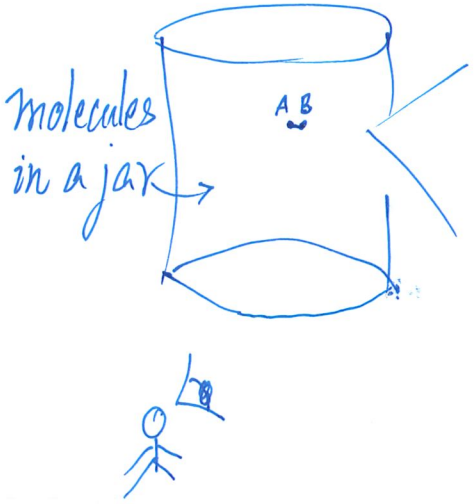
C. Quantum Mechanical Problems of Molecules are hard to solve

- Can't solve simplest molecular problem H_2
- Beauty of developing approximations

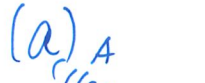
Diatomic "AB" molecules ["simplest" problems]

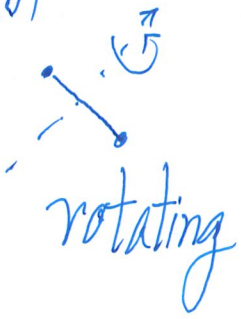


electrons' $|\psi|^2$ (responsible for bonding)

(i)  molecule is moving as a whole [CM is moving] (transitional k.e. in statistical physics)

(ii) Molecules have internal motions

(a)  vibrating!

(b)  rotating

 rotation axis pointing at you

In reality, everything happens at the same time!

molecule flying in the room, vibrating and rotating as it flies!

[Remark: This is the part that gives

$U = \frac{3}{2} N k T$

in statistical physics of (ideal) gas]

In QM: Don't worry about it!

Why? CM motion is free motion

Focus on relative motion

c.f.: Didn't worry about H-atom moving around

QM problems

"bond length"

Schrödinger Eq. for electrons

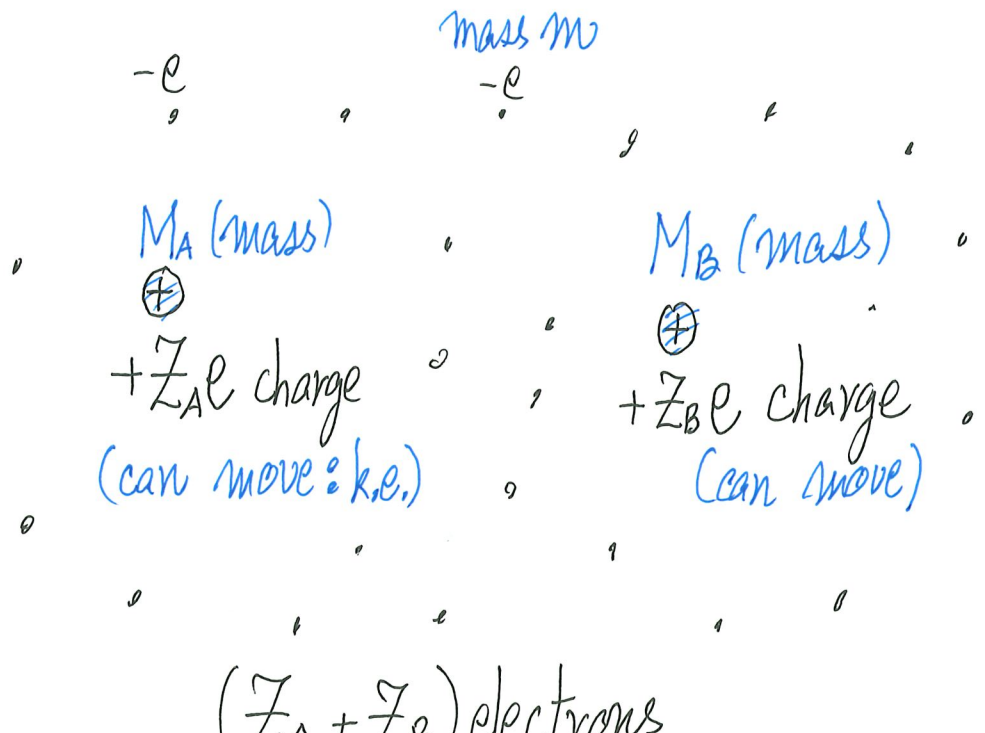
$\Rightarrow$ preferred separation R_0?

