POSTECH 이성익 교수의
양자 세계에 관한 강연
- 14장 -

편집 도우미: POSTECH 학부생 임향택

Chapter 14

About Atoms and Molecules

The helium atom

$$H=\frac{1}{2m}p_1^2+\frac{1}{2m}p_2^2-\frac{ze^2}{r_1}-\frac{ze^2}{r_2}+\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

Ignore : motion of the nucleus
Relativistic effect
Spin-orbit effect
Electron에 의한 Current와 Spin과의 coupling

$$H=H^{(1)}+H^{(2)}+V$$

with

$$H^{(i)}=\frac{1}{2m}p_i^2-\frac{ze^2}{r_i} \quad \text{and} \quad V=\frac{e^2}{|\vec{r}_1-\vec{r}_2|}$$

V가 없으면,

$$u(\vec{r}_1,\vec{r}_2)=\phi_{n_1l_1m_1}(\vec{r}_1)\phi_{n_2l_2m_2}(\vec{r}_2)$$

$$\left[H^{(1)}+H^{(2)}\right]u(\vec{r}_1,\vec{r}_2)=Eu(\vec{r}_1,\vec{r}_2)$$

$$E=E_{n1}+E_{n2}$$

Potential이 없다는 가정을 잊지 말 것

Ground state

$$=+2E_1$$

$$=-mc^2(2\alpha)^2$$

$$=-108.8\text{eV}$$

first excited state

$$E=E_1+E_2$$

$$=-13.6\text{eV}\times 4-\frac{13.6\text{eV}}{4}\times 4$$

$$=-68.0\text{eV}$$

Ionization Energy

ground에서 ∞로 떼어내는 데 필요한 energy

$$E_{\text{ionize}} = E_1 + E_\infty - 2E_1$$
$$= 54.4\text{eV}$$

Ground state wave function

$$u_0(\vec{r}_1, \vec{r}_2) = \phi_{100}(\vec{r}_1)\phi_{100}(\vec{r}_2) X_{\text{singlet}}$$

$$X_{\text{singlet}} = \frac{1}{\sqrt{2}}\left(\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right)$$

first excited state $\rightarrow$ two possibilities

$$u_1^{(s)} = \frac{1}{\sqrt{2}}\left[\phi_{100}(\vec{r}_1)\phi_{2lm}(\vec{r}_2) + \phi_{2lm}(\vec{r}_1)\phi_{100}(\vec{r}_2)\right] X_{\text{singlet}}$$

$$u_1^{(t)} = \frac{1}{\sqrt{2}}\left[\phi_{100}(\vec{r}_1)\phi_{2lm}(\vec{r}_2) - \phi_{2lm}(\vec{r}_1)\phi_{100}(\vec{r}_2)\right] X_{\text{triplet}}$$

$$X_{\text{triplet}} = \begin{cases} \chi_+^{(1)}\chi_+^{(2)} \\ \frac{1}{\sqrt{2}}\left(\chi_+^{(1)}\chi_-^{(2)} + \chi_-^{(1)}\chi_+^{(2)}\right) \\ \chi_-^{(1)}\chi_-^{(2)} \end{cases}$$

Perturbation에 의해 energy shift를 계산하자.

$$\Delta E = \int d^3r_1 d^3r_2 u_0^*(\vec{r}_1, \vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} u_0(\vec{r}_1, \vec{r}_2)$$

$$= \int d^3r_1 d^3r_2 \left|\phi_{100}(\vec{r}_1)\right|^2 \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \left|\phi_{100}(\vec{r}_2)\right|^2$$

$$\left(\phi_{100}(r) = \frac{2}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \cdot e^{-Zr/a_0}\right)$$

$$= \frac{e^2}{\pi}\left(\frac{Z}{a_0}\right)^3 \int d^3r_1 d^3r_2 e^{-2Zr_1/a_0} \cdot e^{-2Zr_2/a_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$= \frac{e^2}{\pi}\left(\frac{Z}{a_0}\right)^3 \int_0^\infty r_1^2 dr_1 \cdot e^{-2Zr_1/a_0} \int_0^\infty r_2^2 dr_2 \cdot e^{-2Zr_2/a_0} \int d\Omega_1 \int d\Omega_2 \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{\left(r_1^2 + r_2^2 - 2r_1r_2\cos\theta\right)^{1/2}}$$

$$\int d\Omega_2 \frac{1}{|\vec{r}_1-\vec{r}_2|} = \int_0^{2\pi} d\phi \int_{-1}^{1} d(\cos\theta)\cdot \frac{1}{\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)^{1/2}}$$

$$= -2\pi\cdot\frac{1}{2r_1r_2}\left[\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)^{1/2}\right]_{\cos\theta=-1}^{\cos\theta=1}$$

