27.02.2013

Lecture - 15 :

Molecules

Consider a typical molecule with K nuclei having charges $Z_1 e$, $Z_2 e$, ... and N electrons. Denote the coordinates of nuclei by $\{\vec{R}_1, \ldots \vec{R}_K\}$ and those of the electrons by $\{\vec{r}_1, \ldots \vec{r}_N\}$.

$$H = \underbrace{T_N + T_e}_{\text{kinetic terms}} + V\left(\{\vec{r}_i\}; \{\vec{R}_i\}\right)$$

(Hamiltonian)

$$\left\{ \begin{aligned} T_N &= \sum_{i=1}^{K} \left(-\frac{1}{2M_i}\right) \vec{\nabla}^2_{\vec{R}_i} \\ T_e &= \sum_{i=1}^{N} \left(-\frac{1}{2m}\right) \vec{\nabla}^2_{\vec{r}_i} \end{aligned} \right\}$$

$$V\left(\{\vec{r}_i\}, \{\vec{R}_i\}\right) = -\sum_{i=1}^{K} \sum_{j=1}^{N} \frac{Z_i e^2}{|\vec{R}_i - \vec{r}_j|} + e^2/2 \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} + e^2/2 \sum_{i,j=1}^{K} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|}$$

Auxilliary problem

Find eigenstates of $(T_e + V)$ by regarding $\vec{R}_1, \ldots, \vec{R}_K$ as fixed parameters

$$(T_e + V)\,\Phi_n = e_n \Phi_n \longrightarrow \text{depend on } (\vec{r}_1, \ldots \vec{r}_N ; \vec{R}_1, \ldots \vec{R}_K)$$

$$|\vec{r}_i - \vec{r}_j| \sim |\vec{r}_i - \vec{R}_j| \sim |\vec{R}_i - \vec{R}_j| \quad \text{(Justify!)}$$

$$|\vec{\nabla}_{\vec{r}_i} \Phi| \sim \frac{1}{|\vec{r}_i|} \Phi \sim |\vec{\nabla}_{\vec{R}_i} \Phi| \sim \frac{1}{|\vec{R}_i|} \Phi .$$

$e_n \equiv e_n(\{\vec{R}_i\})$.

For fixed $\{\vec{R}_i\}$, Φ_n's form complete basis of functions of $\vec{r}_i$'s.

- Any function $\psi(\vec{r}_1, \ldots \vec{r}_N ; \vec{R}_1, \ldots, \vec{R}_K)$ can be expanded as $\sum_n F_n(\{\vec{R}_i\})\, \Phi_n(\{\vec{r}_i\}, \{\vec{R}_i\})$

$$F_n(\{\vec{R}_i\}) = \int d^3r_1\, d^3r_2 \ldots d^3r_N\, \Phi_n^*(\{\vec{r}_i\}, \{\vec{R}_i\})\, \psi(\{\vec{r}_i\}, \{\vec{R}_i\}) \quad (*)$$

• Look for $H\Psi = E\Psi$.

$$\left(T_N + T_e + V\right) \sum_n F_n\left(\{\vec{R}_i\}\right) \Phi_n\left(\{\vec{r}_i\}, \{\vec{R}_i\}\right)$$

$$= E \sum_n F_n\left(\{\vec{R}_i\}\right) \Phi_n\left(\{\vec{r}_i\}, \{\vec{R}_i\}\right)$$

$$\Rightarrow \sum_n e_n\left(\{\vec{R}_i\}\right) F_n\left(\{\vec{R}_i\}\right) \Phi_n\left(\{\vec{r}_i\}, \{\vec{R}_i\}\right) +$$

$$\sum_n \left(T_N F_n\left(\{\vec{R}_i\}\right)\right) \Phi_n\left(\{\vec{r}_i\}, \{\vec{R}_i\}\right) +$$

Terms involving $\left(\frac{1}{M_i} \vec{\nabla}_{\vec{R}_i} \Phi \text{ or } \frac{1}{M_i} \vec{\nabla}^2_{\vec{R}_i} \Phi\right)$ → ignore

$$= E \sum_n F_n\left(\{\vec{R}_i\}\right) \Phi_n\left(\{\vec{r}_i\}, \{\vec{R}_i\}\right)$$

(Born-Oppenheimer Approximation)

$$T_N F_n\left(\{\vec{R}_i\}\right) + e_n\left(\{\vec{R}_i\}\right) F_n\left(\{\vec{R}_i\}\right) = E F_n\left(\{\vec{R}_i\}\right)$$

(equating coefficients of Φ_n - -)

Think of as a potential

. For a fixed n, $F_n(\{\vec{R}_i\})$'s form a complete set in $\{\vec{R}_i\}$ space.

. Expand $e_n\{\vec{R}_i\}$ around a minimum upto quadratic terms.

(good enough approximation when M_i's are large)

$$e_n\left(\{\vec{R}_i\}\right) = e_n\left(\{\vec{R}_i^{(0)}\}\right) + \frac{1}{2} \sum_{j,k=1}^{K} \sum_{\alpha,\beta=1}^{3} A^{(n)}_{j\alpha,\,k\beta} \left(R_{j\alpha} - R^{(0)}_{j\alpha}\right) \left(R_{k\beta} - R^{(0)}_{k\beta}\right) + \cdots$$

$$\left\{ R_{j\beta} = \left(\vec{R}_j\right)_\beta \right\}_{\alpha,\beta = 1,2,3}$$

Change variables to normal modes

$$T_N + e_n\left(\{\vec{R}_i^{(0)}\}\right) + \sum_{s=1}^{3K(?)} \left\{ \frac{p_s^2}{2M_s} + \frac{1}{2} k_s y_s^2 \right\}$$

(for each n)

energy eigenvalue $\sum_s \left(\tilde{n}_s + \frac{1}{2}\right) \omega_s$

Rigid body d.o.f.

→ quantize separately

$\omega_s = \sqrt{k_s/M_s}$

Vibrational level spacing

splitting

ℓ_2 ——— $\frac{m}{M} e^4$

e_1 ———

$\sim \omega_s = \sqrt{\frac{k_s}{\tilde{M}_s}}$ (order of mag.)

$\sim \frac{1}{\sqrt{M}} \sqrt{\frac{\partial^2 e_n}{\partial R_{i\alpha} \partial R_{j\beta}}}$

$\sim \frac{1}{\sqrt{M}} \sqrt{\frac{e_n}{R_i^2}}$

$\sim \frac{1}{\sqrt{M}} \sqrt{\frac{me^4}{1/(me^2)^2}}$

$\sim \frac{m^{3/2} e^4}{\sqrt{M}}$

Conclusion

The vibrational spacing is of order $\left(\sqrt{m/M}\right)$ × electronic level spacing

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28.02.2013 Lecture - 16 :

Main steps

① Electronic part : $(T_e + V)\, \Phi_n(\{\vec{r}_i\}, \{\vec{R}_i\}) = e_n \Phi_n(\{\vec{r}_i\}, \{\vec{R}_i\})$

② $\Psi = \sum_n F_n(\{\vec{R}_i\})\, \Phi_n(\{\vec{r}_i\}, \{\vec{R}_i\})$

③ $(T_N + e_n(\{\vec{R}_i\}) - E)\, F_n(\{\vec{R}_i\}) = 0$ after ignoring terms $\sim 1/M$

