Consider a typical molecule with K nuclei having charges $Z_1e, Z_2e, \ldots$ and N electrons. Denote the coordinates of nuclei by $\{\vec{R}_i\}_1^K$ and those of the electrons by $\{\vec{x}_i\}_1^N$.

$$H = T_N + T_e + V(\{\vec{x}_i\} ; \{\vec{R}_i\})$$

(Hamiltonian)

$$
\begin{align*}
T_N &= \sum_{i=1}^K \left( -\frac{1}{2M_i} \right) \nabla_{\vec{R}_i}^2 \\
T_e &= \sum_{i=1}^N \left( -\frac{1}{2m_i} \right) \nabla_{\vec{x}_i}^2 \\
V &= -\sum_{i=1}^K \sum_{j=1}^N \frac{Z_i e^2}{|\vec{R}_i - \vec{x}_j|}
\end{align*}
$$

Auxiliary problem

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

$$(T_e + V) \Phi_n = e_n \Phi_n$$

$$(\vec{R}_i, \vec{R}_j) \sim |\vec{R}_i - \vec{R}_j| \sim |\vec{R}_i - \vec{R}_j|$$

$$(\vec{x}_i, \vec{x}_j) \sim \frac{1}{|\vec{x}_i|} \Phi \sim |\nabla_{\vec{x}_i} \Phi| \sim \frac{1}{|\vec{x}_i|} \Phi$$

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

Any function $\Psi(\vec{R}_1, \ldots, \vec{R}_K)$ can be expanded as

$$
\begin{align*}
\Psi &= \sum_{n=1}^\infty F_n (\{\vec{R}_i\}) \Phi_n (\{\vec{x}_i\}, \{\vec{R}_i\}) \\
F_n (\{\vec{R}_i\}) &= \int d^3x_1 d^3x_2 \cdots d^3x_N \Phi_n^* (\{\vec{x}_i\}, \{\vec{R}_i\}) \Psi (\{\vec{x}_i\}, \{\vec{R}_i\})
\end{align*}
$$
Look for $\Psi = E\Psi$.

$$(T_N + T_e + V) \sum_n F_n(\{\bar{R}_i\}) \Phi_n(\{\bar{R}_i\}, \{R_i\}) = E \sum_n F_n(\{\bar{R}_i\}) \Phi_n(\{\bar{R}_i\}, \{R_i\})$$

$$\Rightarrow \sum_n e_n(\{\bar{R}_i\}) F_n(\{\bar{R}_i\}) \Phi_n(\{\bar{R}_i\}, \{R_i\}) + \sum_n (T_N F_n(\{\bar{R}_i\})) \Phi_n(\{\bar{R}_i\}, \{R_i\}) = E \sum_n F_n(\{\bar{R}_i\}) \Phi_n(\{\bar{R}_i\}, \{R_i\})$$

Terms involving $\left( \frac{1}{M_i} \bar{v}_{R_i}^2 \Phi_or \frac{1}{M_i} \bar{v}_{R_i}^2 \Phi \right) \rightarrow$ ignore

$$(\text{Born- Oppenheimer Approximation})$$

$T_N F_n(\{\bar{R}_i\}) + e_n(\{\bar{R}_i\}) = F_n(\{\bar{R}_i\})$$

(equating coefficients of $\Phi_n$)

Think of as a potential

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

Expand $e_n(\{\bar{R}_i\})$ around a minimum up to quadratic terms.

(good enough approximation when $M_i$'s are large)

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

$$\left\{ \begin{array}{l} R_{j\alpha} = (\bar{R}_i)^{\beta} \\ \alpha, \beta = 1, 2, 3 \end{array} \right.$$ 

Change variables to normal modes

$$T_N + e_n(\{\bar{R}_i^{(0)}\}) + \sum_{s=1}^{3k} \frac{P_s^2}{2M_s} + \frac{1}{2} k_s y_s^2$$

(for each $n$)

Rigid body d.o.f.

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

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

quantize separately
Vibrational level spacing

\[ \omega_s \approx \sqrt{\frac{K}{M}} \]

(Order of mag.)

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

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

\[ \sim \frac{1}{\sqrt{M}} \sqrt{\frac{me^4}{4(\frac{m}{M})^2}} \]

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

**Conclusion**

The vibrational spacing is of order \( \frac{m}{M} \) x electronic level spacing.

