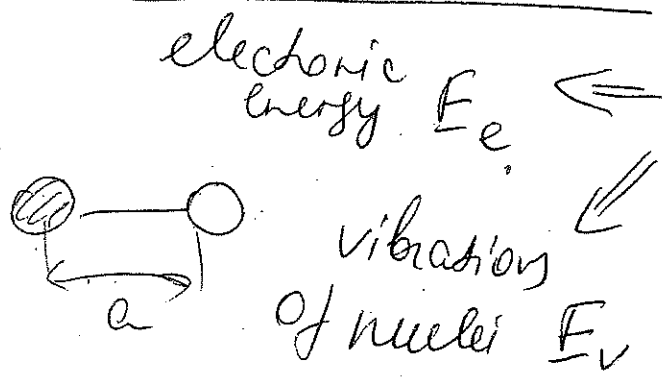


Molecular structure

Diatomic molecules



→ need to consider relative motion of not just electrons, but also nuclei

↓

rotation of nuclei E_r

Estimate:

few eV's $\Rightarrow E_e \sim \frac{\hbar^2}{2ma^2}$ ← momentum $\sim \frac{\hbar}{a}$ (delocalization $\sim a$) $\sim 1 \text{ \AA}$

\Rightarrow UV-VIS average of valence electrons

$E_v = \hbar \omega_N \sim \left(\frac{m}{M}\right)^{1/2} E_e \sim 0.1 \text{ eV}$

distance between nuclei

$\frac{M \omega_N^2 a^2}{2} \sim \frac{\hbar^2}{2ma^2} \Rightarrow \omega_N^2 \sim \frac{\hbar^2}{Mma^4} \Rightarrow \omega_N \sim \frac{\hbar}{\sqrt{M}ma^2} \sim$

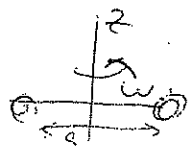
mass of nucleus

Since $\frac{m}{M} \sim 10^{-3-5}$ E_v is in IR \Rightarrow IR

$\sim \frac{\hbar^2}{ma^2} \cdot \sqrt{\frac{m}{M}} \cdot \frac{1}{\hbar}$

$E_r \sim \frac{\hbar^2}{Ma^2} \sim \frac{m}{M} E_e \sim 0.001 \text{ eV} \Rightarrow$ far IR & microwave

$\sim \frac{L^2}{2I} \leftarrow$ moment of inertia $= \frac{Ma^2}{2}$ (same nuclei)



- Ψ must be (A) under interchange of the coordinates of any pair of electrons
- if nuclei A & B are identical $\Rightarrow \Psi$ must also be either (S) or (A) under interchange of A & B

p.s. in deuterium $\Rightarrow 1p + 1n \Rightarrow \text{spin} = 1$ (boson) \leftarrow for integer spin

\Rightarrow e.g. in ^4He nucleus $= 2p \Rightarrow s = \frac{1}{2}$ \leftarrow for half-integer spin

So, we need $(T_N + H_e) \Psi(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) = E \Psi(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$

Hamiltonian $T_e + V$ omit spin variables

$$\Psi(\vec{R}; \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{\mathcal{g}} F_{\mathcal{g}}(\vec{R}) \Phi_{\mathcal{g}}(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$$

So: fix $\vec{R} \Rightarrow$ calculate $F_{\mathcal{g}}, \Phi_{\mathcal{g}}$

$F_{\mathcal{g}}$ depends only on $|\vec{R}| = R$ OR \vec{R} parametrically

$\Phi_{\mathcal{g}}$ expand in the basis of He functions representing nuclear motion when electronic system is in state \mathcal{g}

$\Phi_{\mathcal{g}}$ electronic states

$\text{He } \Phi_{\mathcal{g}}(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) = E_{\mathcal{g}}(\vec{R}) \Phi_{\mathcal{g}}(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$

$\Phi_{\mathcal{g}}$ electronic wave equation

$$\langle \Phi_q | \Phi_p \rangle = \delta_{qp}$$

So, now solve $(T_N + H_e) \sum_q F_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) = E \sum_q F_q(\vec{R}) \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) \Rightarrow$ multiply by $\langle \Phi_s | \Rightarrow$

$$\sum_q \langle \Phi_s | T_N + H_e - E | \Phi_q \rangle F_q(\vec{R}) = 0$$

$$\Downarrow \int \Phi_s^*(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) (T_N + H_e - E) \Phi_q(\vec{R}; \vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N$$

$$\sum_q \langle \Phi_s | T_N | \Phi_q \rangle F_q(\vec{R}) + [E_s(\vec{R}) - E] F_s(\vec{R}) = 0$$

recall $\vec{r}^2 \leftarrow (R, \theta, \phi)$
in spherical coord.