④ Replace $e_n(\{\vec{R}_i\})$ by $E_n(\{\vec{R}_i^{(0)}\}) + \frac{1}{2} \sum_{i\alpha, j\beta} A_{i\alpha, j\beta} \times (R_{i\alpha} - R_{i\alpha}^0)(R_{j\beta} - R_{j\beta}^{(0)})$

$+ \cdots$

$\left(\sum_s -\frac{1}{2\tilde{M}_s} \frac{\partial^2}{\partial u_s^2} + \frac{1}{2} k_s u_s^2 + e_n(\{\vec{R}_i^{(0)}\}) - E \right) F_n(\{\vec{u}_s\}) = 0$

$e_n(\{R_i^{(0)}\}) + \sum_s \left(n_s + \frac{1}{2}\right) \omega_s$ $\quad \omega_s = \sqrt{\frac{k_s}{\tilde{M}_s}}$

· Problem : Zero eigenvalues of the matrix -

Define $\sqrt{M_s}\, u_s = v_s$ ⟵ $A_{i\alpha, j\beta}$

Zero modes

$\frac{\vec{P}^2}{2M}$ → total modes

translational ⟵ trivial

rotational

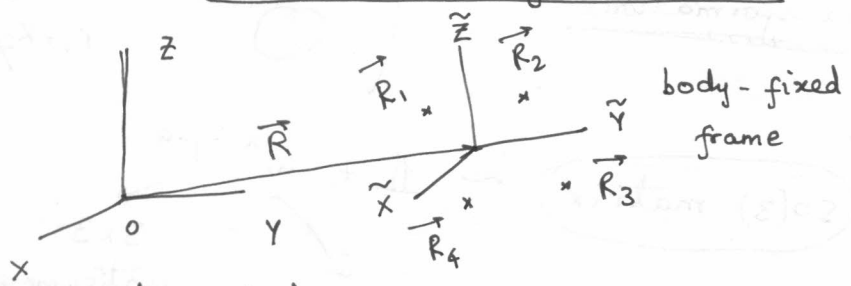
. One can start with COM coordinates.

Effect of rotational zero modes

· How many d.o.f. ? (3) Except Diatomic molecules. (2)

· Think of ~~nucleus~~ molecule as rigid body.

Review : Dynamics of rigid bodies



$\vec{R}_i$: coordinates in space-fixed frame

$\vec{\rho}_i$: coordinates in body-fixed frame

· Choose the origin of the body-fixed frame at the center-of-mass (COM).

Suppose : S is the rotation matrix that take body-fixed coordinates to space-fixed coordinates.

$$R_{i\alpha} = R_\alpha + S_{\alpha\beta}\, \rho_{i\beta}$$

$$\Rightarrow \dot{R}_{i\alpha} = \dot{R}_\alpha + \dot{S}_{\alpha\beta}\, \rho_{i\beta} \qquad (\rho \text{ doesn't change})$$

$$T = \frac{1}{2} \sum_{i,\alpha} \dot{R}_{i\alpha}\, \dot{R}_{i\alpha}\, M_i$$

$$= \frac{1}{2} \sum_i M_i \left(\dot{R}_\alpha \dot{R}_\alpha + 2 \dot{R}_\alpha \dot{S}_{\alpha\beta} \rho_{i\beta} + \dot{S}_{\alpha\beta} \dot{S}_{\alpha\gamma} \rho_{i\beta} \rho_{i\gamma} \right)$$

$\dot{R}_\alpha \dot{S}_{\alpha\beta} \rho_{i\beta} = 0$

$$= \frac{1}{2} \underbrace{\sum_i M_i}_{M} \dot{R}_\alpha \dot{R}_\alpha + \frac{1}{2} \mathrm{Tr}\left(\frac{dS}{dt} K \frac{dS^T}{dt} \right)$$

Define $K_{\alpha\beta\gamma} \equiv \sum_i M_i \rho_{i\beta} \rho_{i\gamma}$

Euler angle representation

$$S = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$K = V K_d V^T$ $\quad V \rightarrow$ SO(3) matrix

$K_d \rightarrow \begin{pmatrix} K_1 & & \\ & K_2 & \\ & & K_3 \end{pmatrix}$ $\quad V \rightarrow$ fixed matrix

$\tilde{S} = SV$

$T = \frac{1}{2} \mathrm{Tr}\left(\frac{d\tilde{S}}{dt} K_d \frac{d\tilde{S}^T}{dt} \right)$

Inertia matrix

$I = \mathrm{Tr}(K)\, \mathbb{1}_{3\times 3} - K$

$= \begin{pmatrix} K_2+K_3 & & \\ & K_1+K_3 & \\ & & K_1+K_2 \end{pmatrix}$

Symmetries & transformations

$\tilde{S} \rightarrow U\tilde{S}$

$U \rightarrow$ SO(3) matrix $\sim \mathbb{1} + \omega^a T^a$

ω^a: infinitesimal parameters; T^a: 3×3 antisymmetric matrices

$\Rightarrow$ Conserved charges

$L_a \equiv (L_x, L_y, L_z)$

- Rotation of space-fixed frame.

$\tilde{S} \rightarrow \tilde{S} W \rightarrow$ SO(3) matrix

- Rotating body-fixed axes - - -

$\rightarrow$ symmetry only if $\left\{ \begin{array}{l} W K_d W^T = K_d \\ \Rightarrow \quad W K_d = K_d W \end{array} \right\}$

- Schur's Lemma

$W = \mathbb{1}$ if all eigenvalues are non-equal.

- What are the generators of $\tilde{S} = \tilde{S} W$?

Call $\tilde{L}_x, \tilde{L}_y, \tilde{L}_z$. $\quad \tilde{S} \rightarrow \tilde{S}(\mathbb{1} + \omega^a T^a)$

$[L_a, \tilde{L}_b] = 0.$

$U\tilde{S}W$, $U\tilde{S}W \rightarrow$ equal

Ex

$$H = \frac{\tilde{L}_x^2}{2I_x} + \frac{\tilde{L}_y^2}{2I_y} + \frac{\tilde{L}_z^2}{2I_z}$$

$$\tilde{L}_x^2 + \tilde{L}_y^2 + \tilde{L}_z^2 = L_x^2 + L_y^2 + L_z^2$$

$\tilde{L}_i \rightarrow$ components of angular momentum along body fixed axes.

$[\tilde{L}_x, H] \neq 0 \ldots$

- Suppose, we have $K_x = K_y$.