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28.02.2013

**Lecture - 16:**

**Main steps**

1. **Electronic part:**
   \[ (Te + V) \Phi_n (\{\vec{r}_i\}, \{\vec{r}^*_{i\alpha}\}) = e_n \Phi_n (\{\vec{r}_i\}, \{\vec{r}^*_{i\alpha}\}) \]

2. \[ \Psi = \sum_{n} F_n (\{\vec{r}_{i\alpha}\}) \Phi_n (\{\vec{r}_i\}, \{\vec{r}^*_{i\alpha}\}) \]

3. \[ (T + e_n (\{\vec{r}_{i\alpha}\}) - \varepsilon) F_n (\{\vec{r}_{i\alpha}\}) = 0 \] after ignoring terms \( \sim \frac{1}{M} \)

4. Replace \( e_n (\{\vec{r}_{i\alpha}\}) \) by \[ E_n (\{\vec{r}^{(o)}_{i\alpha}\}) + \frac{1}{2} \sum_{i\alpha,j\beta} A_{i\alpha,j\beta} x_{i\alpha,j\beta} (R_{i\alpha} - R^{(o)}_{i\alpha}) (R_{j\beta} - R^{(o)}_{j\beta}) \]

\[ \left( \sum_{s} - \frac{1}{2M} \frac{\partial^2}{\partial u_{s}^2} + \frac{1}{2} K_s u_{s}^2 + e_n (\{\vec{r}^{(o)}_{i\alpha}\}) - \varepsilon \right) F_n (\{\vec{u}_s\}) = 0 \]

\[ e_n (\{\vec{r}^{(o)}_{i\alpha}\}) + \sum_{s} (n_s + \frac{1}{2}) \omega_s \]

\[ \omega_s = \sqrt{\frac{Ks}{Ms}} \]
Problem: Zero eigenvalues of the matrix

Define $M_s u_s = \{A_{\alpha \beta}\}$

$\frac{p^2}{2M} \rightarrow$ total modes

$\rightarrow$ zero modes

Translational rotational

Trivial. One can start with COM coordinates.

Effect of rotational zero modes

How many d.o.f.? 3 Except diatomic molecules.

Think of nucleus by as rigid body.

Review: Dynamics of rigid bodies

$$\begin{align*}
\quad & R_i = \text{coordinates in space-fixed frame} \\
\quad & \tilde{R}_i = \text{coordinates in body-fixed frame}
\end{align*}$$

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

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

$$R_i\alpha = R_\alpha + S_{\alpha \beta} \pi_{i\beta}$$

$$\Rightarrow R_i\alpha = \tilde{R}_\alpha + S_{\alpha \beta} \pi_{i\beta} \quad (\pi \text{ doesn't change})$$

$$T = \frac{1}{2} \sum_{i, \alpha} R_i\alpha R_i\alpha M_i$$

$$= \frac{1}{2} \sum_i M_i \left( R_\alpha \tilde{R}_\alpha + 2 R_\alpha S_{\alpha \beta} \pi_{i\beta} + S_{\alpha \beta} \tilde{S}_{\alpha \beta} \pi_{i\beta} \pi_{i\gamma} \right)$$

$$= \frac{1}{2} \sum_i M_i R_\alpha \tilde{R}_\alpha + \frac{1}{2} \text{Tr} \left( \frac{dS}{dt} K \frac{ds}{dt} \right)$$

Define $K_{\alpha \beta \gamma}$

$$\sum_i M_i = \sum_i \frac{1}{2} \text{Tr} \left( \frac{dS}{dt} K \frac{ds}{dt} \right)$$
Euler angle representation

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

$K = V \begin{pmatrix} K_1 & 0 & 0 \\ 0 & K_2 & 0 \\ 0 & 0 & K_3 \end{pmatrix} \quad V \rightarrow \text{fixed matrix}$

$\tilde{S} = SV$

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

Symmetries & Transformations

$\tilde{S} \rightarrow U \tilde{S} \rightarrow \text{so}(3) \text{ matrix}$

$1 = \text{Tr}(K) 1_{3 \times 3} - K$

Inertia matrix

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

Conserved charges

$L_a = (L_x, L_y, L_z)$

Rotation of space-fixed frame.

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

Rotating body-fixed axes.

Symmetry only if

$\begin{cases}
W K_d W^T = K_d \\
W K_d = K_d W
\end{cases}$

Schur's Lemma

$W = 1$ if all eigenvalues are non-equal.

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

Call $\tilde{L}_x, \tilde{L}_y, \tilde{L}_z$. $\tilde{S} \rightarrow \tilde{S} (1 + W \omega \cdot \eta)$
\[ [\tilde{L}_a, \tilde{L}_b] = 0. \]

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

Suppose, we have $K_x = K_y$.

\[ \Rightarrow I_x = I_y \]

\[ \tilde{L}_z \] is conserved.

\[ \tilde{L}_x, \tilde{L}_y, \tilde{L}_z \] are mutually commuting and commute with $H$.

\[ E = \frac{1}{2I_x} (L(L+1) - \tilde{m}_z^2) + \frac{m_w^2}{2I_z} \]

Result is independent of $m_z$.

\[ L = 0, 1, 2, \ldots \]

\[ M_z = -L, -L+1, \ldots, L \]

\[ \tilde{M}_z = -L, -L+1, \ldots, L \]

\[ ? \left( \frac{1}{M} \text{ correction} \right) \]

Wrong analysis (previously).

