D. Born-Oppenheimer Approximation

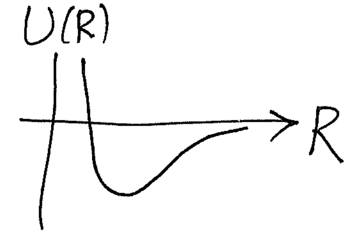
[Max Born] [J. Robert Oppenheimer]

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

nuclei fixed with separation R

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

- 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

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

$$\underset{\text{[slow]}}{\text{time scale of nucleus motion}} \gg \underset{\text{[fast]}}{\text{time scale of electrons' motion}}$$

⇒ 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)

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

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

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

$$+\left(\sum_{i=1}^{N}\frac{-\hbar^2}{2m}\nabla_{\vec{r}_i}^2\right) - \sum_{i=1}^{N}\left(\frac{Z_A e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{R}_A|} + \frac{Z_B e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{R}_B|}\right) + \underbrace{\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}}_{\text{a number for fixed } R}$$

$$+\sum_{i<j}\frac{e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{r}_j|}$$

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

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...

$$\hat{H} \approx \underbrace{-\frac{\hbar^2}{2\mu}\nabla^2_{\underset{\substack{\uparrow\\ \text{nuclear separation}}}{\vec{R}}}}_{\text{Nuclear Variables Only}} + \hat{H}_{\text{electronic}}(\underbrace{\vec{p}_1,\ldots;\vec{p}_N;\vec{r}_1,\ldots,\vec{r}_N}_{\text{electrons' variables Only}};\overset{\substack{\text{[downgraded from operator]}\\ \text{treated as a constant}\\ \text{for now}\\ \downarrow}}{R})$$

Separation of Variables using Eq.(9) and

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

$\Rightarrow$ an equation for $\psi_{el}(\vec{r},\vec{r}_2,\ldots,\vec{r}_N;R)$ (bonding) [see Eq.(10)]

an equation for $\psi_N(\vec{R})$ (vibrational, rotational effects)

2-step process to solve Eq.(9)

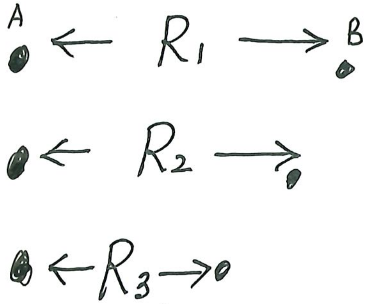
Step 1: Solve electronic part (with R as parameter)

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

- 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 $E_{el}(R_2)$

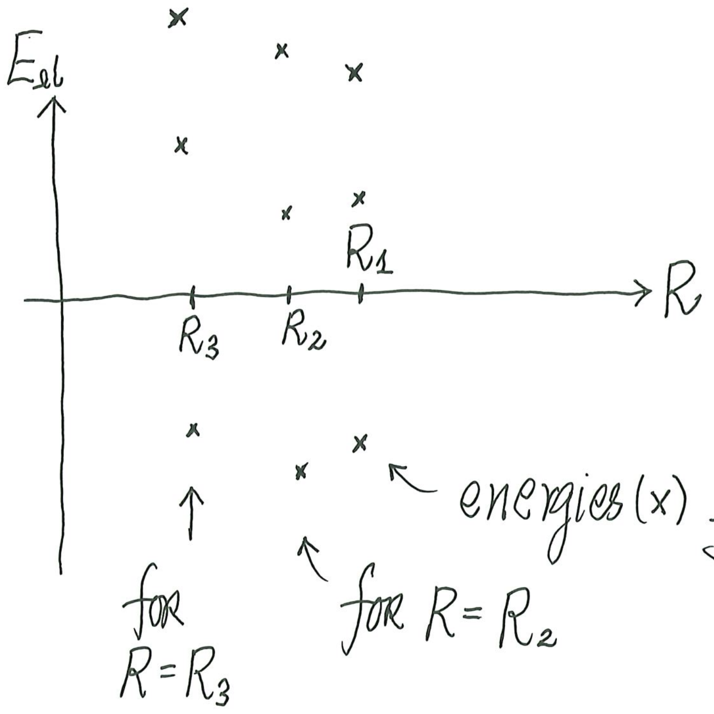
Eq.(10) gives $E_{el}(R_3)$

⋮

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

labels value of R used in solving TISE[†]