$\Rightarrow I_x = I_y$

$\therefore \tilde{L}_z$ is conserved.

$$H = \frac{1}{2I_x}\left(L^2 - \tilde{L}_z^2\right) + \frac{\tilde{L}_z^2}{2I_z}$$

$\tilde{L}_z$, $\tilde{L}^2$ & L_z are mutually commuting & commute with H. $\rightarrow$ Label eigenstates by $\tilde{m}_z$, $l(l+1)$ & m_z

$$E = \frac{1}{2I_x}\left(l(l+1) - \tilde{m}_z^2\right) + \frac{\tilde{m}_z^2}{2I_z}.$$

$m_z = -l, (-l+1), \ldots l$

- Result is independent of m_z.

$$\left\{\begin{array}{l} L = 0, 1, 2, \ldots \\ M_z = -L, -L+1, \ldots, L \\ \tilde{M}_z = -L, -L+1, \ldots, L \end{array}\right\}$$

? ($1/M$ correction)

Energy level spacing

$$\sim 1/I \sim \frac{1}{M\vec{R}_i^2}$$

$\rightarrow 1/me^2$

$$\sim \left(\frac{m}{M}\right)(me^4) \rightarrow \text{electronic energy levels}$$

(Suppression factor)

(*) wrong analysis (previously)

- Go back to the original equations.

$$\sum_n \left(-\sum_i \frac{1}{2M_i}\vec{\nabla}_{R_i}^2 + e_n(\vec{R}) - E\right)\left\{F_n(\{\vec{R}_i\})\,\Phi_n(\{\vec{R}_i\}, \{\vec{r}_i\})\right\} = 0.$$

$$\sum_i \frac{1}{2M_i}\vec{\nabla}_{\vec{R}_i}^2 \longrightarrow \sum_s \frac{1}{2\tilde{M}_s}\frac{\partial^2}{\partial u_s^2} + A_{rot}.$$

$$\int d^3r_1 \ldots d^3r_N\, \Phi_p^{+}(\{\vec{r}_i\}, \{\vec{R}_i\})\,(\ldots)$$

$\Rightarrow$ P.T.O.

$$\left(-\sum_i \frac{1}{2M_i}\vec{\nabla}_{\vec{R}_i}^2 + e_p(\{\vec{R}_i\}) - E\right) F_p\phi_p + \sum_n \sum_i \left(-\frac{1}{2M_i}\right) \langle \phi_p | \vec{\nabla}_{\vec{R}_i} | \phi_n \rangle \vec{\nabla}_{\vec{R}_i} F_n$$

$$+ \sum_n \sum_i \left(-\frac{1}{2M_i}\right) \langle \phi_p | \vec{\nabla}_{\vec{R}_i}^2 | \phi_n \rangle F_n = 0.$$

$$\begin{pmatrix} F_1 \\ F_2 \\ F_3 \\ \vdots \end{pmatrix}$$

- Lesson from first order perturbation theory
- Pick only $n = p$ terms

Unperturbed $\Rightarrow$ $\begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ F_p \\ 0 \\ 0 \\ \vdots \end{pmatrix}$.

$$\langle \phi_p | \left(-\sum_i \frac{1}{2M_i}\vec{\nabla}_{\vec{R}_i}^2 + e_p(\{\vec{R}_i\}) - E\right) \{F_p(\{\vec{R}_i\}) | \phi_p(\{\vec{r}_i\}, \{\vec{R}_i\})\rangle = 0.$$

- Ignore $(1/M^2)$ corrections.

$$= \left(\sum_s -\frac{1}{2\tilde{M}_s}\frac{\partial^2}{\partial u_s^2} + \Delta_{rot.}\right)$$

$\frac{\partial^2}{\partial u_s^2}$: independent of Euler angles (causes shift in vibrational levels)

acts totally on F_p $\rightarrow$ these don't cause any change in level spacing of ~~vibrational~~ rotational levels.

Problem to be solved

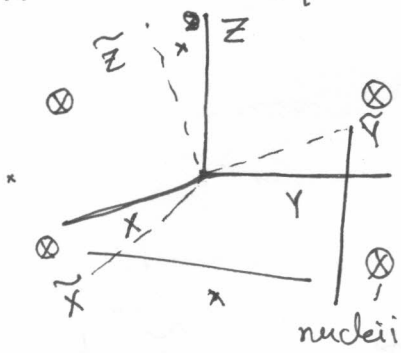
$$\langle \phi_p | \left(-\Delta_{rot} - \tilde{\epsilon}\right)(F_p \phi_p) \rangle = 0.$$

Find $\tilde{\epsilon}$. (vibrational energy levels)

01.03.2013 Lecture - 17 :

Diatomic Molecules :

- $\vec{L}$ will rotate the electronic coordinates $\vec{r}_i$ keeping $\vec{R}_i$ fixed. (Acts on Φ_n and not on F_n).
- $\vec{N}$ rotates $\vec{R}_i$ keeping $\vec{r}_i$ fixed.
  → acts on Φ_n and F_n.
- $\vec{K}$ rotates $\vec{r}_i$ & $\vec{R}_i$ $\left(\vec{K} = \vec{N} + \vec{L}\right)$



× electrons

- $\vec{K}$ acts trivially on Φ_n. (Justify!)
  ↓
  acts non-trivially on F_n

- origin → COM (common CM or CM of $\vec{R}_i$'s only)
  $\bar{e}$ mass - small
- Space-fixed & body-fixed axes.
- $\{L_x, L_y, L_z\}$ → components of $\vec{L}$ in space-fixed frame
- $\{\tilde{L}_x, \tilde{L}_y, \tilde{L}_z\}$ → " " " in body-fixed "
- Same definitions for $\vec{N}$ & $\vec{K}$.
- Nucleii decide on choice of body-fixed frame.

⇓

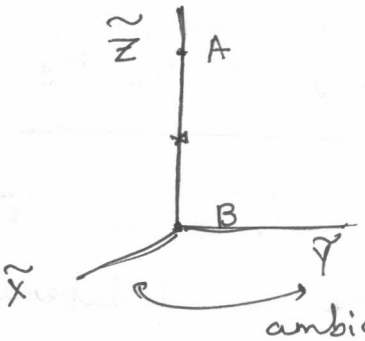
DIATOMIC MOLECULE ??

$\vec{R} = \vec{R}_1 - \vec{R}_2$.

In Body-Fixed Frame

$\vec{\tilde{R}}_1 = (0, 0, \tilde{R}_1)$

$\vec{\tilde{R}}_2 = (0, 0, -\tilde{R}_2)$



ambiguity in choice

$$\left\{ \begin{aligned} \vec{R}_1 &= \vec{R}\,\frac{M_1}{M_1+M_2} \\ \vec{R}_2 &= \vec{R}\,\frac{M_2}{M_1+M_2} \end{aligned} \right\}$$

Solve $H_e \phi_n = e_n(\vec{R})\,\phi_n$

$\boxed{T_e + V}$

$$H_e = -\sum_i \frac{1}{2m_e}\vec{\nabla}^2_{\vec{r}_i} + \sum_{\substack{i,j \\ i<j}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \left\{ \frac{Z_1 e^2}{|\vec{r}_i - \vec{R}_1|} + \frac{Z_2 e^2}{|\vec{r}_i - \vec{R}_2|} \right\}$$

Symmetries of the problem

(1) $\tilde{x}_i \longrightarrow \tilde{x}_i \cos\alpha + \tilde{y}_i \sin\alpha$

$\tilde{y}_i \longrightarrow -\tilde{x}_i \sin\alpha + \tilde{y}_i \cos\alpha$

$\tilde{z}_i \longrightarrow \tilde{z}_i$

$\longrightarrow$ Generated by $\tilde{L}_z \Rightarrow \tilde{L}_z \phi_n = \tilde{M}_L \phi_n$

Define $\Lambda = |\tilde{m}_\ell|$ $\quad \tilde{M}_L = \Lambda$ or $-\Lambda$.

