)

[Important: Will be back to Eq.(8) later]

Aside: For those who like math...

[downgraded from operator]
treated as a constant
for now

$$\hat{H} \approx \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{\underset{\uparrow}{\vec{R}}}}_{\substack{\text{nuclear separation} \\ \text{Nuclear Variables Only}}} + \hat{H}_{electronic}(\underbrace{\vec{p}_1,\ldots;\vec{p}_N;\vec{r}_1,\ldots;\vec{r}_N}_{\text{electrons' variables Only}};\overset{\downarrow}{R})$$

Separation of Variables using Eq.(7)

$$\Psi_{molecule}(\vec{R};\vec{r}_1,\ldots,\vec{r}_N) = \psi_N(\vec{R})\cdot\psi_{el}(\vec{r}_1,\vec{r}_2,\ldots;\vec{r}_N;R)$$

$$\Rightarrow \begin{cases} \text{an equation for } \psi_{el}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N;R) & \text{(bonding)} \\ \text{an equation for } \psi_N(\vec{R}) & \text{(vibrational, rotational effects)} \end{cases}$$

2-step process to solve Eq. (9)

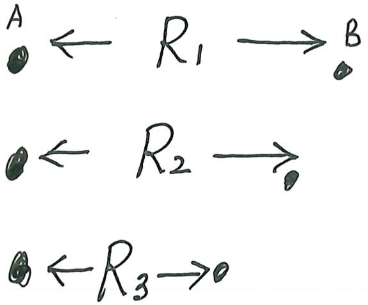
Step 1: Solve electronic part (with R as parameter)

$$\boxed{\hat{H}_{\text{electronic}}\,\psi_{el}(\vec{r}_1,\cdots,\vec{r}_N;R) = E_{\text{electronic}}(R)\,\psi_{el}(\vec{r}_1,\cdots;\vec{r}_N;R)} \quad (10)$$

- Many-electron QM problem (c.f. multi-electron atoms)

Key idea

- Which R to use? [Try different R's. One R is one problem to solve!]



and so on

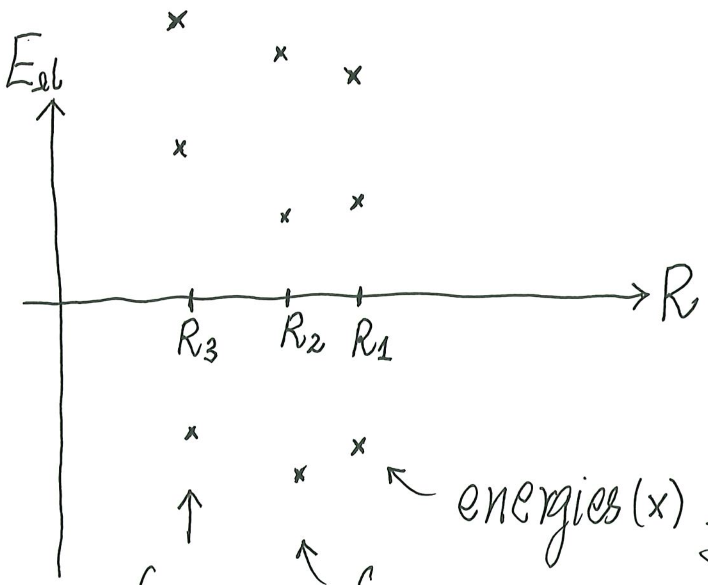
Eq. (10) gives $E_{el}(R_1)$

Eq. (10) gives $E_{el}(R_2)$

Eq. (10) gives $E_{el}(R_3)$

⋮

Each is a different QM problem for solving Eq. (10)



energies (x) $\underbrace{\text{solving Eq.(10) for } R = R_1}_{\text{Recall: Solving TISE gives many energy eigenvalues}}$

for $R = R_2$

for $R = R_3$

labels value of R used in solving TISE†

$$\hat{H}_{\text{electronic}}\,\Psi_{el}(\vec{r}_1,\dots;\vec{r}_N;\overset{\downarrow}{R}) = E_{el}\,\Psi_{el}(\vec{r}_1,\dots;\vec{r}_N;\overset{\downarrow}{R}) \tag{10}$$

