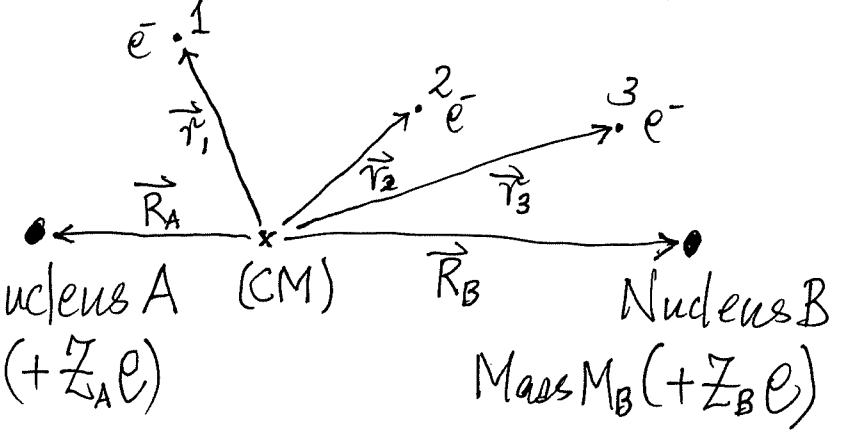
C. The Quantum Mechanical Problem of Molecules

- Realize Complexity of full QM problem of a molecule
- Appreciate the beauty of approximations that follow

Diatomic "AB" molecule ("Simplest")

(2 nuclei + (Z_A+Z_B) electrons)



Hamiltonian H

= k.e. of two nuclei (T_N)
+ k.e. of (Z_A+Z_B) electrons (T_e)
+ interaction between nuclei (p.e.)
+ interaction of electrons and nuclei (p.e.)
+ interaction between electrons (p.e.)

2 nuclei + $N(=Z_A+Z_B)$ electrons

(a many-body problem)

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

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

[$\vec{P}_A$, $\vec{P}_B$, $\vec{p}_i$'s, $\vec{R}_A$, $\vec{R}_B$, $\vec{r}_i$'s are <u>all operators</u> in $\hat{H}$]

$$\hat{H}(\hat{\vec{P}}_A, \hat{\vec{P}}_B, \hat{\vec{R}}_A, \hat{\vec{R}}_B; \{\hat{\vec{p}}_i\}, \{\hat{\vec{r}}_i\})\, \Psi_{\text{molecule}}(\vec{R}_A, \vec{R}_B; \vec{r}_1, \cdots, \vec{r}_N)$$
$$= E^{(\text{molecule})}_{\text{total}}\, \Psi_{\text{molecule}}(\vec{R}_A, \vec{R}_B; \vec{r}_1, \cdots, \vec{r}_N) \qquad (2)$$

- This is the full $(2+N)$-particle QM problem of a diatomic molecule
- Cannot be solved analytically (but know the governing Equation)

- 2-body (2-nucleus) ⇒ Center-of-Mass Motion + Relative motion of reduced mass

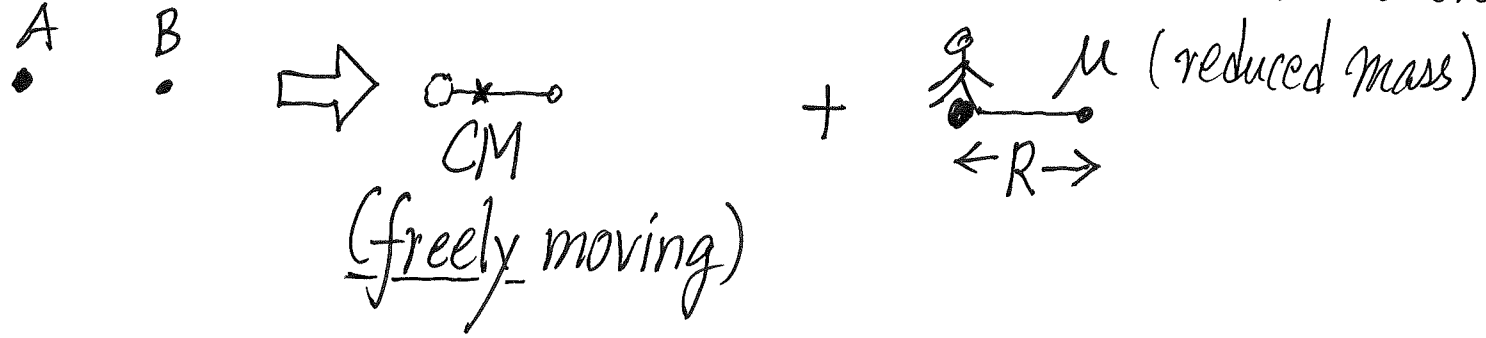
Free motion of CM

$\frac{-\hbar^2}{2(M_A+M_B)} \nabla^2_{CM}$ in $\hat{H}$ by itself

$\begin{cases} \frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B} \\ \vec{R} = \vec{R}_A - \vec{R}_B \end{cases}$

Can separate out CM motion [free] (discard from now on)

[nothing to do with bonding (electrons) and vibrational & rotational (relative) motions]



Even so, the whole molecule's <u>Hamiltonian</u> is

$$\hat{H}_{total} = \underbrace{\frac{-\hbar^2}{2\mu}\nabla_{\vec{R}}^2}_{\text{k.e. nuclei}} + \underbrace{\sum_{i=1}^{N}\left(\frac{-\hbar^2}{2m}\nabla_{\vec{r}_i}^2\right)}_{\text{k.e. electrons}} + \underbrace{\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 R}}_{\text{nucleus-nucleus}}$$

$$\underbrace{-\sum_{i=1}^{N}\left(\frac{Z_A e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{R}_A|} + \frac{Z_B e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{R}_B|}\right)}_{\text{p.e. of each electron and each nucleus}} + \underbrace{\sum_{i<j}\frac{e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{r}_j|}}_{\text{electron-electron}} \qquad (3)$$

$$\boxed{\hat{H}_{total}\,\Psi_{molecule}(\vec{R};\vec{r}_1,\cdots,\vec{r}_N) = E_{total}^{(molecule)}\,\Psi_{molecule}(\vec{R};\vec{r}_1,\cdots,\vec{r}_N)} \qquad (4)$$

"Done!"

- No exact solution (not even H_2)
- Each $\Psi_{molecule}\left[E_{total}^{(molecule)}\right]$ defines a state [energy] of a molecule

Difficulty

In Eq. (3), $\sim \frac{1}{|\vec{r}_i - \vec{R}_A|}$; $\sim \frac{1}{|\vec{r}_i - \vec{R}_B|}$; $\sim \frac{1}{|\vec{r}_i - \vec{r}_j|}$ coupled!

operators operators operators

$\Rightarrow$ $\Psi_{molecule}(\vec{R}; \vec{r}_1, \cdots, \vec{r}_N)$ is formally a function of $\vec{R}$ AND $\{\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N\}$ (electrons' coordinates) (5)

nuclei coordinates

[could also include spins of electrons and nuclei]

$\therefore$ Formally,

$$\Psi_{molecule}(\vec{R}; \vec{r}_1, \cdots, \vec{r}_N) \overset{\text{NOT true}}{\neq} \underbrace{\psi_N(\vec{R})}_{\text{[nuclei part]}} \cdot \underbrace{\psi_{el}(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)}_{\text{[electronic part]}}$$

[Strategy: We will make this approximation]

$\rightarrow$ Anti-symmetric w.r.t. interchanging coordinates of 2 electrons