$[\tilde{L}_z, H_e] = 0$. (Only continuous symmetry)

(2) $\tilde{y}_i \longrightarrow -\tilde{y}_i$

$\tilde{x}_i \longrightarrow \tilde{x}_i$

$\tilde{z}_i \longrightarrow \tilde{z}_i$

Symmetry

Symmetry generator $\longrightarrow A_{\tilde{y}}$

$\tilde{A}_y \phi_n(\{\tilde{x}_i, \tilde{y}_i, \tilde{z}_i\}, \{\vec{R}_1, \vec{R}_2\})$

$= \phi_n(\{\tilde{x}_i, -\tilde{y}_i, \tilde{z}_i\}, \{\vec{R}_1, \vec{R}_2\})$

$A_{\tilde{y}} H_e = H_e A_{\tilde{y}}$

$\tilde{x}_i \longrightarrow -\tilde{x}_i$ is no more an independent symmetry.

Take $\alpha = \pi$.

$A_{\tilde{y}} \tilde{L}_z A_{\tilde{y}}^{-1} = -\tilde{L}_z$

$\tilde{L}_z A_{\tilde{y}} \phi_n = -A_{\tilde{y}} \tilde{L}_z \phi_n$

$= -\tilde{M}_z A_{\tilde{y}} \phi_n$.

- $A_{\tilde{y}}$ takes $\tilde{M}_L = \Lambda$ state to $\tilde{M}_L = -\Lambda$ state with same $e_n(R)$. (Degeneracy) ⟶ Residual...

If $\Lambda = 0$, Φ_n can be chosen to be an eigenstate of $A_{\tilde{y}}$ with eigenvalues ± 1.

Λ :	0	1	2	3	-	-	-	-	-
Symbol :	Σ	Π	Δ	Φ	-	-	-	-	-

$\Sigma^{\pm}$ ⟶ $A_{\tilde{y}} = 1$, ⟶ $A_{\tilde{y}} = -1$

Homonuclear molecules

Special symmetry : $\vec{\tilde{R}}_1 = -\vec{\tilde{R}}_2$ ⟶ extra symmetry

Parity symmetry ⟵ implies ⟶ $(\tilde{x}_i, \tilde{y}_i, \tilde{z}_i) \to (\tilde{x}_i, \tilde{y}_i, -\tilde{z}_i)$

$(\tilde{x}_i, \tilde{y}_i, \tilde{z}_i) \to (-\tilde{x}_i, -\tilde{y}_i, -\tilde{z}_i)$

$[P, H_e] = 0$, $[P, \tilde{L}_z] = 0$

$\Sigma_g^+, \Sigma_u^+, \Sigma_g^-, \Sigma_u^-$ (understand !)

$\Pi_g, \Pi_u, \Delta_g, \Delta_u, \ldots$ { Parity even : g ; " odd : u }

$T_N = \sum_{i=1}^{2} - \frac{1}{2M_i} \nabla^2_{\vec{R}_i}$ (Diatomic case)

$= $ c.m. part $- \frac{1}{2\mu} \vec{\nabla}^2_{\vec{R}}$ ⟶ relative coordinate

$\mu = \frac{M_1 M_2}{(M_1 + M_2)}$ ⟶ { reduced mass }

$$-\frac{1}{2\mu}\vec{\nabla}^2_{\vec{R}} = -\frac{1}{2\mu}\left\{\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{R^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right\}$$

$$-\frac{1}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\frac{1}{2\mu R^2}\vec{N}^2 \longrightarrow \text{(same as } \vec{N}^2\text{)}$$

So, the differential equation to solve looks like —

$$-\frac{1}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial F_n}{\partial R}\right)+\langle\phi_n|\left(+\frac{1}{2\mu R^2}\vec{N}^2\right)|\phi_n\rangle F_n(R)$$

(vibrations) $- e_n(R)\,F_n(R) = E F_n(R)$

- $\vec{K} = \vec{N} + \vec{L}$

  $\vec{N}^2 = \vec{K}^2 + \vec{L}^2 - 2\vec{K}\cdot\vec{L}$.

$\vec{K} \rightsquigarrow$ exact symmetry of the problem.

- We can take the molecular states to be eigenstates of $\vec{K}^2$ & K_z (component of $\vec{K}$ along space-fixed axes)

  $\vec{K}^2 \to K(K+1)$; $K_z \to M_K$ $\rightsquigarrow$ { Different M_K values will be degenerate. }

  $M_K = (-K, -K+1, \text{— — —}, K-1, K)$

$\vec{L}^2 = \tilde{L}_x^2 + \tilde{L}_y^2 + \tilde{L}_z^2$

$2\vec{K}\cdot\vec{L} = 2(\tilde{K}_x\tilde{L}_x + \tilde{K}_y\tilde{L}_y + \tilde{K}_z\tilde{L}_z)$

$\tilde{K}_z = \tilde{N}_z + \tilde{L}_z$

$\tilde{N}_z \to 0$ (? $\to$ $\vec{N} = \vec{R}\times\vec{P}$

$\tilde{N}_z = \dfrac{\vec{R}\cdot(\vec{R}\times\vec{P})}{|\vec{R}|} = 0$.)

$\tilde{K}_x$, $\tilde{K}_y$ $\longrightarrow$ don't act on ϕ_n

$\langle\phi_n|\tilde{L}_x|\phi_n\rangle = 0$, $\langle\phi_n|\tilde{L}_y|\phi_n\rangle = 0$

$$-\frac{1}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial F_n}{\partial R}\right)+\frac{1}{2\mu R^2}\left(K(K+1)-\Lambda^2\right)+\langle\phi_n|\tilde{L}_x^2+\tilde{L}_y^2|\phi_n\rangle\Big) - e_n(R)F_n(R) = E F_n(R)$$

$F_n(R)$

· Ignore ~~[illegible]~~ $-\Lambda^2$ & $\langle \phi_n | \tilde{L}_x^2 + \tilde{L}_y^2 | \phi_n \rangle$ as we are not considering shifts of $O(1/\mu)$ ⟶ no splitting.

$$\begin{cases} K = 0, 1, 2, \ldots \\ M_K = -K, \ldots K \end{cases} \quad \underline{\text{NO!}} \qquad \tilde{K}_z |\ \rangle = \tilde{M}_L |\ \rangle$$

$(2K+1)$ - fold degeneracy

$[K = \Lambda, \Lambda+1, \Lambda+2, \ldots]$ ← dictates this!

{ get from electronic problem }

R_0 : min. of $e_n(R)$

$$E_{rot.} = \frac{K(K+1)}{2\mu R_0^2}$$

$$e_n(R) = e_n(R_0) + \frac{1}{2}(R-R_0)^2 e_n''(R_0) + \ldots$$

$$F_n(R) = \frac{1}{R} G_n$$

$$\left\{ -\frac{1}{2\mu}\frac{\partial^2 G_n}{\partial R^2} + \frac{1}{2}(R-R_0)^2 e_n''(R_0) G_n + G_n\left(e_n(R_0) + \frac{K(K+1)}{2\mu R_0^2}\right) = E G_n \right\}$$

$$E = e_n(R_0) + \left(\tilde{n} + \frac{1}{2}\right)\omega + \frac{K(K+1)}{2\mu R_0^2} \quad \text{--- (A)}$$

$$\omega = \sqrt{\frac{e_n''(R_0)}{\mu}}$$

A few more minutes . . .