Go back to the original equations.

\[ \sum_n \left( -\frac{1}{2M_i} \overrightarrow{V^2_{R_i}} + e_n(R^2) - E \right) \left\{ F_n, \{ R_i \} \right\} \Phi_n,\{ R_i \}, \left\{ \tilde{R}_i \right\} = 0. \]

\[ \sum_i \frac{1}{2M_i} \overrightarrow{V_{R_i}} \rightarrow \sum_i \frac{1}{2m_i} \overrightarrow{u^2} + \text{Arot}. \]

\[ \int d^3r_1 \ldots d^3r_N \Phi^* (\{ \tilde{R_i} \}, \{ \tilde{R}_i \}) \left( \ldots \right) \]

\[ \Rightarrow \text{P.T.O.} \]
\[
\left( - \sum \frac{1}{2M_i} \nabla_{\vec{r}_i}^2 + \varepsilon_p (\{\vec{r}_i\}) - E \right) \Phi_p \Phi_p + \sum \sum \left( - \frac{1}{2M_i} \right) \langle \Phi_p | \nabla_{\vec{r}_i}^2 | \Phi_n \rangle F_n \nabla_{\vec{r}_i} F_n = 0.
\]

\[
\begin{bmatrix}
F_1 \\
F_2 \\
\vdots \\
F_n
\end{bmatrix} \cdot \text{Lesson from first order perturbation theory}
\]

\[
\text{Pick only } n = p \text{ terms}
\]

\[
\text{Unperturbed } \Rightarrow \begin{bmatrix} 0 \\ 0 \\ \vdots \\ F_p \end{bmatrix}
\]

\[
\langle \Phi_p | \left( - \sum \frac{1}{2M_i} \nabla_{\vec{r}_i}^2 + \varepsilon_p (\{\vec{r}_i\}) - E \right) \{\Phi_p (\{\vec{r}_i\}) | \Phi_p (\{\vec{r}_i\}) \} \rangle = 0.
\]

\[
\Delta = \left( \sum \frac{1}{2M_i} \frac{\partial^2}{\partial u_i^2} \right) \bar{\Delta}_{\text{rot.}}
\]

\[
\text{acts totally on } F_p \\
\text{independent of Euler angles}
\]

\[
\text{causes shift in vibrational levels}
\]

\[
\text{Problem to be solved}
\]

\[
\langle \Phi_p | (-\bar{\Delta}_{\text{rot.}} + \varepsilon) (F_p \Phi_p) \rangle = 0.
\]

\[
\text{Find } \tilde{\varepsilon} \quad \text{(vibrational energy)}
\]

\[
\text{levels}
\]
Lecture-17:

Diatomic Molecules:

- $\vec{l}$ will rotate the electronic coordinates $\vec{r}_i$ keeping $\vec{r}_i$ fixed. (Acts on $\Phi_n$ and not on $F_n$).
- $\vec{N}$ rotates $\vec{r}_i$ keeping $\vec{r}_i$ fixed.
  $\rightarrow$ acts on $\Phi_n$ and $F_n$.
- $\vec{k}$ rotates $\vec{r}_i$ & $\vec{r}_i$ ($\vec{k} = \vec{N} + \vec{Z}$)
  \[ \begin{align*}
  \vec{r}_i & \quad \text{electrons} \\
  \vec{r}_i & \quad \Phi_n \quad \text{(Justify!)} \\
  \text{nuclei} & \quad \text{acts non-trivially on} \quad F_n \\
  \text{origin} & \quad \text{COM (common CM or CM of } \vec{r}_i \text{'s only)} \quad \text{e mass small}
  \end{align*} \]
- Space-fixed & body-fixed axes.
- $\{L_x, L_y, L_z\} \rightarrow$ components of $\vec{l}$ in space-fixed frame
- $\{\vec{L}_x, \vec{L}_y, \vec{L}_z\} \rightarrow$ " " " in body-fixed "
- Same definitions for $\vec{N} \& \vec{k}$.
- Nuclei decide on choice of body-fixed frame.

\[ \begin{align*}
\text{DIATOMIC MOLECULE ??} \\
\vec{R}^* &= \vec{r}_1 - \vec{r}_2.
\end{align*} \]

In Body-Fixed Frame

\[ \begin{align*}
\vec{r}_1 &= (0, 0, \vec{r}_1) \\
\vec{r}_2 &= (0, 0, -\vec{r}_2)
\end{align*} \]

\[ \begin{align*}
\vec{R}_1 &= \frac{\vec{R}}{M_1 + M_2} \\
\vec{R}_2 &= \frac{\vec{R}}{M_1 + M_2}
\end{align*} \]
Solve \( H_e \phi_n = e_n(\mathbf{R}) \phi_n \)
\[
H_e = \sum_i \frac{1}{2m_i g} \nabla_{\mathbf{x}_i}^2 + \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \left\{ \frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{R}_L|} + \frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{R}_G|} \right\}
\]

### Symmetries of the problem

1. \( \tilde{x}_i \rightarrow \tilde{x}_i \cos \alpha + \tilde{y}_i \sin \alpha \)
   \( \tilde{y}_i \rightarrow -\tilde{x}_i \sin \alpha + \tilde{y}_i \cos \alpha \)
   \( \tilde{z}_i \rightarrow \tilde{z}_i \)

\( \Rightarrow \) generated by \( \tilde{L}_z \) \( \Rightarrow \) \( \tilde{L}_z \phi_n = \tilde{M}_L \phi_n \)

Define \( \Lambda = |\tilde{m}_e| \) \( \tilde{M}_L = \Lambda \) or \( -\Lambda \).