((O——(N•))

QM of oscillator

QM of (3D) rotor

Diatomic "AB" Molecules



$(Z_A + Z_B + 2)$-body problem

Hamiltonian includes:

- k.e. of nuclei
- k.e. of electrons
- Each electron sees A
- Each electron sees B
- Electron-electron repulsion
- Nucleus-nucleus repulsion

- We know the Hamiltonian and the governing Equation (TISE)
- $\hat{H}\Psi = E\Psi$ is hard to solve $\Rightarrow$ Needs approximations to proceed

Full Hamiltonian of "AB" molecule

$$\hat{H} = \underbrace{\left[\frac{-\hbar^2}{2M_A}\nabla^2_{\vec{R}_A} - \frac{\hbar^2}{2M_B}\nabla^2_{\vec{R}_B}\right]}_{\text{k.e. of nuclei A \& B}} + \underbrace{\sum_{i=1}^{N=(Z_A+Z_B)}\left(\frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_i}\right)}_{\text{k.e. of } Z_A+Z_B=N \text{ electrons}} + \underbrace{\frac{Z_A Z_B e^2}{4\pi\varepsilon_0|\vec{R}_A-\vec{R}_B|}}_{\text{p.e. (Coulomb repulsion) of nuclei}}$$

$$\underbrace{-\sum_{i=1}^{N}\frac{Z_A e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{R}_A|}}_{\text{electrons see nucleus A (p.e.)}} \underbrace{-\sum_{i=1}^{N}\frac{Z_B e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{R}_B|}}_{\text{electrons see nucleus B (p.e.)}} \underbrace{+\sum_{i<j\ (\text{pairs of e's})}\frac{e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{r}_j|}}_{\text{electron-electron Coulomb p.e.}} \qquad (1)$$

Z_A, Z_B = Atomic numbers (A & B) ; $\vec{R}_A, \vec{R}_B$ = positions of nuclei A & B

$\vec{r}_i$ = position of i^{th} electron ; (Z_A+Z_B+2)-body problem ((Z_A+Z_B) electrons + 2 nuclei)

Note: $\vec{r}_i$ (electrons) and $\vec{R}_A$ ($\vec{R}_B$) appear together $\Rightarrow$ Can't separate electron problem and nuclear motion problem

$$\hat{H} = \hat{H}\Big(\overbrace{\hat{\vec{P}}_A, \hat{\vec{R}}_A; \hat{\vec{P}}_B, \hat{\vec{R}}_B}^{\text{nuclei}}; \overbrace{\hat{\vec{p}}_1, \hat{\vec{r}}_1; \hat{\vec{p}}_2, \hat{\vec{r}}_2; \cdots; \hat{\vec{p}}_N, \hat{\vec{r}}_N}^{\text{electrons}}\Big)$$

$$= \hat{H}\left(\hat{\vec{P}}_A, \hat{\vec{R}}_A; \hat{\vec{P}}_B, \hat{\vec{R}}_B; \{\hat{\vec{p}}_i, \hat{\vec{r}}_i\}\right) \qquad (2)^{+}$$

Time-independent Schrödinger Equation

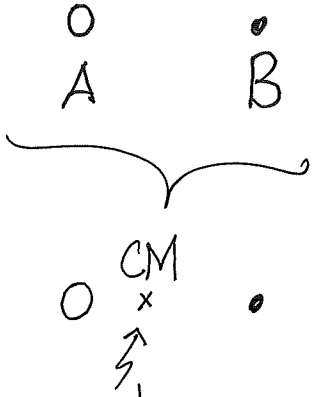
$$\hat{H}\left(\hat{\vec{P}}_A, \hat{\vec{R}}_A; \hat{\vec{P}}_B, \hat{\vec{R}}_B; \{\hat{\vec{p}}_i, \hat{\vec{r}}_i\}\right) \Psi_{molecule}\left(\vec{R}_A, \vec{R}_B; \vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N\right)$$

$$= E_{total}^{(molecule)} \Psi_{molecule}\left(\vec{R}_A, \vec{R}_B; \vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N\right) \qquad (3)$$

to solve for (many) allowed energies of a molecule $E_{total}^{(molecule)}$ and corresponding molecular state $\Psi_{molecule}$.