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



energies (x) $\underbrace{\text{solving Eq.(10) for } R=R_1}$

Recall: Solving TISE gives many energy eigenvalues

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

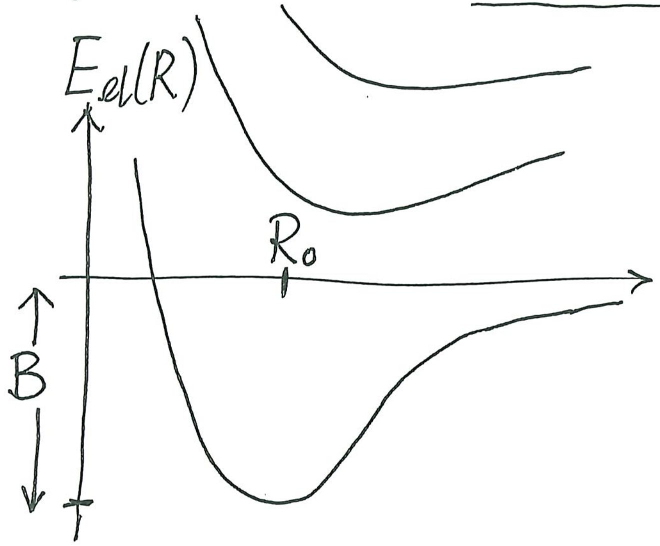
Repeat calculations for many different inter-nucleus separations R

⇒ 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

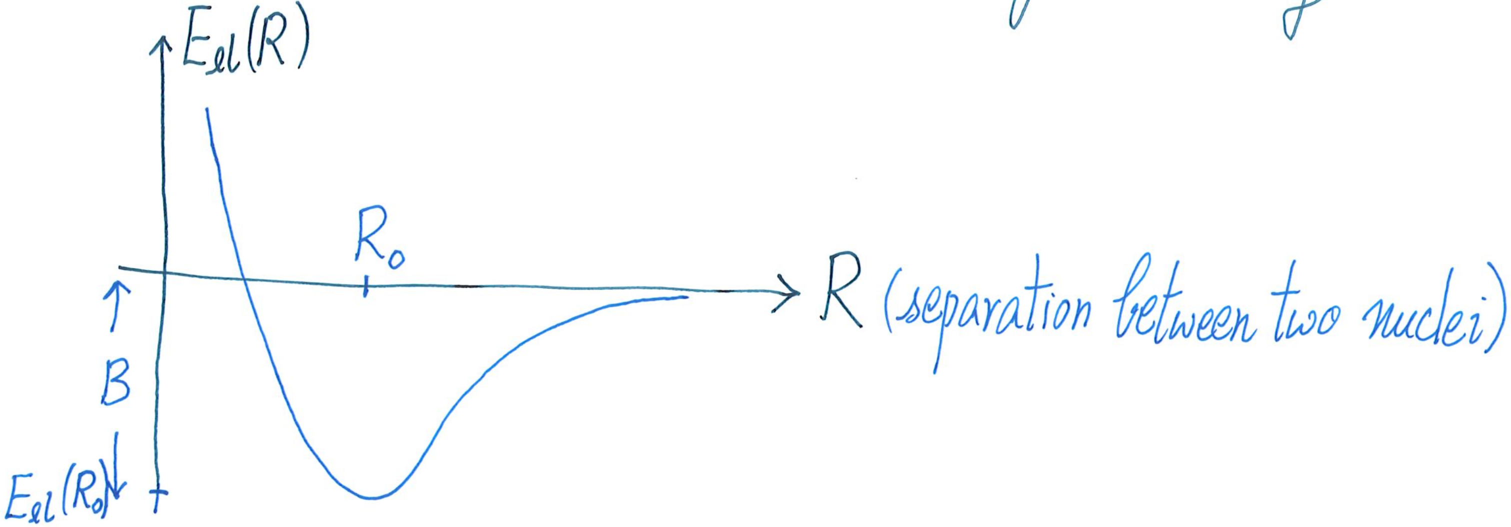
∴ $\boxed{\text{Electronic problem gives the Quantum Physics of Chemical Bonds!}}$

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

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

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 $E_{el}(R_0)$

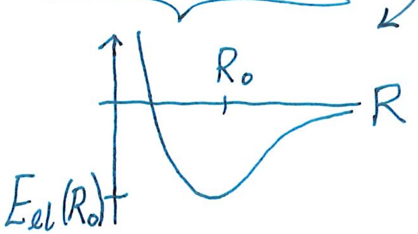
[not true]

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 $\underbrace{\text{their duties}}$.