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

2. \( \tilde{y}_i \rightarrow -\tilde{y}_i \)
   \( \tilde{x}_i \rightarrow \tilde{x}_i \)
   \( \tilde{z}_i \rightarrow \tilde{z}_i \)

Symmetry generator \( \rightarrow A_y \tilde{y} \)

\( A_y \tilde{y} \phi_n \left\{ \tilde{x}_i, \tilde{y}_i, \tilde{z}_i \right\}, \left\{ \mathbf{R}_1, \mathbf{R}_2 \right\} \)

\( = \phi_n \left\{ \tilde{x}_i, -\tilde{y}_i, \tilde{z}_i \right\}, \left\{ \mathbf{R}_1, \mathbf{R}_2 \right\} \)

more an independent symmetry.

Take \( \alpha = \pi \).

\( \tilde{L}_z A_y \tilde{y} \phi_n = - A_y \tilde{L}_z \tilde{y} \phi_n \)
\( = - \tilde{M}_L A_y \tilde{y} \phi_n \).
\( A \) takes \( M_L = \Lambda \) state to \( M_L = -\Lambda \) state with same \( \epsilon_n (R) \). (Degeneracy) \( \longrightarrow \) Residual.

If \( \Lambda = 0 \), \( \Phi_n \) can be chosen to be an eigenstate of \( A \) with eigenvalues \( \pm 1 \).

\[ \begin{align*}
& \Lambda : 0 \quad 1 \quad 2 \quad 3 \quad \cdots \cdots \\
\text{Symbol: } & \sum \Pi \Delta \Phi \quad \cdots \cdots \\
\sum_\pm \quad \longrightarrow \quad & A \gamma = 1 \\
& A \gamma = -1 \\
\end{align*} \]

Homonuclear molecules

Special symmetry: \( \vec{R}_1 = -\vec{R}_2 \) \( \longrightarrow \) extra symmetry

Parity symmetry:

\[ \begin{align*}
\left[ p, \text{He} \right] &= 0 \quad , \quad \left[ p, \text{\L z} \right] = 0 \\
\sum_+ q, \sum_+ u, \sum_- q, \sum_- u, & \quad (\text{understand!}) \\
T q, T u, \Delta q, \Delta u, & \quad \left\{ \begin{array}{l}
\text{Parity even: } q \\
\text{odd: } u
\end{array} \right. \\
\end{align*} \]

\[ T_n = \sum_{i=1}^{2} -\frac{1}{2M_i} \frac{\nabla^2 R_i}{R_i} \quad \text{(Diatomic case)} \]

\[ \mu = \frac{M_1 M_2}{(M_1 + M_2)} \rightarrow \left\{ \begin{array}{l}
\text{reduced mass} \\
\end{array} \right. \]

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

\[ \left. + \frac{1}{\sin^2 \theta} \frac{\partial^2 \phi}{\partial \phi^2} \right] \]
\[- \frac{1}{2\mu R^2} \frac{\partial^2}{\partial R^2} (R^2 \frac{\partial}{\partial R}) + \frac{1}{2\mu R^2} N^2 \rightarrow \text{ (same as } N^2) \]

So, the differential equation to solve looks like:

\[- \frac{1}{2\mu R^2} \frac{\partial^2}{\partial R^2} (R^2 \frac{\partial}{\partial R}) + \left( \langle \phi_n | \frac{1}{2\mu R^2} \frac{\partial}{\partial R} \right) N^2 \left( \langle \phi_n \rangle \right) F_n (R) = \text{
(vibrations)} - \epsilon_n (R) F_n (R) = E F_n (R) \]

\[
\overrightarrow{K} = \overrightarrow{N} + \overrightarrow{L} \\
\overrightarrow{N}^2 = \overrightarrow{K}^2 + \overrightarrow{L}^2 - 2 \overrightarrow{K} \cdot \overrightarrow{L}.
\]

\( \overrightarrow{K} \rightarrow \text{ exact symmetry of the problem.} \)