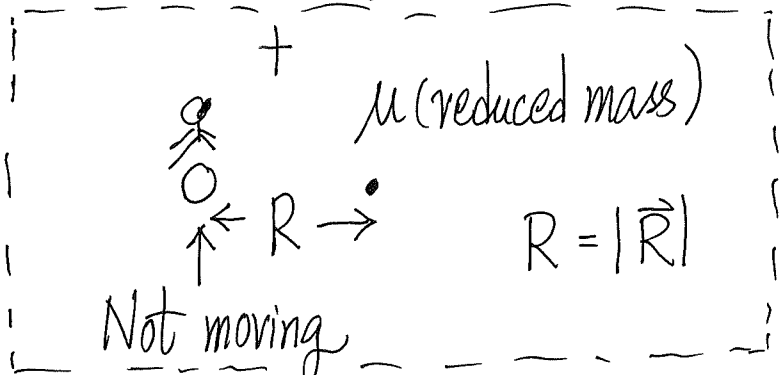
+ Atomic problems are "easier" as $\hat{H}_{atom}(\{\hat{\vec{p}}_i, \hat{\vec{r}}_i\})$ only, with the nucleus at the origin.

- Done! We have TISE (Eq.(3))! All physics has been used.
- Done? Eq.(3) can't be solved for <u>any</u> diatomic ("AB") molecule!
- Even single out the CM (center-of-mass) motion won't help!



$\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B}$; $\vec{R} = \vec{R}_B - \vec{R}_A$ (relative coordinates)

free motion of CM (not our concerns)



one less (CM) coordinate

[still $\underbrace{N(\text{electrons}) + 1(\text{relative, nucleus})}_{(N+1)\text{-body problem}}$]

Retaining relative (nuclear) motion and N ($Z_A + Z_B$) electrons

$$\hat{H}_{total} = \frac{-\hbar^2}{2\mu}\nabla^2_{\vec{R}} + \sum_{i=1}^{N}\left(\frac{-\hbar^2}{2m}\nabla^2_{\vec{r}_i}\right) + \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}$$

$$-\sum_{i=1}^{N}\left(\frac{Z_A e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{R}_A|} + \frac{Z_B e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{R}_B|}\right) + \sum_{i<j}\frac{e^2}{4\pi\varepsilon_0|\vec{r}_i - \vec{r}_j|} \qquad (4)$$

Now, TISE becomes

$$\hat{H}_{total}\,\Psi_{molecule}(\vec{R};\vec{r}_1,\cdots;\vec{r}_N) = E^{(molecule)}_{total}\,\Psi_{molecule}(\vec{R};\vec{r}_1,\cdots;\vec{r}_N) \qquad (5)$$

This is the Full Diatomic Molecule problem

Difficulties: $\frac{-\hbar^2}{2\mu}\nabla^2_{\vec{R}} = \frac{\hat{P}^2}{2\mu}$; momentum of nucleus

$\sim \frac{1}{|\vec{r}_i - \vec{R}|} = \frac{1}{|\hat{\vec{r}}_i - \hat{\vec{R}}|}$ operators! coupled!

CANNOT separate $\hat{H}_{total}$ into terms with nuclear operators only and terms with electron operators only

Implications

- $\Psi_{molecule}$ is formally $\Psi_{molecule}(\vec{R}; \vec{r}_1, \ldots, \vec{r}_N)$ — function of $\vec{R}$ (nuclear) AND $\{\vec{r}_i\}$ (electrons)

- Formally† $\Psi_{molecule}(\vec{R}; \vec{r}_1, \ldots, \vec{r}_N) \neq \underbrace{\psi_N(\vec{R})}_{\text{(Nucleus)}} \cdot \psi_{el}(\vec{r}_1, \ldots, \vec{r}_N)$ (6)

  ($\vec{r}_1, \ldots, \vec{r}_N$: electrons' coordinates only)

[† Recall: When separation of variables works]

- But it will be convenient (thus desirable) to separate nuclear and electronic parts

Key idea →

Way forward? Make the approximation that

$$\Psi_{molecule}(\vec{R}; \vec{r}_1, \ldots, \vec{r}_N) \approx \underbrace{\psi_N(\vec{R})}_{\text{vibration \& rotation (nuclear motion)}} \cdot \underbrace{\psi_{el}(\vec{r}_1, \ldots, \vec{r}_N)}_{\text{nuclei NOT moving (fixed } R\text{)}} \quad (7)$$

($\vec{r}_1, \ldots, \vec{r}_N$: electrons' coordinates only)