$$= \frac{\pi}{r_1r_2}\left(r_1+r_2-|r_1-r_2|\right)$$

$$\Delta E = \frac{e^2}{\pi}\left(\frac{Z}{a_0}\right)^3 \int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0}\int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a_0}\cdot 4\pi^2\left(r_1+r_2-|r_1-r_2|\right)$$

$$\therefore \quad = \frac{e^2}{\pi}\left(\frac{Z}{a_0}\right)^3\cdot 4\pi^2\int_0^\infty r_1^2 dr_1 e^{-2Zr_1/a_0}\cdot\left[\int_0^{r_1} e^{-2Zr_2/a_0}\cdot r_2^2\cdot 2r_1 + \int_{r_1}^\infty e^{-2Zr_2/a_0}\cdot r_2^2\cdot 2r_2\right]$$

$$= \frac{5}{4}Z\left(\frac{1}{2}mc^2\alpha^2\right)$$

When $r_1 > r_2$

$$\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)^{-\frac{1}{2}} = r_1^{-1}\left(1+\frac{r_2^2}{r_1^2}-2\frac{r_2}{r_1}\cos\theta\right)^{-\frac{1}{2}}$$

$$= \frac{1}{r_1}\sum_{l=0}^{\infty}\left(\frac{r_2}{r_1}\right)^l\cdot P_l(\cos\theta)$$

$$\int d\Omega_1\int d\Omega_2 \frac{1}{|\vec{r}_1-\vec{r}_2|} = \int d\Omega_1\int d\Omega_2 \sum_{l=0}^{\infty}\frac{r_<^l}{r_>^{l+1}}P_l(\cos\theta)$$

$$\frac{1}{2}\int_{-1}^{1} d(\cos\theta) P_L(\cos\theta) = \delta_{L0}$$

or

$$\frac{1}{2}\int_{-1}^{1} d(\cos\theta)\cdot P_L(\cos\theta)P_{L'}(\cos\theta) = \frac{\delta_{LL'}}{2L+1}$$

$$= \int d\Omega_1\int d\Omega_2\frac{1}{r_>}\cdot P_0(\cos\theta)$$

$$= \frac{1}{r_>}\int d\Omega_1\cdot 2\pi\int_{-1}^{1} d(\cos\theta)P_0(\cos\theta)$$

$$= 4\pi\cdot 4\pi\cdot\frac{1}{r_>}$$

$$\therefore \quad E = -108.8\text{eV} + 34\text{eV}$$

$$= -74.8\text{eV}$$

그러나 정답 $E_{\exp} = -78.975\text{eV}$ 아직 다르다.

$\because$ Screening을 생각하자

Let

$$E + \Delta E = -\frac{1}{2}mc^2 \cdot \alpha^2 \left(2Z^2 - \frac{5}{4}Z\right)$$

Variational method로 풀자.

Ground state 찾는 법

H의 expectation value를 minimize 하자.

$$\langle \psi | \psi \rangle = 1$$

$$H\psi_n = E_n \psi_n$$

$$\psi = \sum_n C_n \psi_n$$

$$\begin{aligned}
\langle \psi | H | \psi \rangle &= \sum_n \sum_m C_n^* \langle \psi_n | H | \psi_m \rangle C_m \\
&= \sum_n \sum_m C_n^* C_m E_m \delta_{mn} \\
&= \sum |C_n|^2 E_n \\
&\geq E_0 \sum |C_n|^2 \\
&= E_0
\end{aligned}$$

$\therefore \langle \psi | H | \psi \rangle \geq E_0$ Variational method

예. Helium

Choose $\psi(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)$

where $\left(\frac{p^2}{2m} - \frac{Z^* e^2}{r}\right)\psi_{100}(\vec{r}) = \varepsilon \psi_{100}(\vec{r})$ with $\varepsilon = -\frac{1}{2}mc^2 \left(z^* \alpha\right)^2$

$$\langle \psi | H | \psi \rangle$$

$$= \int d^3 r_1 \int d^3 r_2 \psi_{100}^*(\vec{r}_1) \psi_{100}^*(\vec{r}_2) \left(\frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right) \psi_{100}(\vec{r}_1) \psi_{100}(\vec{r}_2)$$

$$\int d^3 r_1 \psi^*_{100}(\vec{r}_1)\left(\frac{p_1^2}{2m}-\frac{Z^* e^2}{r_1}+\frac{(Z^*-Z)e^2}{r_1}\right)\psi_{100}(\vec{r}_1)$$

$$=\varepsilon+(Z^*-Z)e^2\int d^3 r_1\left|\psi_{100}(\vec{r}_1)\right|^2\frac{1}{r_1}$$