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

\( K(K+1) M_K \rightarrow \text{ Different } M_K \text{ values will be degenerate.} \)

\[
M_K = \{- K, -K+1, \cdots, K-1, K\}.
\]

\[
\overrightarrow{L}^2 = \overrightarrow{L}_x^2 + \overrightarrow{L}_y^2 + \overrightarrow{L}_z^2 = 2 \overrightarrow{K} \cdot \overrightarrow{L} = 2 \left( \overrightarrow{K}_x \overrightarrow{L}_x + \overrightarrow{K}_y \overrightarrow{L}_y + \overrightarrow{K}_z \overrightarrow{L}_z \right)
\]

\[
\overrightarrow{K}_x, \overrightarrow{K}_y, \overrightarrow{K}_z
\]

\( \rightarrow \text{ don't act on } \phi_n \)

\[
\langle \phi_n | \overrightarrow{L}_x | \phi_n \rangle \quad , \quad \langle \phi_n | \overrightarrow{L}_y | \phi_n \rangle \quad , \quad \langle \phi_n | \overrightarrow{L}_z | \phi_n \rangle
\]

\[- \frac{1}{2\mu R^2} \frac{\partial^2}{\partial R^2} (R^2 \frac{\partial}{\partial R}) + \frac{1}{2\mu R^2} K(K+1) - \lambda^2 \frac{\partial}{\partial R} \Theta (R) + \langle \phi_n | \overrightarrow{L}_x^2 + \overrightarrow{L}_y^2 + \overrightarrow{L}_z^2 \rangle \]

\[- \epsilon_n (R) F_n (R) = EF_n (R) \]

\( F_n (R) \)
Ignore $\lambda^2$ & $\langle \phi_n | \Sigma_x^2 + \Sigma_y^2 | \phi_n \rangle$ as we are not considering shifts of $O(1/\mu) \rightarrow$ no splitting.

$$\begin{cases} K = 0, 1, 2, \ldots \rightarrow \text{NO!} & \tilde{K}_z | \tilde{M}_L | > \\ M_K = -K, \ldots, K \end{cases}$$

(2K+1) - fold degeneracy

$$[K = \Lambda, \Lambda+1, \Lambda+2, \ldots]$$

dictates this!

$R_o : \text{min. of } e_n(R)$

$$E_{\text{rot.}} = \frac{k(k+1)}{2\mu R_o^2}$$

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

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

$$\begin{cases} -\frac{1}{2\mu} \cdot \frac{2G_n}{dR^2} + \frac{1}{2} (R - R_o)^2 e_n''(R_o) G_n + \\ G_n (e_n(R_o) + \frac{k(k+1)}{2\mu R_o^2}) = \lambda G_n \end{cases}$$

$$E = e_n(R_o) + \left( \frac{\tilde{n}}{2} + \frac{1}{2} \right) \omega + \frac{k(k+1)}{2\mu R_o^2}$$

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

A few more minutes...

Alternative description derivation of rotational spectrum

An axisymmetric rigid body.

$I_x = I_y \neq I_z$.

$I_z \rightarrow$ small

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

$$M_K = \Lambda^2$$

Recall that for axisymmetric rigid body,

\begin{align*}
\text{Etot.} & = \frac{1}{2I_z} K(K+1) + \left( \frac{1}{2I_z} - \frac{1}{2I_x} \right) \tilde{M}_K^2 \\
\text{overall shift} & \text{same as in (A)}
\end{align*}
\[ H^+_2 \]

\[ H_e = -\frac{\hbar^2}{2m} \nabla^2_n - \frac{e^2}{|r - R_A|} - \frac{e^2}{|r - R_B|} + \frac{e^2}{R} \]

\[ R = |\overrightarrow{R_A} - \overrightarrow{R_B}| \]

\[ \overrightarrow{R_A} = (0, 0, \frac{R}{2}) \quad \overrightarrow{R_B} = (0, 0, -\frac{R}{2}) \]

\[ r_A = |\overrightarrow{r} - \overrightarrow{R_A}| \quad r_B = |\overrightarrow{r} - \overrightarrow{R_B}| \]

Symmetries:

1. Rotation about \( z \rightarrow \) \( L_z \) conserved

\[ L_z |\Psi\rangle = M_L |\Psi\rangle \]

\[ |M_L| = \Lambda. \]

2. \( y \rightarrow -y \quad A_y \]

\[ r_A \rightarrow r_A \]

\[ r_B \rightarrow r_B \]

3. Special to homonuclear molecule

Parity \( \overrightarrow{r} \rightarrow -\overrightarrow{r} \rightarrow r_A \leftarrow -r_B \]

\[ \overrightarrow{R_A} = -\overrightarrow{R_B} \]

- Propose (guess!) a ground state

- Intuition \( \rightarrow \) For large \( R \),

\[ \phi = \frac{1}{\sqrt{2}} \left( \psi_{1s}(r_A) \pm \psi_{1s}(r_B) \right) \]

- H-atom ground state

- Reason for taking linear combination \( \rightarrow \) symmetries

\[ \Lambda = 0, \quad A_y = 1, \quad \sum^+ g/u \rightarrow \{ \text{Symbol for} \}