Alternative description derivation of rotational spectrum

· An axisymmetric rigid body.

$I_x = I_y \neq I_z$.

$I_z \longrightarrow$ small

$$I_x = I_y = \frac{M_1 M_2 R^2}{(M_1 + M_2)} = \mu R^2$$

$$M_K^2 = \Lambda^2$$

Recall that for axisymmetric rigid body,

$$E_{rot.} = \frac{1}{2I_x} K(K+1) + \left(\frac{1}{2I_z} - \frac{1}{2I_x}\right) \tilde{M}_K^2$$

same as in (A)

overall shift

06.03.2013

Lecture - 18 :

H_2^+

$$H_e = -\frac{1}{2m}\vec{\nabla}_r^2 - \frac{e^2}{|\vec{r}-\vec{R}_A|} - \frac{e^2}{|\vec{r}-\vec{R}_B|} + \frac{e^2}{R}$$

$$R = |\vec{R}_A - \vec{R}_B|$$

$$\vec{R}_A = \left(0, 0, \frac{R}{2}\right) \; ; \quad \vec{R}_B = \left(0, 0, -\frac{R}{2}\right).$$

$$r_A = |\vec{r} - \vec{R}_A| \; ; \quad r_B = |\vec{r} - \vec{R}_B|$$

Symmetries : · ① Rotation about $z \Rightarrow$ L_z conserved

$$L_z|\psi\rangle = M_L|\psi\rangle$$

$$|M_L| = \Lambda.$$

② $y \to -y$ (A_y)

$r_A \to r_A$

$r_B \to r_B$

③ Special to homonuclear molecule

Parity $\vec{r} \longrightarrow -\vec{r} \implies r_A \leftrightarrow r_B$.

$\vec{R}_A = -\vec{R}_B$

· Propose (guess !) a ground state

· Intuition $\longrightarrow$ For large R,

$$\phi = \frac{1}{\sqrt{2}}\left(\psi_{1s}(r_A) \pm^{g}_{u} \psi_{1s}(r_B)\right).$$

ψ_{1s} : H-atom ground state

· Reason for taking linear combination $\to$ symmetries

· $\Lambda = 0$. $A_y = 1$. } $\Sigma^+_{g/u} \to$ {symbol for states}

Parity $\to \pm 1$. }

· Take this as an approximation even for finite R.

$$E_{g,u} = \frac{\int d^3r\, \phi^*_{g,u}\, H_e\, \phi_{g,u}}{\int d^3r\, \phi^*_{g,u}\, \phi_{g,u}}$$

Exercise : Check that, $E_{g,u} = E_{1s}$ + correction

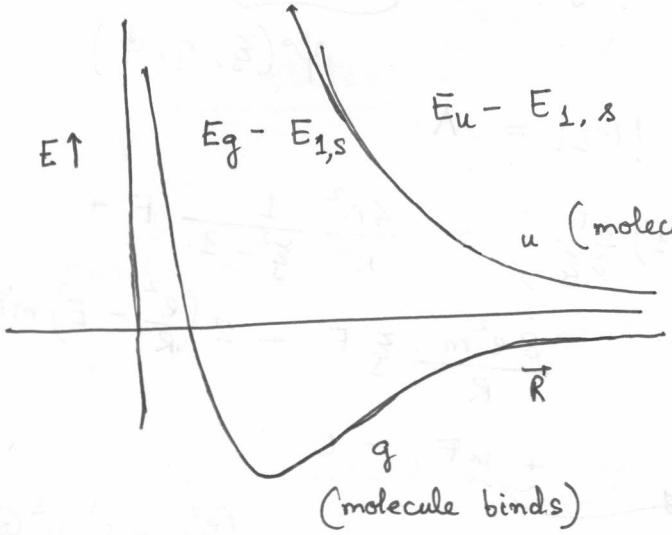
(E_{1s} ↓ ground state energy for single-electron atom)

Correction

$$= me^4 \left[\frac{1}{\hat{R}} \frac{(1+\hat{R})e^{-2\hat{R}} \pm (1-\frac{2\hat{R}^2}{3})e^{-\hat{R}}}{1 \pm e^{-\hat{R}}(1+\hat{R}+\frac{\hat{R}^2}{3})} \right]$$

~~single-electron atom~~

$\hat{R} = me^2 R$



{ • Gives an upper bound on the energy. }

"Exact" solution

$$\xi = \frac{1}{R}(r_A + r_B)$$
$$\eta = \frac{1}{R}(r_A - r_B)$$

Elliptic coordinates

$\{\xi, \eta, \phi\}$ → set of independent coordinates.

r_A r_B

Ex Check that, $\vec{\nabla}_r^2 \psi = \frac{4}{R^2(\xi^2-\eta^2)} \left[\frac{\partial}{\partial\xi}\left\{(\xi^2-1)\frac{\partial\psi}{\partial\xi}\right\} + \frac{\partial}{\partial\eta}\left\{(1-\eta^2)\frac{\partial\psi}{\partial\eta}\right\} + \frac{\xi^2-\eta^2}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2}{\partial\phi^2} \right]$

$\xi \to \xi$, $\eta \to -\eta$ } parity

A_y : doesn't change ξ, η, $\phi \to \phi + \pi$

L_z : rotates ϕ.

$$H = -\frac{1}{2m}\vec{\nabla}_r^2 - \frac{2e^2}{R(\xi_s+\eta)} - \frac{2e^2}{R(\xi_s-\eta)} + \frac{e^2}{R}.$$

$$\left.\begin{aligned} r_A &= R\left(\frac{\xi_s+\eta}{2}\right) \\ r_B &= R\left(\frac{\xi_s-\eta}{2}\right) \end{aligned}\right\} \quad H_e\psi = E\psi.$$

Multiply both sides by $(\xi_s^2-\eta^2)$.

$\partial^2/\partial\phi^2 \rightarrow \underbrace{-\Lambda^2}$ · The variables separate

· Look for solutions of the form – $\underbrace{e^{iM_L\phi}F(\xi_s)G(\eta)}_{\psi(\xi,\eta,\phi)}$

Equations for F & G

$$|M_L| = \Lambda$$

Exercise :

$$4/R^2\frac{\partial}{\partial\xi}\left((\xi_s^2-1)\frac{\partial F}{\partial\xi}\right) - \frac{4\Lambda^2}{R^2}\frac{1}{\xi^2-1}F + \frac{8e^2m}{R}\xi F - 2\left(\frac{e^2}{R}-E\right)m\xi^2F$$

new constant $\leftarrow$ $+\mu F = 0$

$$4/R^2\frac{\partial}{\partial\eta}\left((1-\eta^2)\frac{\partial G}{\partial\eta}\right) - \frac{4\Lambda^2}{R^2}\frac{1}{1-\eta^2}G - 2\left(e^2/R-E\right)\eta^2G - \mu G = 0.$$

(*) (No linear η term $\rightarrow$ Parity symmetry)

· Numerical solution

· Look for ground state in both g sector (even under $\eta\rightarrow-\eta$) and u sector (odd under $\eta\rightarrow-\eta$)

(*) CAN BE DONE NUMERICALLY.

$\Rightarrow$ gives $E_g(R)$ & $E_u(R)$.