↑ ↑ ↑

Different $\hat{H}_{\text{electronic}}$ ⇒ Different TISE's

Repeat calculations for many different inter-nucleus separations R

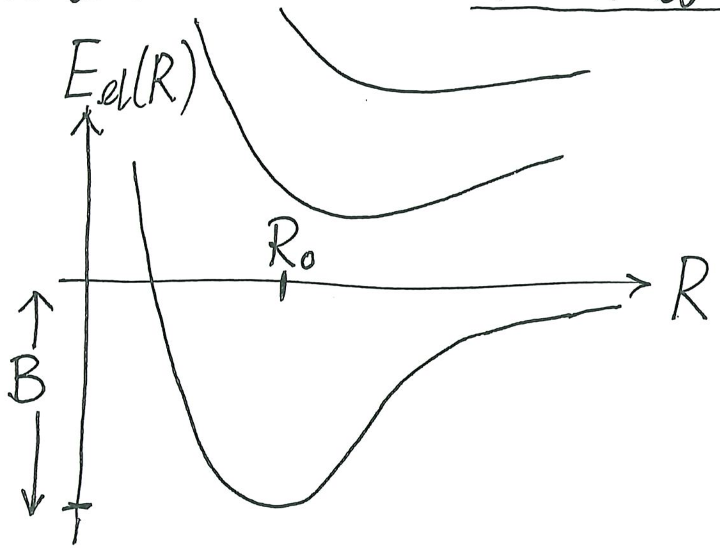
⇒ many curves $E_{el}(R)$

---

† Eq.(10) is a many-electron TISE just like atomic problems. How can we "solve" it? As in atomic problems, we need to make further approximations.

- At the end, we have how E_{el} depends on R, i.e. $E_{el}(R)$

Possibly,



shows $\underbrace{\text{preferred separation}}_{\text{bond length } R_0}$

and Binding energy B

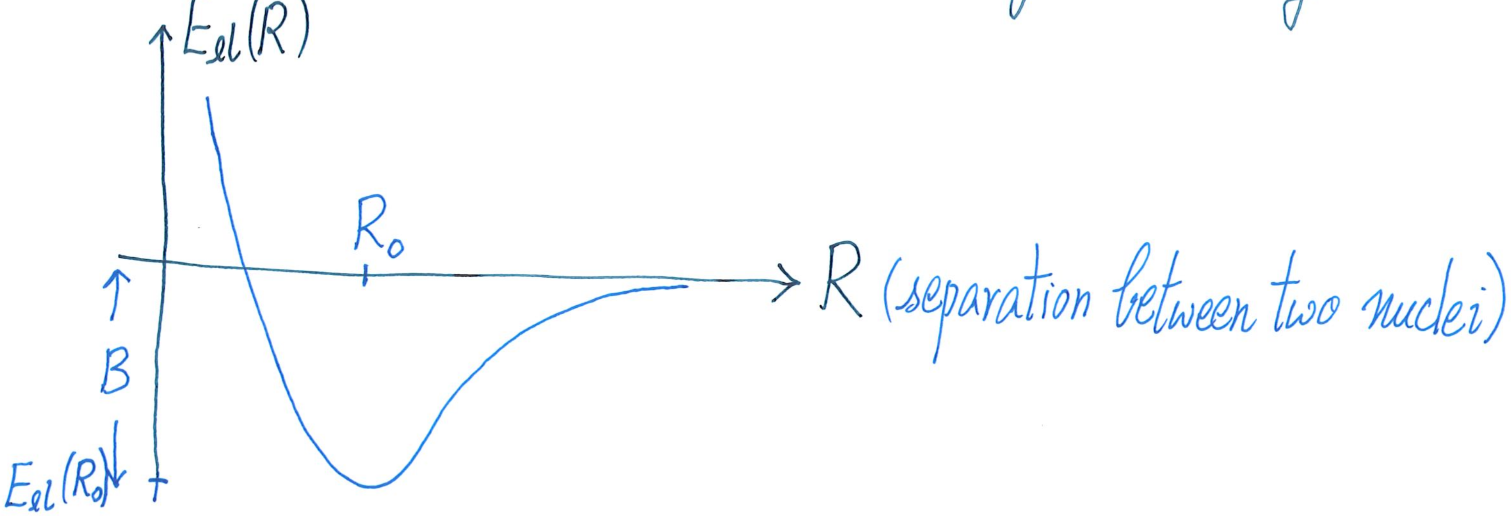
∴ Electronic problem gives the Quantum Physics of Chemical Bonds!

