Lecture 14 – Molecules

03/24/16

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1. Finish Atoms
2. Molecules

1. Concluding Atoms

nitrogen $(1s)^2(2s)^2(2p)^3$

closed shells → do not contribute

$\ell = 1$

m_ℓ: ↑ 1, ↑ 0, ↑ −1 → $L_z = 0$

$S = 3/2$, $L = 0$, $J = 3/2$

configuration: $^4S_{3/2}$

oxygen $(1s)^2(2s)^2(2p)^4$

m_ℓ: ↑↓ 1, ↑ 0, ↑ −1 → $1 + 0 + (-1) = L = 1$

$S = S_z = 1/2 + 1/2 = 1$ ← because that is the maximized spin values

$S = 1$, $L = 1$, $J = 2$

configuration: $^3P_2$

Zeeman effect for multi-electron atoms

General Zeeman magnetic Hamiltonian

$$H_z = -\vec{\mu}\cdot\vec{B}, \quad \vec{B} = B\hat{z}$$

$$\vec{\mu} = \frac{e}{2mc}\sum_i (\vec{L}_i + g_e \vec{S}_i), \quad g_e \approx 2.002\ldots$$

$e = -e_0$ for an electron

$$= \frac{-e_0}{2mc}\sum_i (\vec{J}_i + (g_e - 1)\vec{S}_i)$$

$\frac{-e_0}{2mc} = \mu_B/\hbar$

$$= -\frac{\mu_B}{\hbar}(\vec{J} + (g_e - 1)\vec{S})$$

$\Delta E_z^{(1)}$ ← first-order correction due to Zeeman

$$\Delta E_z^{(1)} = \langle \omega J L S m_J | H_z | \omega J L S m_J \rangle$$

→

then by the projection theorem ($\vec{S} \propto \vec{J}$)

$$\vec{S} \to \frac{(\vec{S}\cdot\vec{J})\vec{J}}{\vec{J}(\vec{J}+1)}, \quad (\vec{S}\cdot\vec{J}) = \frac{1}{2}(J^2 + S^2 - L^2)$$

proportionaly constant; $L^2 = (\vec{J}-\vec{S})^2$

$$\Delta E_{\text{JLS}}^{(1)} = m_J \mu_B B \underbrace{\left(1 + (g_e - 1)\frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}\right)}_{\equiv g_{JLS},\ \text{The Landé g-factor } (1 \le g_{JLS} \le 2)}$$

2. Molecules

very complicated compared to atoms

Required simplification: the mass of the nuclei, M, is much, much greater than the mass of the electron, m_e.

- allows a good approximation which separates the problem of electron states from that of nuclei

small parameter $\frac{m_e}{M_N} \sim 10^{-3} - 10^{-5}$

Take a wavefunction of the form

(exact form) $\Psi(x_e, x_n)$ = (approximate form) $\psi(x_e|x_n)\Phi(x_n)$

nuclear & electron coordinates; spin embedded in x's

$$H = \underbrace{T_e + V_{en} + V_{ee}}_{H_e} + \underbrace{T_n + V_{nn}}_{H_n}$$

(T_e: total Kinetic Energy (of e^-); $V_{en} + V_{ee}$: potential of interaction (between e^- & n))

$H\Psi = E\Psi$ — the configuration energy

$\hookrightarrow H_e\psi(x_e|x_n) = E_e(x_n)\psi(x_e|x_n)$

this is the "Born-Oppenheimer Approximation"

which allows us to approximate, for the whole molecule,

$$(T_n + V_{nn} + E_e(x_n))\Phi(x_n) = E\Phi(x_n)$$

→

When is this valid?: Valid up to corrections involving...

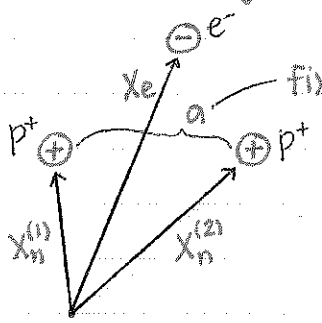
$$\frac{\partial}{\partial x_n}\psi(x_e|x_n) \sim \sqrt{\frac{m}{M_N}} \quad \text{(vibrational correction)}$$

$$\frac{\partial^2}{\partial x_n^2}\psi(x_e|x_n) \sim \frac{m}{M_N} \quad \text{(rotational correction)}$$

→ Dr. Yakovenko takes over here ←

[Schwabl 15.1] We want to make approximations in the Hamiltonian that take advantage of our "small parameter."

ex. H_2^+ The Hydrogen Ion (simplest molecule)



fixed relation in nucleus (the equilibrium distance)

$$E_{e^-} = \frac{p^2}{2m_e}$$ — by the uncertainty relation, the equilibrium distance ∝ the size of the electron → $p \sim \hbar/a$

$$\sim \frac{\hbar^2}{2m_e a^2}$$

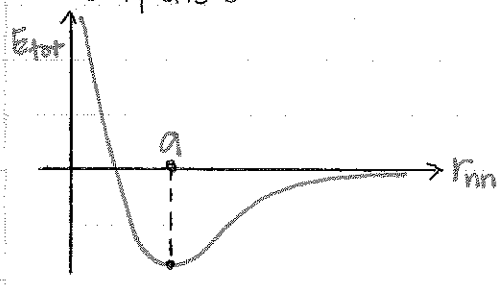
Why do molecules even form? (Neglect KE)