(agrees with our intuition)

Neutral hydrogen H_2

$$H_e = -\frac{1}{2m}\left(\vec{\nabla}_{r_1}^2 + \vec{\nabla}_{r_2}^2\right) - \frac{e^2}{r_{A_1}} - \frac{e^2}{r_{A_2}} - \frac{e^2}{r_{B_1}} - \frac{e^2}{r_{B_2}} + \frac{e^2}{R}$$

$r_{A1} = |\vec{r}_1 - \vec{R}_A|$

$r_{12} = |\vec{r}_1 - \vec{r}_2|$

and so on... (!!!)

- Single electron → spin doesn't matter

BUT, HERE IT MATTERS !!!

- Think of nucleus as fixed classical object.

Electron spin states

$|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$.

Choose a different basis,

S = 1 states

$\chi_{S\, m_S}$ → S_z eigenvalue

↓ total spin

$\chi_{11} = |\uparrow\uparrow\rangle$

$\chi_{10} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$

$\chi_{1-1} = |\downarrow\downarrow\rangle$

$\chi_{00} = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$

- Two independent methods → Molecular Orbital Method
  → ? (Valence Bond Method)

Molecular Orbital Method

- First, solve the single electron moving in the background of both nucleii.
- Use products of these to build multi-electron states.

$\phi_g(\vec{r})$, $\phi_u(\vec{r})$ → solutions to single-electron problem.

$\chi_{1\, M_S}$ → $\{\phi_g(\vec{r}_1)\,\phi_u(\vec{r}_2) - \phi_g(\vec{r}_2)\,\phi_u(\vec{r}_1)\}$

$^{(2S+1)}\Sigma^+_u$ → understand → $^3\Sigma^+_u$

χ_{00} → $\{\phi_g(\vec{r}_1)\,\phi_u(\vec{r}_2) + \phi_g(\vec{r}_2)\,\phi_u(\vec{r}_1)\}$

$^1\Sigma^+_u$ ✓

$\chi_{00}\,\phi_g(\vec{r}_1)\,\phi_g(\vec{r}_2)$ → $^1\Sigma^+_g$

$\chi_{00}\,\phi_u(\vec{r}_1)\,\phi_u(\vec{r}_2)$ → $^1\Sigma^+_g$

Let's call $^1\Sigma_g^+$ states as Φ_A & Φ_B.

(These can mix)

- Suppose, we use the approximation –

$$\phi_g(\vec{r}) = \frac{1}{\sqrt{2}}\left(\psi_{1s}(r_A) + \psi_{1s}(r_B)\right)$$

$$\phi_u(\vec{r}) = \frac{1}{\sqrt{2}}\left(\psi_{1s}(r_A) - \psi_{1s}(r_B)\right)$$

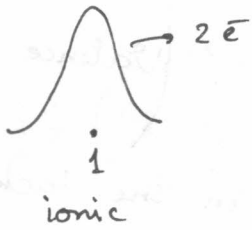
Exercise :

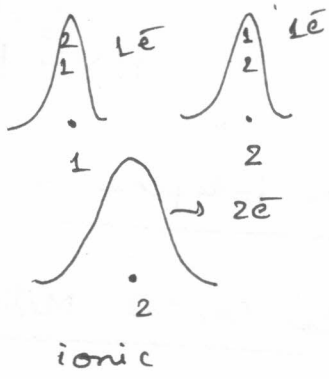
$$\begin{bmatrix} \Phi_A = \phi^{cov} + \phi^{ion} \\ \Phi_B = \phi^{cov} - \phi^{ion} \end{bmatrix}$$

$$\phi^{cov} = \frac{1}{2}\left(\psi_{1s}(r_{A1})\,\psi_{1s}(r_{B2}) + \psi_{1s}(r_{A2})\,\psi_{1s}(r_{B1})\right)$$

$$\phi^{ion} = \frac{1}{2}\left(\psi_{1s}(r_{B1})\,\psi_{1s}(r_{B2}) + \psi_{1s}(r_{A1})\,\psi_{1s}(r_{A2})\right)$$

$1 \leftrightarrow 2$ exchange symmetry





- In MO method, one doesn't mix electronic wavefunctions.

Valence Bond Method

We first construct the ground state wave function of each atom & then take linear combination of their product. (!)

$\psi_{1s}(r_A)$

$$\left\{\psi_{1s}(r_{A1})\,\psi_{1s}(r_{B2}) \pm \psi_{1s}(r_{A2})\,\psi_{1s}(r_{B1})\right\}$$

$+$: $S = 0$

$-$: $S = 1$

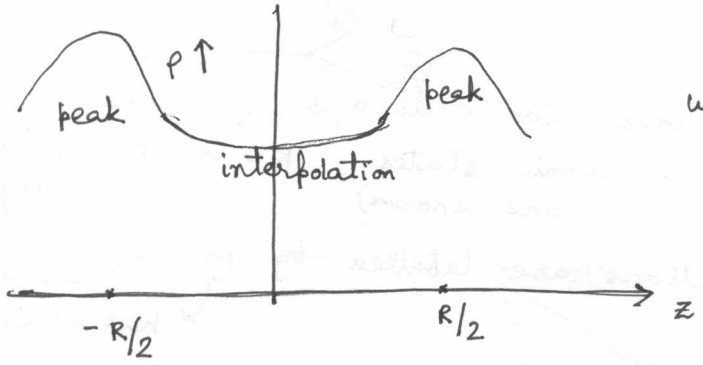
$\hookrightarrow \phi^{cov}$. (starting point)

LOWER ENERGY $\equiv$ Ground state

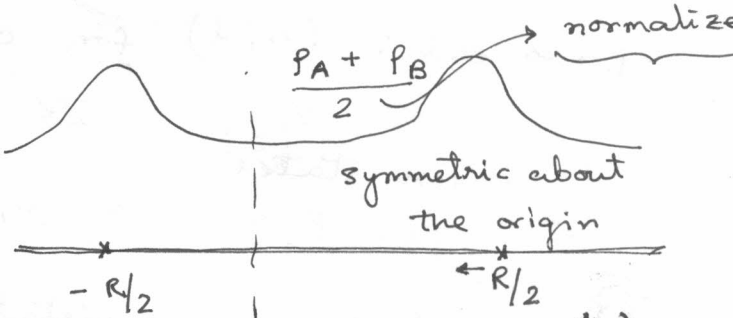
- Effectiveness of a particular approx. depends on the system concerned.

07.03.2013 Lecture - 19 :

Take trial wavefunction Φ.



• Compare this with what we get by summing the contribution from individual atoms.



(for H_2^+)

(*) If the earlier distribution is above or below the second one throughout the region (intermediate range of R), we can say the nucleii bind / ~~unb~~ don't bind.