\text{states}

\[ \text{Parity} \rightarrow \pm 1. \]

- Take this as an approximation even for finite \( R \).
\[ E_{g,u} = \frac{\int d^3r \phi_{g,u}^* \phi_{g,u}}{\int d^3r \phi_{g,u} \phi_{g,u}} \]

**Exercise**: Check that, \( E_{g,u} = E_{1s} + \text{correction} \)

**Correction**

\[
\text{ground state energy for single-electron atom} = \text{single-electron atom} = \frac{e^2}{2R} \left[ \frac{1}{1 + \hat{R}} \right] \left( 1 + \frac{2}{3} \right) e^{-\hat{R}} = \frac{e^2}{2} \left( 1 + \frac{2}{3} \right) e^{-\hat{R}}
\]

\[ \hat{R} = \frac{me^2}{R} \]

\[ E^\uparrow \quad E_g - E_{1s} \quad E_u - E_{1s} \quad \{ \text{molecule doesn't bind} \} \quad \{ \text{Exact solution} \} \]

\[ \bar{z}_g = \frac{1}{R} (r_A + r_B) \quad \{ \text{Elliptic coordinates} \} \]

\[ \eta = \frac{1}{R} (r_A - r_B) \]

\[ \{ \bar{z}_g, \eta, \phi \} \rightarrow \text{set of independent coordinates} \]

\[ E_x \quad \text{Check that,} \quad \nabla^2 \psi = \frac{4}{R} \left( \frac{1}{\eta^2} \right) \left[ \frac{2}{\sqrt{3}} \left( \frac{y^2 - 1}{(y^2 - \eta^2)} \right) \frac{2}{\sqrt{3}} \frac{2y}{\sqrt{3}} \right] \]

\[ \bar{z}_g \rightarrow \bar{z}_g \quad \{ \text{parity} \} \quad \frac{2}{\eta} \left\{ \left( 1 - \eta^2 \right) \frac{d^2}{d\eta^2} \right\} + \frac{\eta^2 - \eta^2}{(\eta^2 - 1)(1 - \eta^2)} \frac{d^2}{d\phi^2} \]

\[ \eta \rightarrow -\eta \]

\[ A_y : \text{doesn't change} \quad \bar{z}_g, \eta, \phi \rightarrow \phi + \pi \]

\[ L_z : \text{rotates} \phi \]
\[ H = -\frac{1}{2m} \nabla_n^2 - \frac{2e^2}{R(\zeta_1 + \eta)} - \frac{2e^2}{R(\zeta_2 - \eta)} + \frac{e^2}{R} \]

\[ \begin{align*}
\alpha_A &= R\left(\frac{\eta + 1}{2}\right) \\
\alpha_B &= R\left(\frac{\eta - 1}{2}\right)
\end{align*} \]

\[ \text{Multiply both sides by } (\frac{\eta^2}{4} - \eta^2) \]

\[ \frac{\partial^2 \phi^2}{\partial \eta^2} \rightarrow - \Lambda^2 \]

- The variables separate

- Look for solutions of the form \( e^{i M L \phi} F(\frac{\zeta}{R}) G(\eta) \)

Equations for \( F \& G \)

\[ |ML| = \Lambda \]

Exercise:

\[ 4 \int R^2 \frac{\partial}{\partial \eta} \left( (\zeta^2 - 1) \frac{\partial F}{\partial \eta} \right) - \frac{4 \Lambda^2}{R^2} \frac{1}{\zeta^2 - 1} F + \frac{8e^2 m}{R} \frac{\zeta}{R} F - 2 \frac{(e^2}{R} - E) m^2 F \]

new constant \(+ \Lambda F = 0 \)

\[ \frac{1}{R^2} \frac{\partial}{\partial \eta} \left( (1 - \eta^2) \frac{\partial G}{\partial \eta} \right) - \frac{4 \Lambda^2}{R^2} \frac{1}{1 - \eta^2} G - 2 \frac{(e^2}{R} - E) \eta^2 G \]

- 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

\[ \implies \text{gives } E_g(R) \& E_u(R) \]

( agrees with our intuition)

Neutral hydrogen \( H_2 \)

\[ H_e = -\frac{1}{2m} \left( \nabla_{\zeta_1}^2 + \nabla_{\zeta_2}^2 \right) - \frac{e^2}{\zeta A_1} - \frac{e^2}{\zeta A_2} - \frac{e^2}{\zeta B_1} - \frac{e^2}{\zeta B_2} + \frac{e^2}{R} \]
\[ n_{\text{A1}} = |\vec{r}_1 - \vec{r}_A| \quad \text{and so on} \quad (!!!) \]

\[ n_{12} = |\vec{r}_1 - \vec{r}_2| \]

- Single electron \rightarrow spin doesn't matter

**BUT, HERE IT MATTERS !!!**

- Think of nucleus as fixed classical object.