$$=\varepsilon+(Z^*-Z)e^2\cdot\frac{Z^*}{a_0}$$

$$=\varepsilon+Z^*(Z^*-Z)mc^2\alpha^2 \qquad \text{where } \varepsilon=-\frac{1}{2}mc^2(Z^*\alpha)^2$$

$$=-\frac{1}{2}mc^2(Z^*\alpha)^2+Z^*(Z^*-Z)mc^2\alpha^2$$

$$=mc^2\alpha^2\left[-\frac{1}{2}Z^{*2}+Z^{*2}-Z^*Z\right]$$

$$=mc^2\alpha^2\left[\frac{1}{2}Z^{*2}-Z^*Z\right]$$

$$\langle\psi|H|\psi\rangle=mc^2\alpha^2\left[Z^{*2}-2Z^*Z\right]+\int d^3 r_1\int d^3 r_2\psi^*_{100}(\vec{r}_1)\psi^*_{100}(\vec{r}_2)\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2)$$

$$\therefore \qquad =mc^2\alpha^2\left[Z^{*2}-2Z^*Z\right]+\left(\frac{1}{2}mc^2\alpha^2\right)\left(\frac{5}{4}Z^*\right)$$

$$=mc^2\alpha^2\left[Z^{*2}-2Z^*Z+\frac{5}{8}Z^*\right]$$

minimize with respect to Z^*

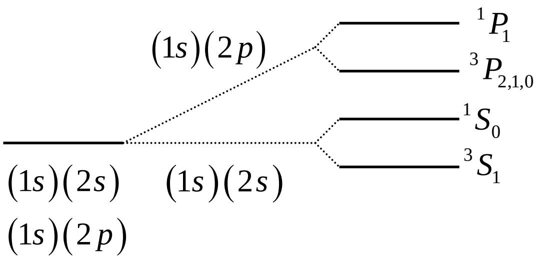
$$2Z^*-2Z+\frac{5}{8}=0 \qquad\qquad \therefore Z^*=Z-\frac{5}{16}$$

minimum energy

$$E_0\le-\frac{1}{2}mc^2\alpha^2\left[2\left(Z-\frac{5}{16}\right)^2\right]$$

$$=-77.38\text{eV} \quad (Z=2)$$

Schematic sketch of splitting of the first excited states of helium



특 징

Spin parallel과 antiparallel의 차이

Spin parallel과 antiparallel의 차이

total wave function은 anti-symmetric

$$\psi(\vec{r}_1,\vec{r}_2) = \text{Space} \cdot \text{Spin}$$

S	A	singlet
A	S	triplet

$$\frac{1}{\sqrt{2}}\left\{\phi_{100}(\vec{r}_1)\phi_{2l0}(\vec{r}_2) \pm \phi_{2l0}(\vec{r}_1)\phi_{100}(\vec{r}_2)\right\}$$

$$\Delta E_1^{(s,t)} = \frac{1}{2}e^2\int d^3r_1\int d^3r_2\left[\phi_{100}(\vec{r}_1)\phi_{2l0}(\vec{r}_2) \pm \phi_{2l0}(\vec{r}_1)\phi_{100}(\vec{r}_2)\right]^* \cdot \frac{1}{|\vec{r}_1-\vec{r}_2|}$$

$$\cdot\left[\phi_{100}(\vec{r}_1)\phi_{2l0}(\vec{r}_2) \pm \phi_{2l0}(\vec{r}_1)\phi_{100}(\vec{r}_2)\right]$$

$$= \frac{1}{2}e^2 \cdot 2\int d^3r_1\int d^3r_2\left|\phi_{100}(\vec{r}_1)\right|^2 \cdot \left|\phi_{2l0}(\vec{r}_2)\right|^2 \frac{1}{|\vec{r}_1-\vec{r}_2|}$$

$$\pm e^2\int d^3r_1\int d^3r_2\phi^*_{100}(\vec{r}_1)\phi^*_{2l0}(\vec{r}_2)\frac{1}{|\vec{r}_1-\vec{r}_2|}\phi_{2l0}(\vec{r}_1)\phi_{100}(\vec{r}_2)$$

= electron에 의한 coulomb interaction + No classical interpretation Pauli's principle

$n=1, n=2$의 결합 or $(1,n)$

$$\Delta E_{n,l}^{(t)} = J_{nl} - K_{nl}$$

$$\Delta E_{n,l}^{(s)} = J_{nl} - K_{nl}$$

triplet

Spin $|1,1\rangle$, $|1,0\rangle$, $|1,-1\rangle$

electron이 멀어져 있다.

$r_1 = r_2 \to \psi = 0$

singlet

Spin $|0,0\rangle$

electron이 가까이 있다.