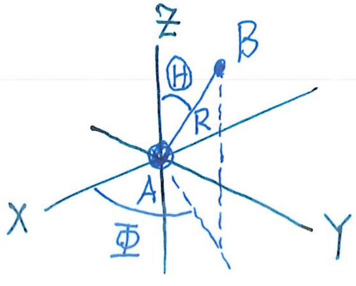
- What's left is $\underbrace{\text{the relative motion problem}}$.

$\underline{\text{3D}}$ $\underline{\text{One}}$-body of $\underline{\text{mass}}$ $\underline{\mu}$ under the influence of $E_{el}(R)$

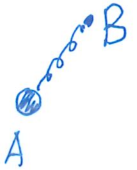
↖ depends on $\underline{\text{separation}}$ R $\underline{\text{only}}$ (spherically symmetric)

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

Picture



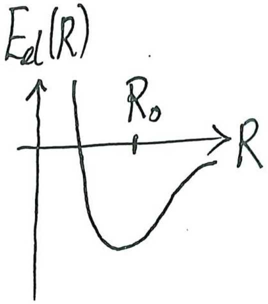
- rod could rotate

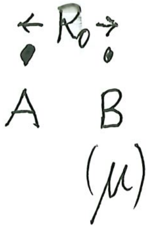


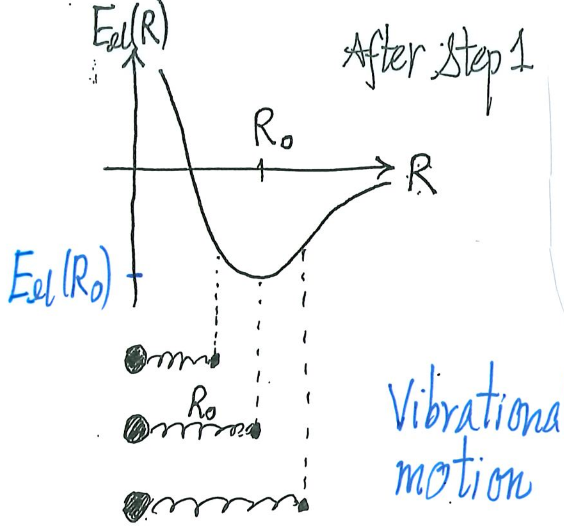
- could vibrate (radial direction)

The situation has a 2D analogy (easier to visualize)

Radial motion is approximately harmonic oscillator







Vibrational motion

Near minimum,

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

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

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

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

stiffness of the chemical bond

"Spring Constant"?

- Curvature near R_o

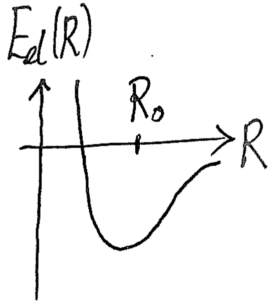
<u>QM of harmonic oscillator</u>

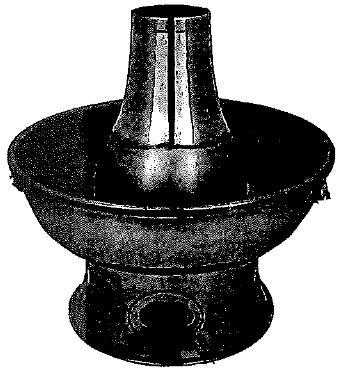
allowed energies are

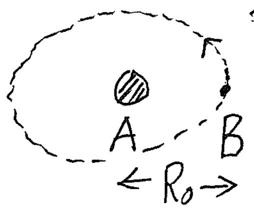
$$\left(n+\frac{1}{2}\right)\hbar\omega$$

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

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

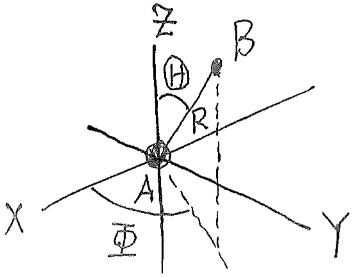
$$\frac{L^2}{2I} = \frac{L^2}{2\mu R_0^2}$$

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

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

"rotational levels"

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

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

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

[Key result without going through the mathematics!]