Q: Why does the CO (carbon monoxide) molecule have bond length 1.128 Å?

We have $\hat{H}^{(CO)}_{\text{electronic}} \to \text{TISE} \to E_{el}(R) \to R_0$

electrons behavior ($|\Psi_{el}|^2$) that selects preferred separation R_0

Due to the electrons, there emerges binding



If nuclear motion is ignored, electrons [their distribution] select a certain bond length R_0 and certain bond strength B

and energy of the molecule would be $E_{el}(R_0)$

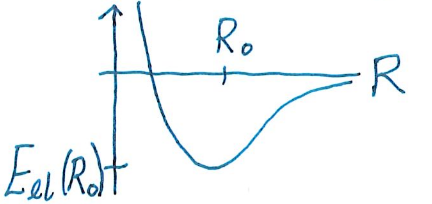
[not true]

The picture of the molecule up to here is

[no vibration, no rotation YET!]

Step 2 : Go back to $\underbrace{\hat{H}_{total}}_{\text{with } -\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}\text{ term}}$ and consider $\underbrace{\text{nuclear motion}}_{\text{new physics in molecules}}$

At this point, the electrons are done with $\underbrace{\text{their duties}}$.

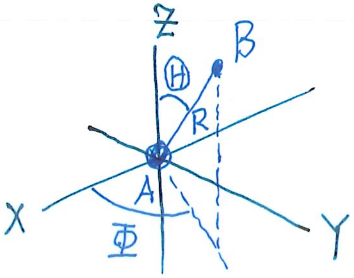


- What's left is $\underbrace{\text{the relative motion problem}}_{\text{3D One-body of mass } \mu \text{ under the influence of } E_{el}(R)}$.

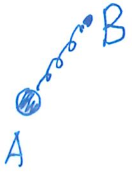
← depends on separation R only (spherically symmetric)

[Generally $\underbrace{R, \Theta, \Phi}_{\text{capital symbols used for nucleus B's coordinates}}$ of mass μ]

Picture

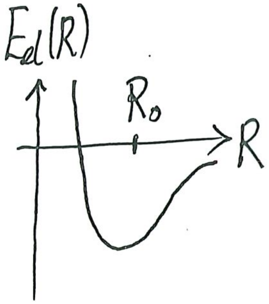


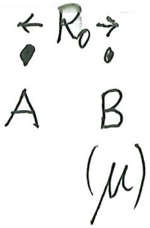
- rod could rotate



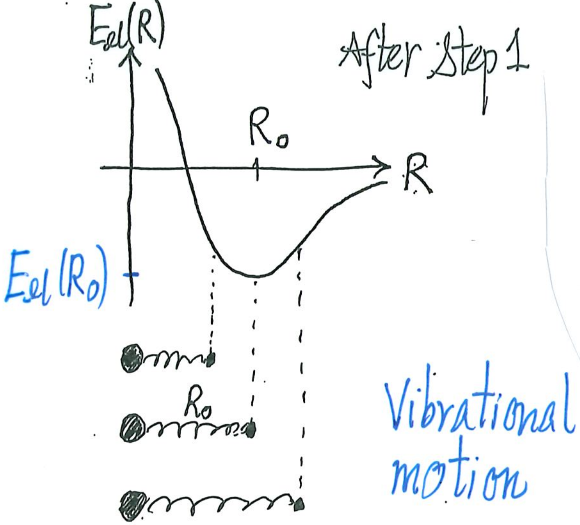
- could vibrate (radial direction)

The situation has a <u>2D analogy</u> (easier to visualize)





Radial motion is approximately harmonic oscillator



Near minimum,

$$E_{el}(R\approx R_0) = E_{el}(R_0) + \frac{1}{2}\left(\frac{d^2E_{el}}{dR^2}\right)_{E_0}(R-R_0)^2$$

$$= E_{el}(R_0) + \frac{1}{2}k\,(R-R_0)^2$$

$$k \equiv \frac{1}{2}\left(\frac{d^2E_{el}}{dR^2}\right)_{E_0}$$ (due to electrons)

R_0 = equilibrium separation (bond length)
= "natural length" of spring (bond)

"Spring Constant"?