$r_1 = r_2 \to \psi \neq 0$

Pauli의 exclusion principle에 의해 높은 에너지 상태가 된다.

Pauli’s exclusion principle

$\rightarrow$ spin dependent

$$\Delta E_{nl}^{(t)} = J_{nl} - K_{nl}$$

$$\Delta E_{nl}^{(s)} = J_{nl} + K_{nl}$$

$$S^2 = \left(S_1 + S_2\right)^2 = S_1^2 + S_2^2 + 2\vec{S}_1 \cdot \vec{S}_2$$

$$2\vec{S}_1 \cdot \vec{S}_2 = S^2 - \left(S_1^2 + S_2^2\right)$$

$$\text{If} \quad S = 1 \quad 2\hbar^2 - 2\cdot\frac{3}{4}\hbar^2 = \frac{1}{2}\hbar^2$$

$$S = 0 \quad 0 - 2\cdot\frac{3}{4}\hbar^2 = -\frac{3}{2}\hbar^2$$

$$\therefore \begin{pmatrix} 1 = \dfrac{2\vec{S}_1 \cdot \vec{S}_2}{\hbar^2} + \dfrac{1}{2} & S = 1 \\ -1 = \dfrac{2\vec{S}_1 \cdot \vec{S}_2}{\hbar^2} + \dfrac{1}{2} & S = 1 \end{pmatrix} \qquad \therefore \begin{matrix} 1 = \left(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right) & S = 1 \\ -1 = \left(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right) & S = 0 \end{matrix}$$

$$\Delta E_{nl}^{(t)} = J_{nl} - K_{nl}\left(\frac{1}{2} + \frac{2\vec{S}_1 \cdot \vec{S}_2}{\hbar^2}\right)$$

$$\therefore \quad \left(\vec{S}_1 = \frac{\hbar}{2}\vec{\sigma}_1, \vec{S}_2 = \frac{\hbar}{2}\vec{\sigma}_2\right)$$

$$= J_{nl} - K_{nl}\left(\frac{1}{2} + \frac{1}{2}\vec{\sigma}_1 \cdot \vec{\sigma}_2\right)$$

$$= J_{nl} - \frac{K_{nl}}{2}\left(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right)$$

$$\Delta E_{nl}^{(s)} = J_{nl} - \frac{K_{nl}}{2}\left(1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right)$$

Spin dependent Hamiltonian

$$H = H_0 + V_1(r) + V_2(r) \cdot [1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2]$$

Spin dependent force between atoms are quite weak

예. Spin-orbit, relativistic correction

energy, force α^2 또는 $\left(\frac{v}{c}\right)^2$

However, $[1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2]$: very strong

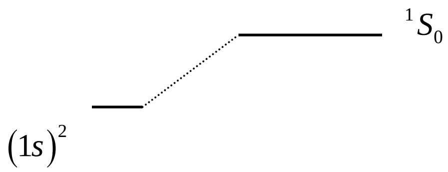
Why? $\rightarrow$ Coulomb interaction

머리 좋은 Heisenberg – Responsible for the phenomena of ferromagnetism

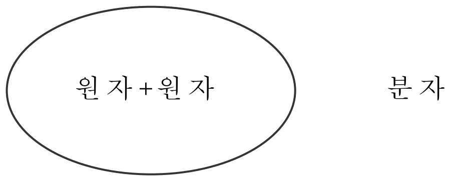
Hund Rule : other things being equal, the state of highest spin will have the lowest energy

Helium의 excitation : ultraviolet light를 비추고

selection rule $\Delta L = 1$, $\Delta S = 0$



Molecules



예. H_2^+ : two proton + one electron

still 6 degree of freedom

가정 1. $\frac{M_p}{m_e} \geq 10^3$

motion of nuclei is slow

2. 핵이 느끼는 field는 electron의 average field이다.

핵과 전자가 만족하는 Schrödinger equation

$$\left[T_R + T_r + V(r,R)\right]\psi(r,R) = E\psi(r,R)$$

Hamiltonian 중 electron의 운동방정식을 fixed R에 대해 풀자.