$$T_N = -\frac{\hbar^2}{2M} \left[\frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) - \frac{\vec{N}^2}{\hbar^2 R^2} \right]$$

orbital angular momentum of nucleus

$$\vec{N}^2 = -\hbar^2 \left[\frac{1}{\sin^2 \theta} \frac{\partial}{\partial \theta} (\sin^2 \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

Φ_q varies very slowly with R, θ, ϕ
 \uparrow since nuclear motion is much slower $\Rightarrow \frac{\partial \Phi_q}{\partial R} \rightarrow 0$
 compared to F_q

$$\sum_q \langle \Phi_s | -\frac{\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) - \frac{\vec{N}^2}{\hbar^2 R^2} \right] | \Phi_q \rangle F_q(\vec{R}) \quad (5)$$

$$= \sum_q \langle \Phi_s | T_N F_q(\vec{R}) | \Phi_q \rangle = \sum_q \langle \Phi_s | -\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R}$$

Born-Oppenheimer approximation \Rightarrow $\left[\frac{\partial \Phi_q}{\partial R} \rightarrow 0 \right]$
 (or adiabatic approximation) \Rightarrow $\left[\vec{N} \text{ doesn't affect electronic state} \right]$

$$\cdot \left(R^2 \frac{\partial F_q(\vec{R})}{\partial R} \right) | \Phi_q \rangle + \frac{\hbar^2}{2\mu \hbar^2} \sum_q \langle \Phi_s | \frac{\vec{N}^2}{R^2} F_q(\vec{R}) | \Phi_q \rangle$$

$$= \sum_q \left(-\frac{\hbar^2}{2\mu} \right) \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial F_q(\vec{R})}{\partial R} \right) \underbrace{\langle \Phi_s | \Phi_q \rangle}_{\delta_{sq}} +$$

$$+ \frac{\hbar^2}{2\mu \hbar^2} \langle \Phi_s | \frac{\vec{N}^2}{R^2} F_q(\vec{R}) | \Phi_s \rangle$$

So, Born-Oppenheimer equations \Rightarrow uncoupled \Rightarrow

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) + \frac{\langle \Phi_s | \vec{N}^2 | \Phi_s \rangle}{2\mu R^2} + E_s(R) -$$

$$- E \right] F_s(\vec{R}) = 0 \quad \Rightarrow \text{describes vibrational \& rotational motion of the molecule when the electronic system is in state } S$$

$$S = 0, 1, 2, \dots$$

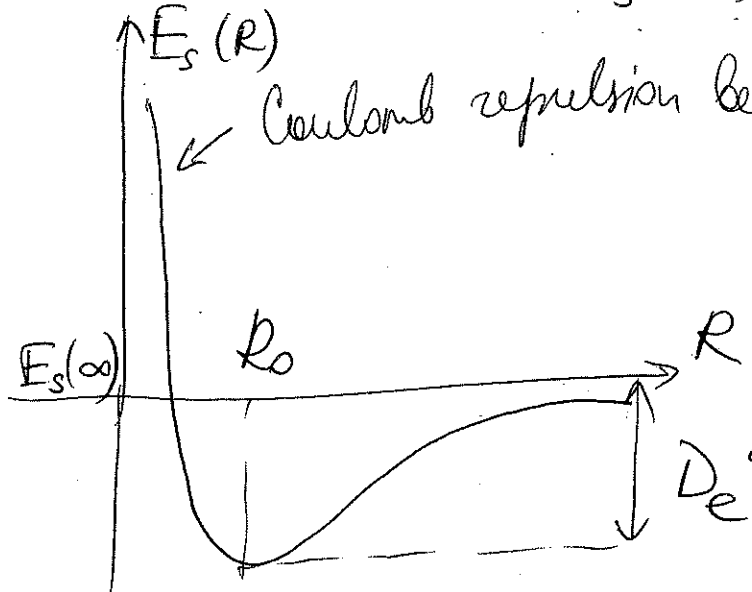
Then, $\Psi_S = E_S(R) \Phi_S(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$ (6)

Recipe: B.-O. approximation

- Solve ~~B.O.~~ electronic wave eqn for different $R \Rightarrow$ get $E_S(R)$
 $\Phi_S(\vec{R}; \vec{r}_1, \dots, \vec{r}_N)$

- Use $E_S(R)$ in B.-O. equations \Rightarrow get E

General form of $E_S(R)$: \leftarrow for a bound state $E_S(R)$



\leftarrow Coulomb repulsion between A & B dominates
 sum of energies of isolated atoms
 $D_e = E_S(\infty) - E_S(R_0)$
 electronic (or spectroscopic) dissociation energy of the molecule in the electronic state S

When B.-O. is insufficient:

- if $E_S(R)$ is degenerate \rightarrow can't ignore $\langle \Phi_S | T | \Phi_S \rangle$
- atom-atom collisions (relative motion of nuclei is not slow)
- Rydberg molecules (e^- is in a highly excited electronic state)
 e^- motion \leftarrow is slow