- Curvature near R_0

stiffness of the chemical bond

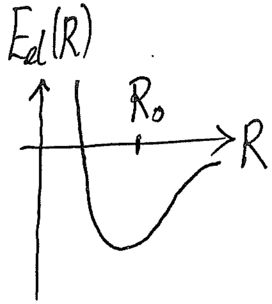
<u>QM of harmonic oscillator</u>

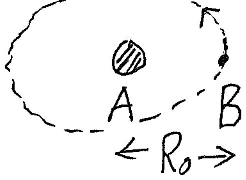
allowed energies are

$(n+\frac{1}{2})\hbar\omega$

$= (n+\frac{1}{2})\hbar\sqrt{\frac{k}{\mu}}$ (11)

2D analogy





rotational motion at the minimum (assume $R=R_0$)

Angular Motion

rotational motion

"2D rigid rotor"

means $R=R_0$

Allowed energies are

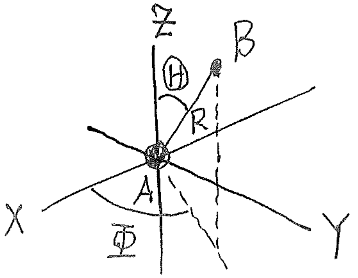
$$\frac{L^2}{2I}=\frac{L^2}{2\mu R_0^2}$$

moment of inertia

Diatomic Molecules

Angular motion is rotational motion

"3D rigid rotor"



B freely moves on sphere of radius R_0

Allowed energies are

$$\frac{\ell(\ell+1)\hbar^2}{2\mu R_0^2} \qquad (12)^{\dagger}$$

"rotational levels"

[†Chemists use $\frac{J(J+1)\hbar^2}{2\mu R_0^2}$]

At the end (Steps 1+2), an <u>allowed energy</u> <u>of a molecule</u> is specified by

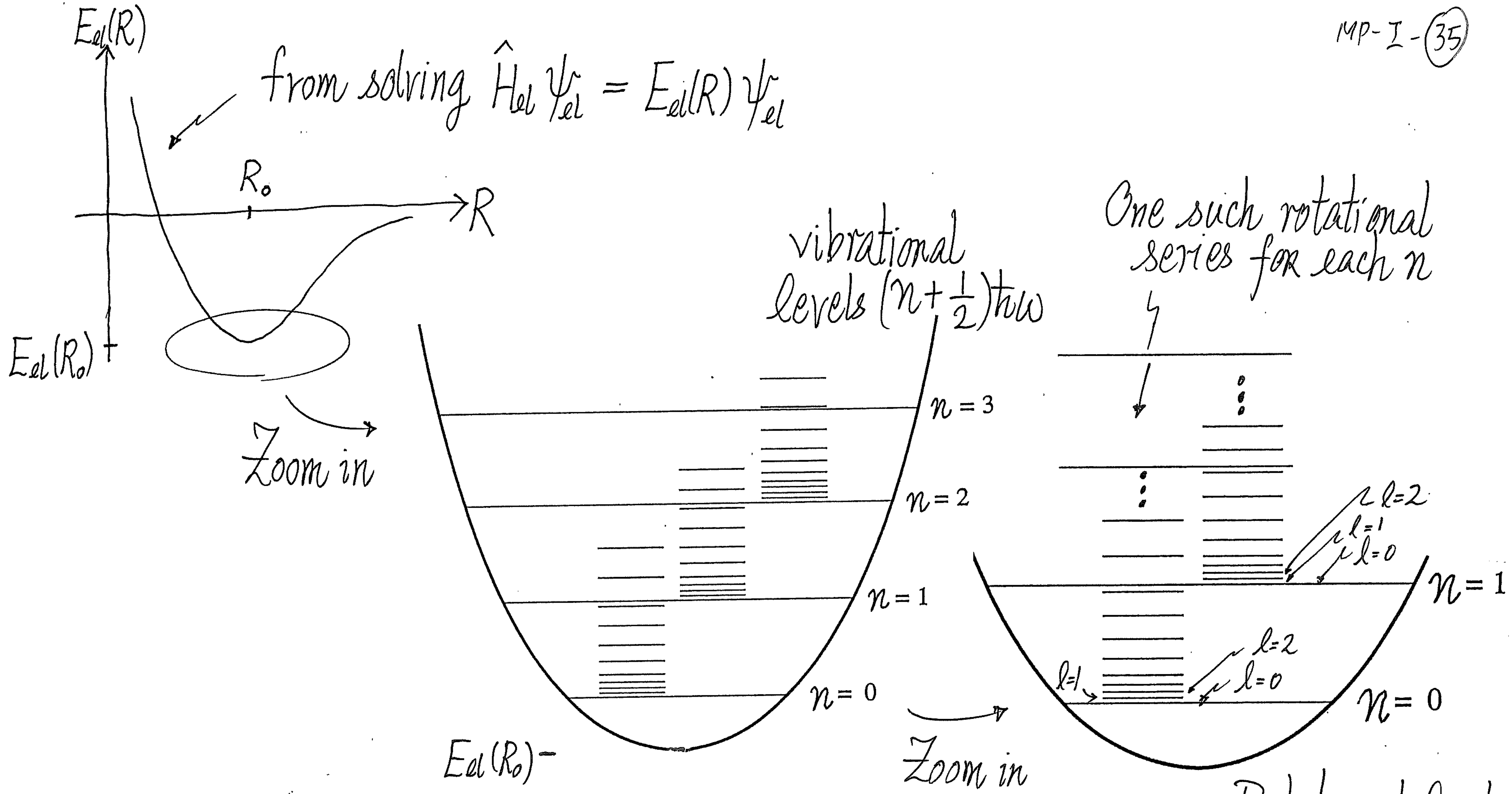
$$\boxed{E_{\text{total}}^{(\text{molecule})} = \underbrace{E_{el}(R_0)}_{\text{electronic part}} + \underbrace{\overset{\text{which vibrational state}}{\left(n+\tfrac{1}{2}\right)\hbar\omega}}_{\text{vibrational part}} + \underbrace{\overset{\text{which rotational state}}{\frac{l(l+1)\hbar^2}{2\mu R_0^2}}}_{\text{rotational part}}} \qquad (13)$$