↑ ①

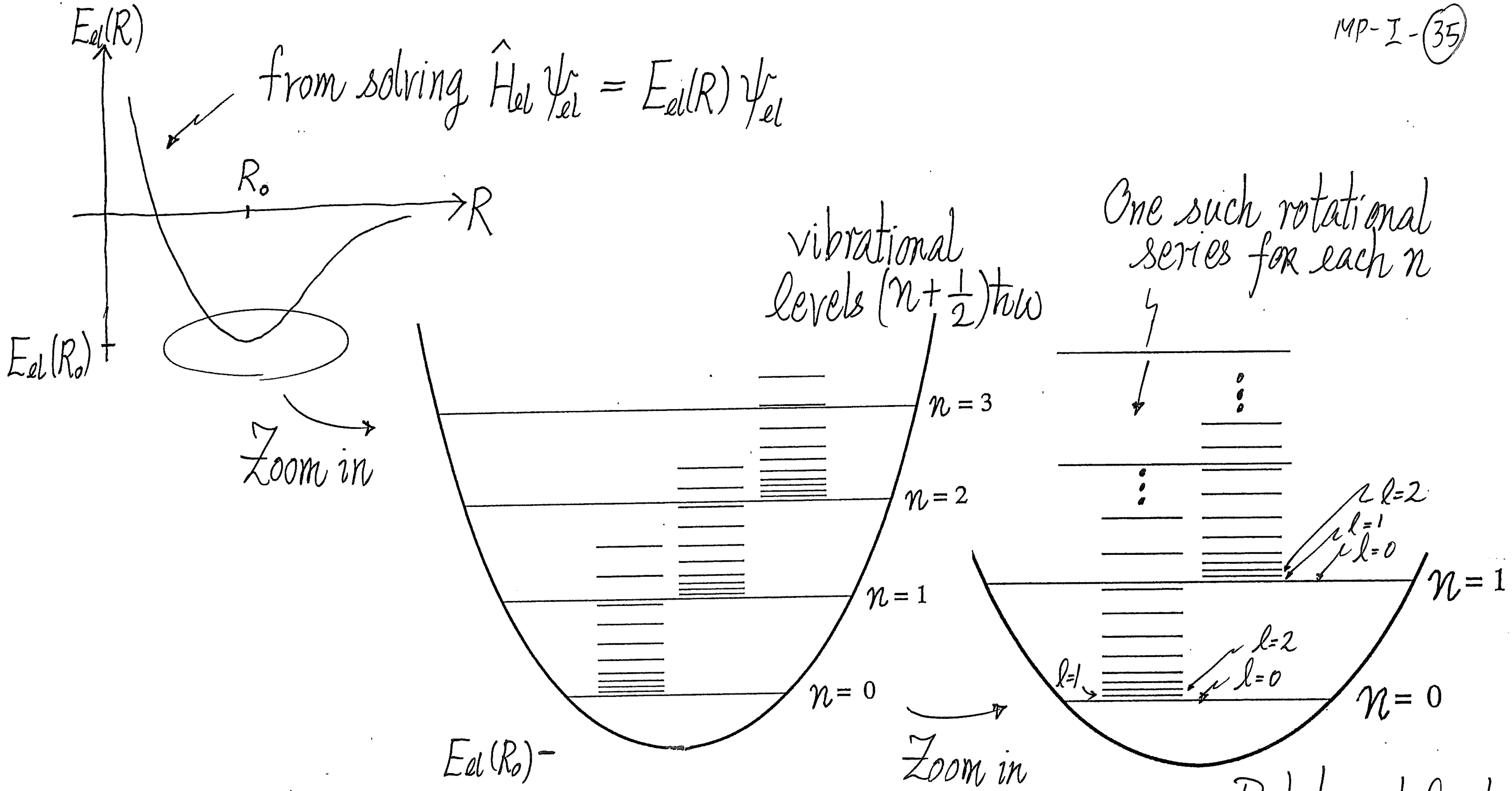
electrons bind the atoms at set the scale of the binding $E_{el}(R_0)$, the spring constant k (thus ω) and equilibrium bond length R_0 for...

↑ 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

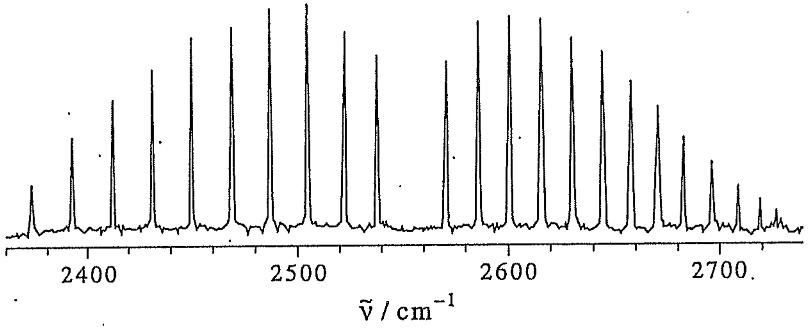
$$\frac{l(l+1)\hbar^2}{2I}$$

[each l, $(2l+1)$ 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 same physics works in understanding solids. ["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 Big Picture of the QM theory of molecular states