$$H_0 = T_r + V(r,R)$$

The eigenvalue problem can be solved

$$\left[T_r + V(r,R)\right]u_n(r,R) = \varepsilon_n(R)u_n(r,R)$$

Let $\psi(r,R) = \sum_m \phi_m(R)u_m(r,R)$

$$T_R\sum_m \phi_m(R)u_m(r,R) + \sum_m \varepsilon_m(R)\phi_m(R)u_m(r,R) = E\sum_m \phi_m(R)u_m(r,R)$$

first term은

$$\left(-\frac{\hbar^2}{2M_1}\nabla_{R_1}^2 + \cdots\right)\sum_m \phi_m(R)u_m(r,R) = \sum_m \left[T_R\phi_m(R)\right]u_m(r,R)$$
$$-\frac{\hbar^2}{2M_1}\sum_m \nabla_{R_1}\phi_m(R)\cdot\nabla_{R_1}u_m(r,R)$$
$$-\frac{\hbar^2}{2M_1}\phi_m(R)\nabla_{R_1}^2 u_m(r,R)$$

first approximation

$u_m(r,R)$ are slowly varying function of R

둘째, 셋째 zero

$$\therefore T_R\sum_m \phi_m(R)u_m(r,R) \approx \sum_m \left[T_R\phi_m(R)\right]u_m(r,R)$$

Take the scalar product with $u_n(r,R)$

$$\int\prod_i d^3r_i u_n^*(r,R)u_m(r,R) = \delta_{nm}$$

$$\therefore T_R\phi_m(R) + \varepsilon_m(R)\phi_m(R) = E\phi_m(R)$$

이것은 $\varepsilon_n(R)$ potential 내의 핵운동

$$\varepsilon_m(R) \simeq \varepsilon_m(R_0) + \frac{1}{2}(R-R_0)^2\left(\frac{\partial^2\varepsilon_m}{\partial R^2}\right)_0 + \cdots$$

Uncertainty Relation에 의해

$$\varepsilon \simeq \frac{1}{2m}\left(\frac{\hbar}{a}\right)^2$$

$$M\omega^2 \simeq \frac{\partial^2 \varepsilon(R)}{\partial R^2}$$

$$= \frac{\partial^2}{\partial R^2}\left(\frac{1}{2m}\left(\frac{\hbar}{a}\right)\right)^2$$

$$\simeq \frac{\hbar^2}{ma^4}$$

$$\therefore \omega \simeq \left(\frac{m}{M}\right)^{\frac{1}{2}} \cdot \frac{\hbar}{ma^2}$$

The ratio of the vibrational energy of the nuclei:
to the electronic energy is

$$\frac{E_{\text{vib}}}{\varepsilon} \simeq \frac{\hbar\omega}{\hbar^2 / ma^2} = \frac{ma^2\omega}{\hbar} = \frac{\cancel{ma}^2}{\cancel{\hbar}} \cdot \left(\frac{m}{M}\right)^{\frac{1}{2}} \frac{\cancel{\hbar}}{\cancel{ma}^2} = \left(\frac{m}{M}\right)^{\frac{1}{2}}$$

이 molecule은 Center of mass에 대한 Rotation 가능

$$E_{\text{rot}} \simeq \frac{J(J+1)\hbar^2}{2I} \simeq \frac{\hbar^2}{2Ma^2} = \frac{\varepsilon ma^2}{Ma^2} = \varepsilon \cdot \frac{m}{M}$$

wavelength의 비교

(a). $a \equiv \dfrac{2\hbar}{mc\alpha}$

$$h\nu = 2\pi\hbar \cdot \frac{c}{\lambda} \simeq mc^2\alpha^2$$

$$\therefore \lambda = \frac{2\pi\hbar c}{mc^2\alpha^2}$$

$$= \frac{2\pi\hbar}{mc\alpha^2}$$

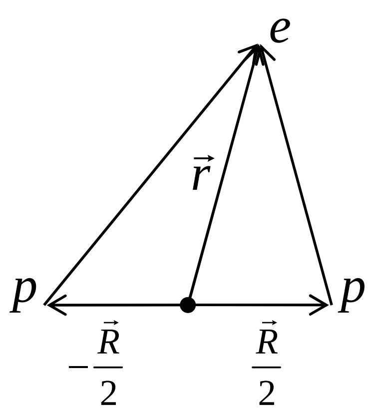
$$\sim 3500\,\text{Å}$$

(b). Vibrational transition $\quad 3500\,\text{Å} \cdot \sqrt{\dfrac{M}{m}}$ infra-red

(c). Rotational transition $\quad 3500\,\text{Å} \cdot \dfrac{M}{m}$ ~ 0.1 ~ 1cm

가장 간단한 molecule H_2^+

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2m}\nabla_r^2-\frac{e^2}{\left|\vec{r}-\frac{\vec{R}}{2}\right|}-\frac{e^2}{\left|\vec{r}+\frac{\vec{R}}{2}\right|}+\frac{e^2}{R}-E\right)\psi(r,R)=0$$



C.M.에 대하여 생각

$$M=\frac{M_p^2}{M_p+M_p}=\frac{1}{2}M_p$$

$$-\frac{\hbar^2}{2M_p}\frac{\partial^2}{\partial\left(\frac{R}{2}\right)^2}\cdot 2=-\frac{\hbar^2}{2M_p}\cdot 2\cdot 4\frac{\partial^2}{\partial R^2}=-\frac{\hbar^2}{2\left(\frac{M_p}{2}\right)}\frac{\partial^2}{\partial\left(\frac{R}{2}\right)^2}$$

