D. Born-Oppenheimer Approximation

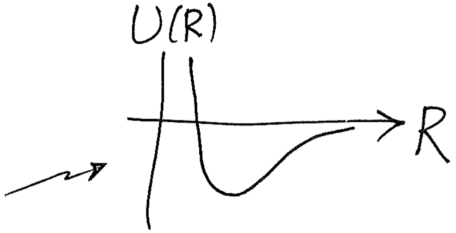
[Max Born] [J. Robert Oppenheimer]

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

nuclei fixed with separation R

$$\Psi_{molecule}(\vec{R};\vec{r}_1,\ldots,\vec{r}_N) \approx \psi_N(\vec{R})\cdot\psi_{el}(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N;\vec{R}) \quad (6)$$

- 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

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

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

$\Rightarrow$ 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

$\Rightarrow$ Solve Schrödinger Equation for electrons only with nuclei separated by R (with R being a parameter, not an operator any more) (7)

Meaning:

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

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

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

$$= \left(-\frac{\hbar^2}{2\mu}\nabla^2_{\vec{R}}\right) + \boxed{\hat{H}_{electronic}(\vec{p}_1, \ldots, \vec{p}_N; \vec{r}_1, \ldots, \vec{r}_N; \underline{R})} \qquad (8)$$

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...

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

Separation of Variables using Eq. (6)

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

$\Rightarrow$ an equation for $\psi_{el}(\vec{r},\vec{r}_2,\cdots,\vec{r}_N;R)$ (bonding)

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

2-step process to solve Eq.(8)

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

$$\boxed{\hat{H}_{electronic}\, \psi_{el}(\vec{r}_1, \cdots, \vec{r}_N; R) = E_{electronic}(R)\, \psi_{el}(\vec{r}_1, \cdots, \vec{r}_N; R)} \quad (9)$$

- Many-electron QM problem (c.f. multi-electron atoms)
- Which R to use? [Try different R's. <u>One R is one problem to solve!</u>]

$\bullet \leftarrow R_1 \rightarrow \bullet$ Eq.(9) gives $E_{el}(R_1)$

$\bullet \leftarrow R_2 \rightarrow \bullet$ Eq.(9) gives $E_{el}(R_2)$

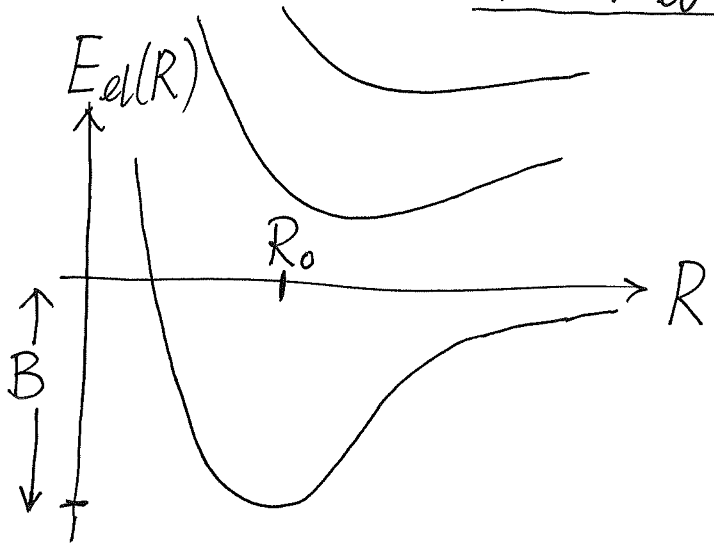
$\bullet \leftarrow R_3 \rightarrow \bullet$ Eq.(9) gives $E_{el}(R_3)$

and so on $\vdots$

Each is a different QM problem for solving Eq.(9)

- 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!

The resulting electronic states are called Molecular Orbitals (MOs)

Is this a sensible expectation?

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

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

$$\hat{H}_{total} \approx \left(-\frac{\hbar^2}{2\mu}\nabla_{\vec{R}}^2\right) \boxed{+ \left(\sum_{i=1}^{N} \frac{-\hbar^2}{2m}\nabla_{\vec{r}_i}^2\right) - \sum_{i=1}^{N}\left(\frac{Z_A e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{R}_A|} + \frac{Z_B e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{R}_B|}\right)_{①} + \underbrace{\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}}_{②\ \text{a number for fixed } R} + \sum_{i<j}\frac{e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{r}_j|}\ ③}$$

$\hat{H}_{electronic} \rightarrow$

$$= \left(-\frac{\hbar^2}{2\mu}\nabla_{\vec{R}}^2\right) + \boxed{\hat{H}_{electronic}(\vec{p}_1, \cdots, \vec{p}_N; \vec{r}_1, \cdots, \vec{r}_N; R)} \qquad (7)$$

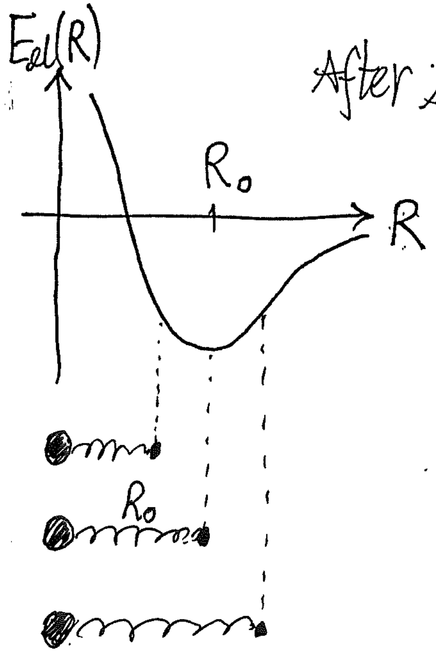
- Term ①: electrons can stablize a molecule by attractive Coulomb interactions of nuclei
- Term ②: Repulsive term between nuclei destablizes molecule
- Term ③: el-el repulsive term destablizes molecule

- larger R: ① [bad] ② [good] ③ [good]
- smaller R: ① [good] ② [bad] ③ [bad]

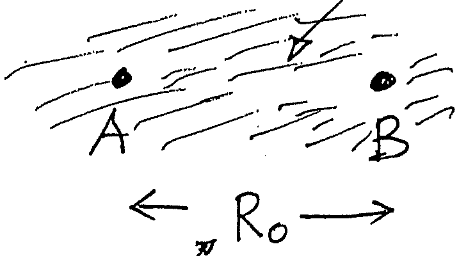
Existence of preferred separation R_0?