**Electron spin states**

\[ |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle. \]

\[ S = 1 \quad \text{states} \]

\[ \mathcal{N}_{S, m_S} \rightarrow S^z \text{ eigenvalue} \]

\[ \mathcal{N}_{00} = \frac{1}{\sqrt{2}} (|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle) \]

**Two independent methods**

**Molecular Orbital Method**

\[ \mathcal{N}_{10} = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \]

\[ \mathcal{N}_{11} = |\downarrow\downarrow\rangle \]

\[ \mathcal{N}_{01} \rightarrow \text{Molecular Orbital Method} \]

**? \quad \text{(Valence Bond Method)}**

- First, solve the single electron moving in the background of both nuclei.

- Use products of these to build multi-electron states.

\[ \phi_g (\vec{x}), \phi_u (\vec{x}) \rightarrow \text{solutions to single-electron problem}. \]

\[ \mathcal{N}_{1 \text{ Ms}} \rightarrow \{ \phi_g (\vec{x}_1) \phi_u (\vec{x}_2) - \phi_q (\vec{x}_2) \phi_u (\vec{x}_1) \} \]

\[ \sum \phi \rightarrow \text{understand} \]

\[ \mathcal{N}_{00} \rightarrow \{ \phi_g (\vec{x}_1) \phi_u (\vec{x}_2) + \phi_q (\vec{x}_2) \phi_u (\vec{x}_1) \} \]

\[ \mathcal{N}_{00} \quad \mathcal{N}_{01} \quad \mathcal{N}_{02} \]
Let's call \( \sum \) as \( \Phi_A \) & \( \Phi_B \).

(These can mix)

- Suppose, we use the approximation -

\[
\Phi_A (r) = \frac{1}{\sqrt{2}} (\psi_{1S} (r_A) + \psi_{1S} (r_B))
\]

\[
\Phi_B (r) = \frac{1}{\sqrt{2}} (\psi_{1S} (r_A) - \psi_{1S} (r_B))
\]

**Exercise:**

\[
\begin{bmatrix}
\Phi_A \\
\Phi_B
\end{bmatrix} =
\begin{bmatrix}
\phi_{cov} + \phi_{ion} \\
\phi_{cov} - \phi_{ion}
\end{bmatrix}
\]

\[
\phi_{cov} = \frac{1}{2} \left( \psi_{1S} (r_{A1}) \psi_{1S} (r_{B2}) + \psi_{1S} (r_{A2}) \psi_{1S} (r_{B1}) \right)
\]

\[
\phi_{ion} = \frac{1}{2} \left( \psi_{1S} (r_{B1}) \psi_{1S} (r_{B2}) + \psi_{1S} (r_{A1}) \psi_{1S} (r_{A2}) \right)
\]

1 ↔ 2 exchange symmetry

1 \( \rightarrow \) 2 covalent

1 \( \rightarrow \) 2 ionic

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. (1)

\[
\psi_{1S} (r_A)
\]

\[
\left\{ \psi_{1S} (r_{A1}) \psi_{1S} (r_{B2}) \pm \psi_{1S} (r_{A2}) \psi_{1S} (r_{B1}) \right\}
\]

\( S = 0 \)

\( S = 1 \)

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

\( \phi_{cov} \)

(Starting point)

\( \Phi \)
Take trial wavefunction $\phi$. 

If the earlier distribution is above or below the second one throughout the region (intermediate range of $R$), we can say the nuclei bind \textit{yet don't bind}.

$H_2 \phi_u \phi_g$

Diatomic molecules with larger nuclei (more electrons)

General strategy:

Assume that molecular orbitals are $\psi_1 (\mathbf{r}_1, \mathbf{r}_2), \psi_2 (\mathbf{r}_2, \mathbf{r}_1), \ldots$

Initial guess for $\psi_i$'s.

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

- Compare the pictures

$H_2^+ \phi_u \rightarrow \text{doesn't bind}$

$\phi_g \rightarrow \text{binds}$

- Carry out Hartree-Fock.

- Make an initial guess for $\psi_i$'s (Zeroth order approx.)
energies of these two ends are fixed (if atomic states are known)

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

R = ∞ end: (n, l) for charge ZE for each nucleus.