H_2	ϕ_u	ϕ_g

$\left\{ \begin{array}{ll} H_2^+ & \phi_u \rightarrow \text{doesn't bind} \\ & \phi_g \rightarrow \text{binds} \end{array} \right.$

• Compare the pictures

• ϕ_u has a node at $R = 0$

Diatomic molecules with larger nucleii (more electrons)

General strategy :

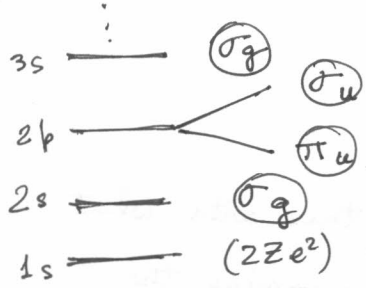
Assume that lowest lying molecular orbitals are $u_1(\vec{r}_1, q_1)$, $u_2(\vec{r}_2, q_2)$, ... $u_N(\vec{r}_N, q_N)$ (m_s)

$$\begin{pmatrix} u_1(q_1) & u_2(q_1) & \cdots & u_N(q_1) \\ u_1(q_2) & u_2(q_2) & \cdots & u_N(q_2) \\ \vdots & & & \\ u_{\otimes 1}(q_N) & \cdots & & u_N(q_N) \end{pmatrix}$$

→ Carry out Hartree-Fock.

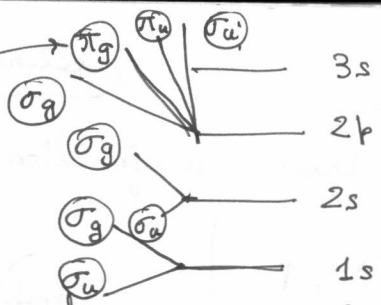
• Make an initial guess for u's (Zeroth order approx.)

Initial guess for u_i's.



HW

Check this!



$R=0$ ← energies of these two ends are fixed (if atomic states are known) → $R=\infty$

{each state → twofold degenerate}

$R=0$ end : Wavefunctions are labelled by (n, ℓ) nucleus has charge $2Ze$

$R=\infty$ end : (n, ℓ) for charge Ze for each nucleus.

- Two states for each (n, ℓ) → bound to either of the nucleii
- Choose basis → eigenstates of parity operator.

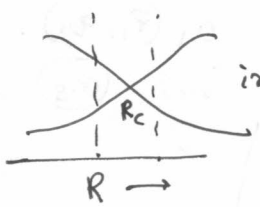
$$\phi_{g/u\ n\ell} \propto \left(u_{n\ell}(r_A) \pm u_{n\ell}(r_B)\right)$$

- Conserved quantum numbers : $|M_L| = \Lambda$, parity g, u

$$\Lambda = \begin{cases} 0, & 1, & 2, & 3, & \cdots \\ \sigma & \pi & \delta & \phi, & \cdots \end{cases}$$

Result : { Levels with same quantum number don't cross as functions of R. }

Proof :



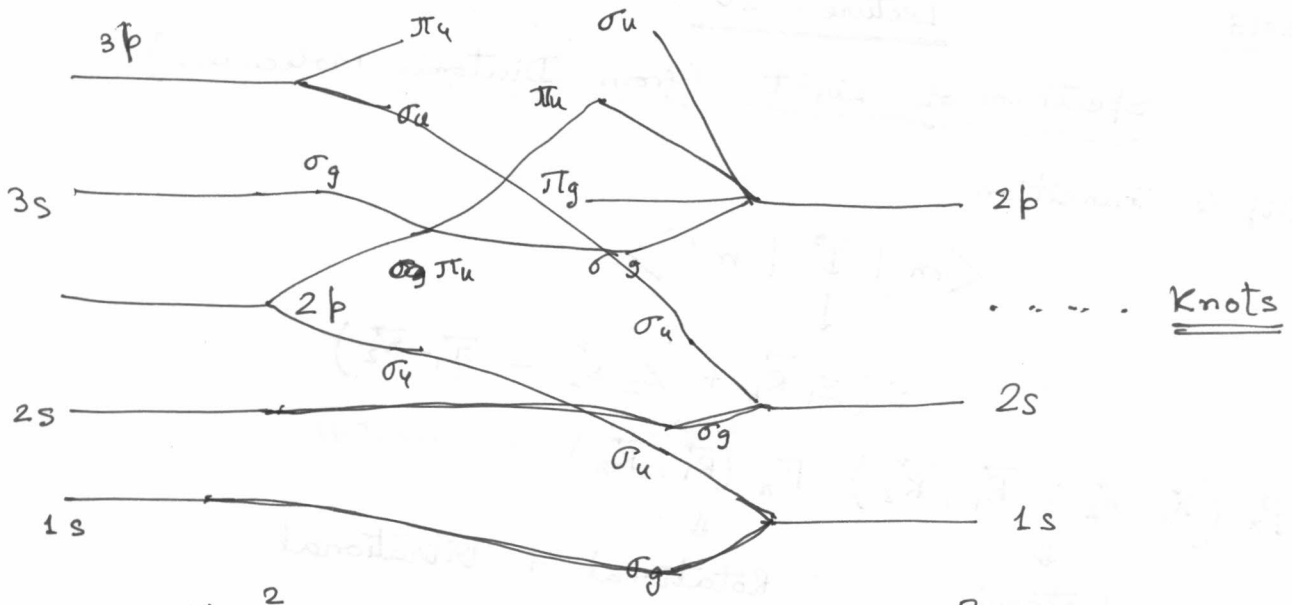
imagine (!) → map to 2-level system

$$H_{\text{eff}} = \begin{pmatrix} H_{11}(R) & H_{12}(R) \\ H_{12}^*(R) & H_{22}(R) \end{pmatrix}$$

effective Hamiltonian.

condition for level crossing { $H_{12}(R_c) = 0$; $H_{11}(R_c) - H_{22}(R_c) = 0$; at $R = R_c$ }

- Simultaneous vanishing is not likely.



He^2 : $(\sigma_g\, 1s)^2\ (\sigma_u\, 1s)^2$.

HW : Calculate $E(R)$ & check if it has a minimum

Li^2 : $(\sigma_g\, 1s)^2 (\sigma_u 1s)^2 (\sigma_g\, 2s)^2$. → it binds

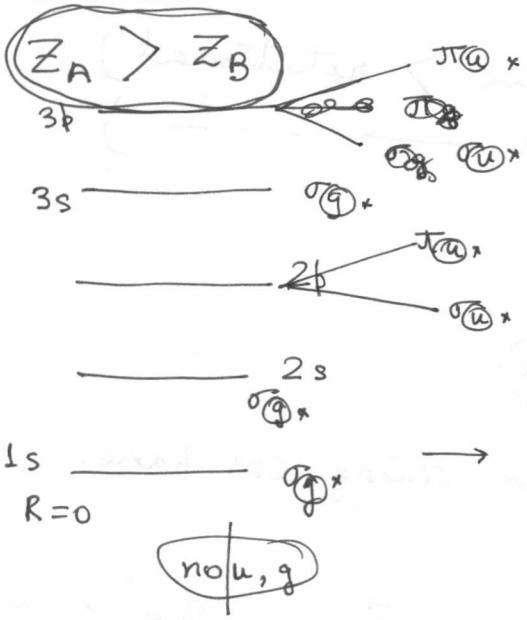
Sum of these contributions → very small

$$\frac{1+A}{1+B} + \frac{1-A}{1-B} = \frac{2(1-AB)}{(1-B^2)}$$

Heteronuclear molecule (diatomic)

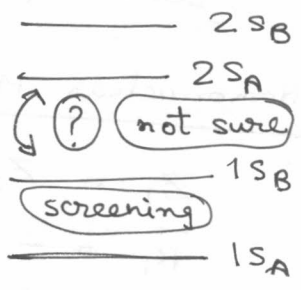
$u_{n l m_l}(r_A) \pm u_{n l m_l}(r_B)$

$Z_A > Z_B$



LiH molecule

$Z_A = 3$; $Z_B = 1$



Connect in same way

LiH → $(1s_A)^2 (1s_B)^2$.