Electronic Energy

만약 $R\to\infty$이면 electron은 하나에 핵에 attach

$$E=-13.6\text{eV}$$

$R=0,\quad Z=2$ case

$$E=-13.6Z^2\text{eV}=-54.4\text{eV}$$

Electronic eigenvalue

$$H_0u_0\left(\vec{r},\vec{R}\right)=\left(\frac{p_e^2}{2m}-\frac{e^2}{\left|\vec{r}-\frac{\vec{R}}{2}\right|}-\frac{e^2}{\left|\vec{r}+\frac{\vec{R}}{2}\right|}+\frac{e^2}{R}\right)u_0\left(\vec{r},\vec{R}\right)$$

$$=\varepsilon_0(R)u_0\left(\vec{r},\vec{R}\right)$$

이 문제는 Elliptical coordinate를 써서 정확히 풀 수 있다.

Reasonable trial function

$$\psi_1\left(\vec{r},\vec{R}\right)=\left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}}\cdot e^{-\left|\vec{r}-\frac{\vec{R}}{2}\right|/a_0}$$

$$\psi_2\left(\vec{r},\vec{R}\right)=\left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}}\cdot e^{-\left|\vec{r}+\frac{\vec{R}}{2}\right|/a_0}$$

$$\psi_g\left(\vec{r},\vec{R}\right)=C_+(R)\cdot\left[\psi_1\left(\vec{r},\vec{R}\right)+\psi_2\left(\vec{r},\vec{R}\right)\right]$$

$$\psi_u\left(\vec{r},\vec{R}\right)=C_-(R)\cdot\left[\psi_1\left(\vec{r},\vec{R}\right)-\psi_2\left(\vec{r},\vec{R}\right)\right]$$

이 때의 normalization factor는?

$$\frac{1}{C_\pm}=\left\langle\psi_1\pm\psi_2\middle|\psi_1\pm\psi_2\right\rangle$$
$$=2\pm2\int d^3r\psi_1\left(\vec{r},\vec{R}\right)\psi_2\left(\vec{r},\vec{R}\right)$$

$$S(R)=\int d^3r\psi_1\left(\vec{r},\vec{R}\right)\psi_2\left(\vec{r},\vec{R}\right)$$
$$=\frac{1}{\pi a_0^3}\int d^3re^{-\frac{\left|\vec{r}-\frac{\vec{R}}{2}\right|}{a_0}}\cdot e^{-\frac{\left|\vec{r}+\frac{\vec{R}}{2}\right|}{a_0}}$$
$$=\frac{1}{\pi a_0^3}\int d^3r'e^{-\frac{\left|\vec{r}'-\vec{R}\right|}{a_0}}\cdot e^{-\frac{r'}{a_0}}$$
$$=\frac{1}{\pi a_0^3}\int d^3r'r'^2\sin\theta d\theta d\phi\cdot e^{-\left(r'^2+R^2-2r'R\cos\theta\right)^{\frac{1}{2}}/a_0}\cdot e^{-r'/a_0}$$
$$=\left(1+\frac{R}{a_0}+\frac{R^2}{3a_0^2}\right)e^{-\frac{R}{a_0}}$$

The expectation value of H_0

$$\langle H\rangle_{g,u}=\frac{1}{2\left[1\pm S(R)\right]}\left\langle\psi_1\pm\psi_2\middle|H_0\middle|\psi_1\pm\psi_2\right\rangle$$
$$=\frac{1}{2\left[1\pm S(R)\right]}\left\{\left\langle\psi_1\middle|H_0\middle|\psi_1\right\rangle+\left\langle\psi_2\middle|H_0\middle|\psi_2\right\rangle\pm\left\langle\psi_1\middle|H_0\middle|\psi_2\right\rangle\pm\left\langle\psi_2\middle|H_0\middle|\psi_1\right\rangle\right\}$$
$$=\frac{\left\langle\psi_1\middle|H_0\middle|\psi_1\right\rangle\pm\left\langle\psi_1\middle|H_0\middle|\psi_2\right\rangle}{1\pm S(R)}$$