[Key result without going through the mathematics!]

① electrons bind the atoms at set the scale of the binding $E_{el}(R_0)$, the spring constant k (thus ω) and equilibrium bond length R_0 for...

② ... the vibrational motion of the nuclei with $\omega = \sqrt{\frac{k}{\mu}}$ ...

③ ...and the rotational motion of the nuclei



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

Picture of Key Result Eq. (13)

Rotational levels

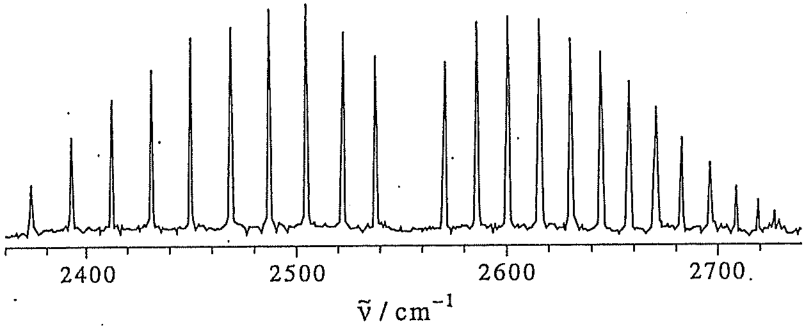
$$\frac{\ell(\ell+1)\hbar^2}{2I}$$

[each ℓ, $(2\ell+1)$ values of m]
degeneracy

Experimental consequences

- Transitions between one molecular state $[n, l]$ to another state $[n', l']$ give finger-print molecular spectrum of the molecule

IR range



Rotational-vibrational Spectrum of HBr

[Questions: Get R_0 and $\omega = \sqrt{\frac{k}{\mu}}$ out from spectrum?]

- Must understand the physical picture behind Born-Oppenheimer approximation first, before going into more detail
- It is important also because the <u>same physics</u> works in understanding <u>solids</u>. ["Solid is just a huge molecule"]
- Eq.(13) is the key result for understanding molecular spectrum [c.f. atomic spectra motivated the development of QM]
- This ends the discussion on the <u>Big Picture</u> of the QM theory of molecular states