- Read Bransden & Joachain

14/03/2013

Lecture - 20 :

Spectrum of Light (from Diatomic Molecules)

- Dipole transition

$$\langle n | \vec{D} | n' \rangle$$

$$\downarrow$$

$$e\left(Z_1 \vec{R}_1 + Z_2 \vec{R}_2 - \vec{r}_1 - \vec{r}_2\right)$$

$$\phi_n\left(\vec{r}_1, \vec{r}_2 ; \vec{R}_1, \vec{R}_2\right) \quad F_n\left(\vec{R}_1, \vec{R}_2\right)$$

$\Downarrow$ electronic states — $\Downarrow$ Rotational + Vibrational States

$e_{s;n,k}$ → rotational $= e_s(R_0) - \frac{\Lambda^2}{2\mu R_0^2} +$

electronic, vibrational

$$\frac{1}{2\mu R_0^2} \langle \phi_s | \left(\tilde{L}_x^2 + \tilde{L}_y^2\right) | \phi_s \rangle$$

$$+ \left(n + \frac{1}{2}\right)\omega + \frac{k(k+1)}{2\mu R_0^2}$$

n: 0, 1, 2, - - - (vibrational q. no.)

$\Lambda, \Lambda+1, - - -$ (m_L value)

$$\omega = \sqrt{\frac{e_n''(R_0)}{\mu}} \,.$$

- Hierarchy

(electronic > vibrational > rotational)

(Level spacing goes down ⟶ - - -)

Homonuclear Molecule

$$\left.\begin{aligned} Z_1 &= Z_2 \\ \vec{R}_1 &= -\vec{R}_2 \end{aligned}\right\} \text{ COM frame}$$

- ignore electronic masses in fixing CM frame.

$$\vec{D} = +e\left(\vec{r}_1 + \vec{r}_2\right)$$

$$\langle \phi_s | \vec{D} | \phi_s \rangle = 0 \,.$$

$$\int d^3r_1\, d^3r_2 \cdots$$

(only electronic part)

For homonuclear molecules, $|\phi_s\rangle$ → parity eigenstates.

• There is no rotational, vibrational spectrum of homonuclear molecule due to electric dipole transition.

. THIS IS SOMETHING UNFORTUNATE (!!!)

• Remedy : Raman Scattering (Scatter photons).

(Info about ω, R_0).

Heteronuclear Molecule

$$e \langle \phi_s | \left(Z_1 \vec{R}_1 + Z_2 \vec{R}_2 - \vec{r}_1 - \vec{r}_2 \right) | \phi_s \rangle$$

• $|\phi_s\rangle$'s are no longer parity eigenstates.

⊛ (transitions are possible)

• What about selection rules ??

$\vec{D}$ => vector under $\vec{R}$, $\vec{r}$ rotations.

$\langle s, n, k, m_k | \vec{D} | s, n', k', m_k' \rangle$

↳ non-zero for $k = k' \pm 1$ or k'

(Clebsch-Gordon coefficients. --) $m_k = m_k' \pm 1$ or m_k'

• A stronger selection rule ? (say for $\Lambda = 0$).

Naively, ϕ_s will depend on $\vec{r}_i \cdot \vec{r}_j$ and $\vec{r}_i \cdot \vec{R}_j$

for $i = 1, 2$; $j = 1, 2$.

THIS IS TRUE FOR POLYATOMIC MOLECULES...

• Rotate $\vec{r}_1, \vec{r}_2$ by ϵ about $\vec{R}_{12}$ axis. (Problem for diatomic molecules).

$\phi_s \rightarrow e^{i \tilde{m}_L \epsilon} \phi_s$.

• In spl. case ($\Lambda = 0$), ϕ_s is invariant.

• Information about overall rotations is encoded within $F_s(\vec{R}_1, \vec{R}_2)$.

$$F_S(\vec{R}) = F_S(R)\, Y_{K,m_K}(\theta,\phi)$$

R ↓ $|\vec{R}_1 - \vec{R}_2|$; (θ,ϕ) → (orientation of space-fixed frame.)

- Under $\vec{r}_i \longrightarrow -\vec{r}_i$

AND $\vec{R}_i \longrightarrow -\vec{R}_i$; ϕ_S is unchanged.

$F_S(R)$ is also unchanged.

- $Y_{K,m_K}(\theta,\phi) \longrightarrow (-1)^K Y_{K M_K}(\theta,\phi)$

$\vec{D} \longrightarrow (-\vec{D})$

- For $\Lambda = 0$; $K' = K \pm 1$ (not K)

$m_K = m_K' \pm 1, m_K'$

Selection rules for vibrational states

$$\langle \vec{D}(\vec{R}) \rangle = \langle \phi_S | \vec{D} | \phi_S \rangle$$

(integrate over electronic coordinates)

Define → (Taylor expand)

$$\longrightarrow \langle D_i(\vec{R}_0) \rangle + (\vec{R} - \vec{R}_0)\cdot \vec{\nabla}_{R'} D_i(\vec{R})\Big|_{\vec{R}=\vec{R}_0} + O(\vec{R}-\vec{R}_0)^2$$

$\langle D_i(\vec{R}_0) \rangle$ doesn't depend on $\vec{R}$ (doesn't cause any transition)

$O(\vec{R}-\vec{R}_0)^2$ ← ignore

- $n = n' \pm 1$

These give the most intense lines.

Like x in 1D → $|\vec{R} - \vec{R}_0|$

$\dfrac{(\vec{R}-\vec{R}_0)}{|\vec{R}-\vec{R}_0|}\cdot \vec{\nabla}_R D_i(\vec{R})\Big|_{\vec{R}=\vec{R}_0}$: angular part (don't care)

Rotational Spectrum

- No change in vibrational state ($n = n'$)

$S = S'$

~~$(n, s, k) \longrightarrow (n, s, k+1)$~~

$(s, n, k) \longrightarrow (s, n, k-1)$

Frequency Ω : $\frac{1}{2\mu R_0^2}$ $\frac{K(K+1) - (K-1)K}{1}$

$= \frac{K}{\mu R_0^2}$. $K = \Lambda, \Lambda+1, \Lambda+2, \ldots$

• Equally spaced lines.

• There's a lower cutoff

Vibrational - Rotational spectrum

1. ~~(s, n, k)~~ $\longrightarrow$ $(s, n+1, k+1) \rightarrow (s, n, k)$

R - branch $\Omega = \omega + \frac{(k+1)}{\mu R_0^2}$

(Band - like) $K = \Lambda, \Lambda+1, \ldots$

2. P - branch $(s, n+1, k-1) \longrightarrow (s, n, k)$

small gap $\Omega = \omega - \frac{K}{\mu R_0^2}$ $K = \Lambda+1, \ldots$

3. $\Lambda \neq 0$ $\longrightarrow$ Q - branch $(s, n+1, K) \rightarrow (s, n, k)$

$\Omega = \omega$.

Electronic spectrum

$(s, n, k) \longrightarrow (s', n', k')$