Consider, instead of equilibrium distance = a, you solve the Schrödinger equation for a nucleus distance of r_{nn}

ignore KE

$$H = T_e + V_{en} + \cancel{V_{ee}} + \cancel{T_n} + V_{nn}$$

only one e⁻ $\quad V_{nn} \sim e^2/r_{nn}$



$$E_{tot} = E_e + V_{nn}$$
$$<0 \quad >0$$

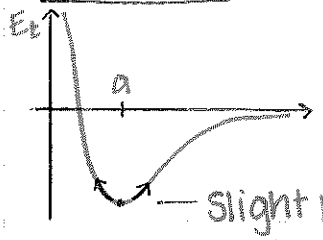
For two protons, the Schrödinger equation solution will have a minimum @ $r_{nn} = a$

Molecules form because their equilibrium distance is the most stable nuclear / Nucleus distance.

→ Now, reinstate KE

There are two kinds of motion:

① Vibration



$$(T_N + V_{nn} + \overbrace{E_e(X_n)}^{E_{tot}(X_n)})\Phi(X_n) = E\Phi(X_n)$$

where $E_e(X_n)$ is an effective potential as a function of nuclear position

— Slight motions within the well

⇒ Approximate as a Simple Harmonic Oscillator

$$E_{tot} \sim \frac{M_N \omega^2}{2}(\delta r_{nn})^2$$

└ this is an estimate of the average displacement from equilibrium where T_N is the standard kinetic energy in terms of nuclear position ;2

$$T_N = \frac{-1}{2M_N}\frac{\partial^2}{\partial X_N^2}$$

But what if $\delta r_{nn} \sim a$?

→ causes distortion to energy

$$\delta r \sim a \; ; \; \delta E \sim E_{e^-} = \frac{\hbar^2}{2ma^2}$$

Plugging into displacement to find ω, the vibrational frequency ;2

$$\frac{M_N \omega^2}{2} a^2 \sim \frac{\hbar^2}{2m_e a^2}$$

$$\hbar^2\omega^2 = \frac{m_e}{M_N}\left(\frac{\hbar^2}{a^2 m_e}\right)\left(\frac{\hbar^2}{a^2 m_e}\right)$$

$$\hbar\omega = \sqrt{\frac{m_e}{M_N}}\overbrace{\frac{\hbar}{m_e a^2}}^{E_{e^-}} = \sqrt{\frac{m_e}{M_N}}E_{e^-} \Rightarrow \hbar\omega \ll E_{e^-}$$

(ħω: vibration; E_{e^-}: electron energy)

* The characteristic quantum vibration within nuclei is <u>much</u> smaller than the electron energy (energy of nuclear motion)

⇒ This justifies our previous approximations!

→

② Rotation

→ the second consequence of the standard KE, T_N (angular momentum)

$$E_{rot} = \frac{\hbar^2 \ell(\ell+1)}{2I}$$ ← moment of inertia of the molecule

$$\sim \frac{\hbar^2}{M_N a^2} = \frac{m_e}{M_N}\underbrace{\left(\frac{\hbar^2}{m_e a^2}\right)}_{E_{e^-}}$$

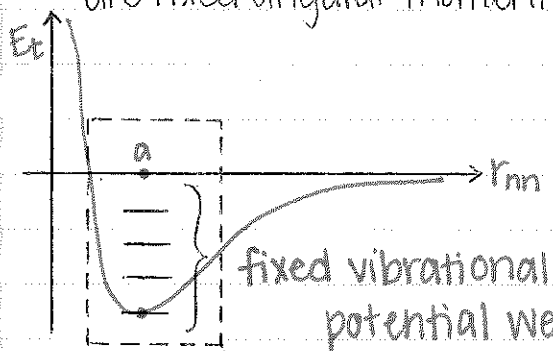
decrease by a factor of $\sqrt{m_e/M_N}$ each time

$$= \frac{m_e}{M_N} E_{e^-} \implies E_{rot} \ll \hbar\omega \ll E_{e^-}$$

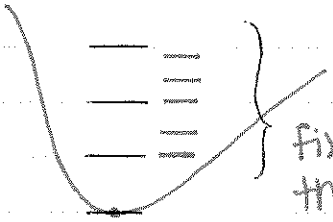
$$E_{tot} = E_{e^-} + E_{vib} + E_{rot}$$

- E_{e^-}: electron Q#
- $E_{vib} = \hbar\omega(n+\tfrac{1}{2})$
- $E_{rot} = \frac{\hbar^2 \ell(\ell+1)}{2I}$

Recall: for a fixed discrete energy spectrum of a molecule, there are fixed angular momentum levels



fixed vibrational levels within the E_{e^-} potential well



fixed rotatational levels within the vibrational levels

This graphically confirms $E_{tot} = E_{e^-} + E_{vib} + E_{rot}$