수소 에너지

$$\left\langle\psi_1\middle|H_0\middle|\psi_1\right\rangle=\int d^3r\psi_1^*\left(\vec{r},\vec{R}\right)\left(\boxed{\frac{p_e^2}{2m}-\frac{e^2}{\left|\vec{r}-\frac{\vec{R}}{2}\right|}}-\frac{e^2}{\left|\vec{r}+\frac{\vec{R}}{2}\right|}+\frac{e^2}{R}\right)\cdot\psi_1\left(\vec{r},\vec{R}\right)$$
$$=E_1+\frac{e^2}{R}-e^2\int d^3r\frac{\left|\psi_1\left(\vec{r},\vec{R}\right)\right|}{\left|\vec{r}+\frac{\vec{R}}{2}\right|}$$

$$E_1 = 13.6\text{eV}$$

$$\langle \psi_1 | H_0 | \psi_1 \rangle = E_1 + \frac{e^2}{R}\left(1 + \frac{R}{a_0}\right) e^{-\frac{2R}{a_0}}$$

같은 방법으로

$$\langle \psi_1 | H_0 | \psi_2 \rangle = \int d^3 r \psi_1^*\left(\vec{r}, \vec{R}\right) \cdot \left(E_1 + \frac{e^2}{R} - \frac{e^2}{\left|\vec{r} + \frac{\vec{R}}{2}\right|} \right) \cdot \psi_2\left(\vec{r}, \vec{R}\right)$$

$$= \left(E_1 + \frac{e^2}{R} \right) S(R) - e^2 \int d^3 r \cdot \frac{\psi_1^*\left(\vec{r}, \vec{R}\right) \psi_2\left(\vec{r}, \vec{R}\right)}{\left|\vec{r} + \frac{\vec{R}}{2}\right|}$$

$$= \left(E_1 + \frac{e^2}{R} \right) S(R) - \frac{e^2}{a_0}\left(1 + \frac{R}{a_0}\right) e^{-\frac{R}{a_0}}$$

어떻게 eigenstate 기술하나?

$$\left[H,\ \text{rotation about the } z\text{-axis}\right] = 0$$

R을 z축으로 잡자.

$e^{im\phi}$의 angular dependence가 있을 것이다.

$m = 0, \pm 1, \pm 2, \cdots,\quad S, P, D, \cdots$ 대신 $\sigma, \pi, \delta, \cdots$

g, u symmetric, anti-symmetric

Pauli의 exclusion principle을 만족하는 homonuclear molecules

핵의 spin $\frac{1}{2}$

total 핵의 wave function = anti-symmetric

= Rotation · Spin

even L · singlet

odd L · triplet

Rotation은 equally probable

$\therefore$ 확률 $\frac{P_{\text{even L}}}{P_{\text{odd L}}} = \frac{1}{3}$

만약 Spin I가 integer이면

Symmetric = Rotation · Spin

even L · even state $(2I, 2I-2, \cdots)$

odd L · odd state $(2I-1, 2I-3, \cdots)$

Even state의 수

$$=\left[2\cdot(2L)+1\right]+\left[2(2L-2)+1\right]+\cdots\left[2\cdot(2)+1\right]+\left[2\cdot 0+1\right]$$
$$=\frac{(I+1)(4I+1+1)}{2}$$
$$=(I+1)(2I+1)$$

Even + odd

$$=\left[2(2I)+1\right]+\left[(2I-1)+1\right]+\cdots+\left[2\cdot 1+1\right]+\left[2\cdot 0+1\right]$$
$$=\frac{(2I+1)(4I+1+1)}{2}$$
$$=(2I+1)^2$$

비율

$$\frac{\text{Even state}}{\text{Odd state}}=\frac{(2I+1)(I+1)}{(2L+1)^2-(2I+1)(I+1)}$$
$$=\frac{(2I+1)(I+1)}{(2I+1)I}$$
$$=\frac{I+1}{I}$$

Fermion의 경우

Spin I가 half interger인 경우는

$$\frac{\text{Even L}}{\text{Odd L}}=\frac{I}{I+1}$$

Rotational state energy

$$E_{\text{rot}}=\frac{\hbar^2 L(L+1)}{2I}$$

Energy of radiation

$$\omega(L+1\to L)=\frac{\hbar^2}{2I}\left[(L+1)(L+2)-L(L+1)\right]$$
$$=\frac{\hbar^2}{2I}\left(L^2+3L+2-L^2-L\right)$$
$$=\frac{\hbar^2}{2I}(2L+2)$$
$$=\frac{\hbar^2}{I}(L+1)$$

N_2 atom을 14개 proton + 7개 electron이라 이해하다.

∵위의 spectrum의 density 때문이다.

후에 Neutron이 발견된 후 7개 proton + 7개 neutron임을 알았다.