[Remark: The story is richer than this! There is a QM part in it.]

Step 2 : Go back to Eq.(8) and consider Nuclei Motion



After Step 1



electron distribution binds atoms to form molecule

equilibrium separation (bond length)

"bond" $\boxed{\text{(due to electrons)}}$

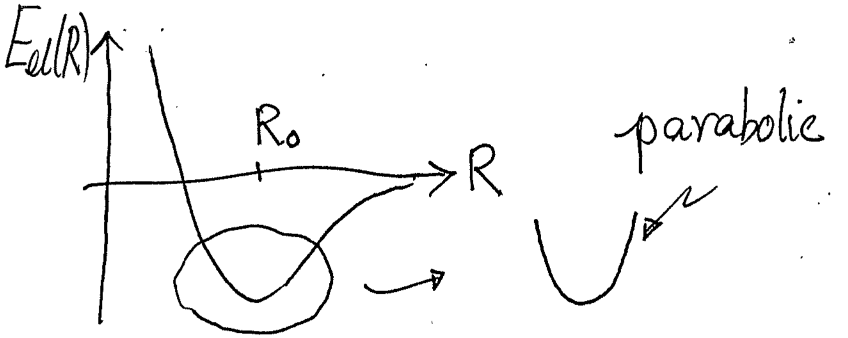
Key Concept emerged from Step 1

Answer to "What is the spring?"

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

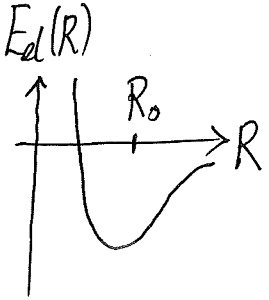
"Spring Constant"?

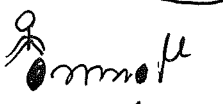
- Curvature near R_0



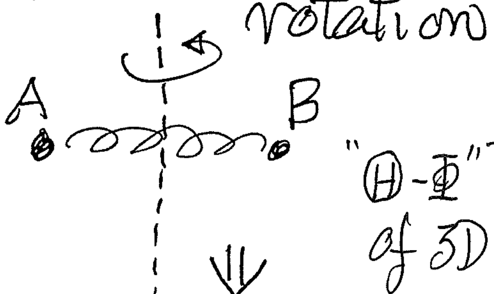
spring constant k $\left[\overset{c.f.}{\frac{1}{2}k(R-R_0)^2}\right]$

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





[reduced mass μ]



vibrational motion

⇓

vibrational states

(harmonic oscillator)

"R"-part of 3D problem

"Θ-Φ" Part of 3D problem

⇓

rotational motion

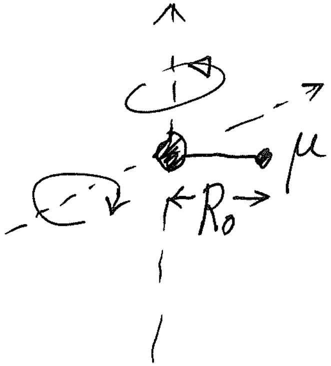
⇓

rotational states

$$(n+\tfrac{1}{2})\hbar\omega = (n+\tfrac{1}{2})\hbar\sqrt{\frac{k}{\mu}} \quad (9)$$

$$\text{energy} = \frac{L^2}{2I} = \frac{\ell(\ell+1)\hbar^2}{2\mu R_0^2} \quad (10)$$

(3D rigid rotor)

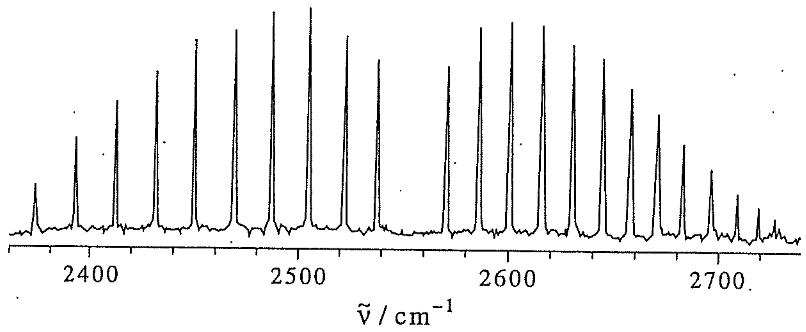


At the end (Steps 1+2), an allowed energy of a molecule is specified by

$$\boxed{E_{total}^{(molecule)} = \underbrace{E_{el}(R_0)}_{\text{electronic part}} + \underbrace{(\overset{\text{which vibrational state}}{n}+\tfrac{1}{2})\hbar\omega}_{\text{vibrational part}} + \underbrace{\frac{\overset{\text{which rotational state}}{l}(l+1)\hbar^2}{2\mu R_0^2}}_{\text{rotational part}}} \qquad (11)$$

[Key result without going through the mathematics!]

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



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.(11) 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