Two states for each (n, l) → bound to either of the nuclei

Choose basis → eigenstates of parity operator.

\[ \phi_{\ell m} \propto (n_{A} (r_{A}) \pm n_{B} (r_{B})) \]

Conserved quantum numbers: \[ |M_{\ell}| = \ell \]

\[ \lambda = \{ 0, 1, 2, 3, \ldots \} \]

\[ \sigma \pi \delta \phi \]

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

Proof:

Imagine (!) map to \[ H_{\text{eff.}} \]

2-level system \[ H_{11}(R) \quad H_{12}(R) \]

condition for level crossing \[ \begin{align*}
H_{11}(R_{c}) &= 0 \\
H_{12}(R_{c}) &= 0
\end{align*} \]

at \[ R = R_{c} \]

\[ \text{Simultaneous vanishing is not likely.} \]
\[
\text{He}^2 : \quad (\sigma_g 1s)^2 \quad (\sigma_u 1s)^2
\]

\[
\text{Li}^2 : \quad (\sigma_g 1s)^2 \quad (\sigma_u 1s)^2 \quad (\sigma_g 2s)^2
\]

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

Heteronuclear molecule (diatomic)

\[
\begin{align*}
Z_A &> Z_B \\
\end{align*}
\]

\[
\text{LiH molecule} \\
Z_A = 3 \quad Z_B = 1
\]

Connect in same way

\[
\text{LiH} \rightarrow (1s_a)^2 (1s_b)^2
\]

Read Bransden & Joacham
Lecture 20:

Spectrum of Light (from Diatomic Molecules)

- Dipole transition

\[ \langle m | \vec{D} | m' \rangle \]

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

\[ \phi_n (\vec{r}_1, \vec{r}_2) \quad F_n (\vec{r}_1, \vec{r}_2) \]

\( \downarrow \) rotational + vibrational states

\( \epsilon_S, n, k \rightarrow \) rotational

\[ \hbar \langle \phi_S | (\hat{L}_x^2 + \hat{L}_y^2) | \phi_S \rangle \]

\[ \frac{1}{2 \mu R_0^2} \left( \epsilon_S (R_0) - \frac{\Lambda^2}{2 \mu R_0^2} + \right. \]

\[ \left. \right. \quad \left. \left. \left. \right. \left. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \right. \righ...
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 $\omega$, $R_0$).

Heteronuclear Molecule

$$e \langle \phi_s | (Z_1 \bar{R}_1 + Z_2 \bar{R}_2 \cdot \bar{R}_1 - \bar{R}_2) | \phi_s \rangle$$

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

Transitions are possible.

What about selection rules ?

$\bar{D} \Rightarrow$ vector under $\bar{R}$, $\bar{r}$ rotations.

$$\langle s, n, k, m | \bar{D} | s', n', k', m' \rangle$$

$\Rightarrow$ non-zero for $k = k' \pm 1$ or $k' \pm 1$ or $k'$

(Clebsch - Gordon coefficients ---)

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

Naively, $\phi_s$ will depend on $\bar{r}_i \cdot \bar{r}_j$ and $\bar{r}_i \cdot \bar{R}_j$

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

This is true for polyanionic molecules...

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

$\phi_s \rightarrow e^{i \phi} \phi_s$.

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

Information about overall rotations is encoded within $F_s(\bar{R}_1, \bar{R}_2)$. 
\[ F_s (\vec{R}) = F_s (\vec{R}) Y^m_k (\theta, \phi) \]

Under \( \vec{J}_i \rightarrow - \vec{J}_i \) AND \( \vec{R}_i \rightarrow - \vec{R}_i \), \( \phi_s \) is unchanged.

\( F_s (\vec{R}) \) is also unchanged.

\[ Y^m_k (\theta, \phi) \rightarrow (-1)^k Y^m_k (\theta, \phi) \]
\[ \vec{D} \rightarrow (-\vec{D}) \]

For \( \Lambda = 0 \):

\[ K' = K \pm 1 \quad (\text{not } K) \]
\[ m_k = m'_k \pm 1, m'_k \]

**Selection rules for vibrational states**

\[ \langle \vec{D} (\vec{R}) \rangle = \langle \phi_s | \vec{D} | \phi_s \rangle \]

(Integrate over electronic coordinates)

(Taylor expand)

doesn't depend on \( \vec{R} \)

(doesn't cause any transition)

\[ n = n' \pm 1 \]

These give the most intense lines.

**Rotational Spectrum**

No change in vibrational state \( n = n' \)

\[ S = s' \]

\[ (n, s, k) \rightarrow (n, s, k' - 1) \quad (s, n, k) \rightarrow (s, n, k' - 1) \]
Frequency $\Omega$:
\[ \frac{1}{2\mu R_0^2} \quad \frac{k(k+1)-(k-1)k}{1} \]
\[ = \frac{k}{\mu R_0^2} \]

Equally spaced lines.

- There's a lower cutoff

Vibrational - Rotational spectrum

1. $\text{R-branch}$
   \[ \Omega = \omega + \frac{(k+1)}{\mu R_0^2} \]
   
   (Band-like)
   \[ K = n, n+1, \ldots \]

2. $\text{P-branch}$
   \[ \Omega = \omega - \frac{k}{\mu R_0^2} \]
   
   (Small gap)
   \[ K = n+1, \ldots \]

3. $\Lambda \neq 0$
   \[ \text{Q-branch} \]
   \[ \Omega = \omega - \frac{(s, n+1, k)}{(s, n, k)} \]
   
   Electronic spectrum
   \[ (s, n, k) \rightarrow (s', n', k') \]