Excitation energy

$$C_V=N_0\frac{\partial}{\partial T}\bar{E}(T)$$

$$\bar{E}(T)=\frac{\int dE\cdot E\cdot g(E)e^{-\frac{E}{k_BT}}}{\int dEg(E)e^{-\frac{E}{k_BT}}}$$
$$=-\frac{\partial}{\partial\beta}\ln Z$$
$$=k_BT^2\frac{\partial}{\partial T}\ln\int dEg(E)e^{-\frac{E}{k_BT}}$$

$g(E)$: degeneracy of states

average energy

$$\bar{E}(T)=\bar{E}_{\text{trans}}(T)+\bar{E}_{\text{rot}}(T)+\bar{E}_{\text{vib}}(T)+\cdots$$

$$\int dEg(E)e^{-\frac{E}{k_BT}}=\int\frac{d^3p}{(2\pi\hbar)^3}e^{-\frac{p^2}{2Mk_BT}}$$
$$=\frac{1}{(2\pi\hbar)^3}\left(\pi\cdot 2Mk_BT\right)^{\frac{3}{2}}$$

$$I^2 = \int_{-\infty}^{\infty} e^{-\alpha x^2} \cdot dx \int_{-\infty}^{\infty} e^{-\alpha y^2} \cdot dy$$

$$= \int_0^{\infty} e^{-\alpha r^2} r dr \cdot 2\pi$$

$$= \frac{2\pi}{2\alpha} \cdot e^{-\alpha r^2} \Big|_{\infty}^{0}$$

$$= \frac{\pi}{\alpha}$$

$$\bar{E} = k_B T^2 \frac{\partial}{\partial T} \left[\left(\frac{1}{2\pi\hbar} \right)^3 \cdot \left(\pi 2 M k_B T \right)^{\frac{3}{2}} \right]$$

$$\therefore \quad = k_B T^2 \cdot \frac{\partial}{\partial T} \left(\ln T^{\frac{3}{2}} \right)$$

$$= \frac{3}{2} k_B T$$

$$C_V = \frac{\partial}{\partial T} \left(\frac{3}{2} N_0 k_B T \right)$$

$$\therefore \quad = \frac{3}{2} N_0 k_B$$

$$= \frac{3}{2} R$$

Rotation

$$\frac{\hbar^2}{2I} \cdot \frac{1}{k_B} \quad \text{for} \quad H_2$$

$$= 84.8K$$

$$\bar{E}_{\text{rot}} = \frac{\sum_L (2L+1) \cdot \frac{\hbar^2 L(L+1)}{2I} \cdot e^{-\frac{\hbar^2 L(L+1)}{2 I k_B T}}}{\sum_L (2L+1) \cdot e^{-\frac{\hbar^2 L(L+1)}{2 I k_B T}}}$$

$$
\begin{aligned}
Z &= \sum_L (2L+1) e^{-\frac{\hbar^2 L(L+1)}{2Ik_B T}} \\
&= \int dl \cdot 2l \cdot e^{-\frac{\hbar^2 l^2}{2Ik_B T}} \qquad \text{Let } x = l^2, dx = 2ldl \\
&= \int dx \cdot e^{-\frac{\hbar^2}{2Ik_B T}x} \\
&= \frac{2Ik_B T}{\hbar^2} e^{-\frac{\hbar^2}{2Ik_B T}x} \Bigg|_{\infty}^{0} \\
&= \frac{2Ik_B T}{\hbar^2}
\end{aligned}
$$

$$
\begin{aligned}
E &= k_B T^2 \cdot \frac{\partial}{\partial T} \ln\left(\frac{2Ik_B T}{\hbar^2}\right) \\
&= k_B T^2 \cdot \frac{1}{T} \\
&= k_B T
\end{aligned}
$$

$$\therefore C_V = k \cdot n_0 = R$$

vibrational state

$$E = \hbar\omega_x\left(n_x + \frac{1}{2}\right) + \hbar\omega_y\left(n_y + \frac{1}{2}\right) + \hbar\omega_z\left(n_z + \frac{1}{2}\right)$$

first excited state까지만 생각

$$
\begin{aligned}
\bar{E} &= \frac{E_0 e^{-\frac{E_0}{k_B T}} + E_1 e^{-\frac{E_1}{k_B T}}}{e^{-\frac{E_0}{k_B T}} + e^{-\frac{E_1}{k_B T}}} \\
&= \frac{E_0 + E_1 e^{-\frac{\hbar\omega_z}{k_B T}}}{1 + e^{-\frac{\hbar\omega_z}{k_B T}}} \\
&\simeq E_0\left(1 + \frac{E_1}{E_0} e^{-\frac{\hbar\omega_z}{k_B T}}\right)\left(1 - e^{-\frac{\hbar\omega_z}{k_B T}}\right) \\
&\simeq E_0 + \hbar\omega_z e^{-\frac{\hbar\omega_z}{k_B T}}
\end{aligned}
$$

$$E_0 = \hbar\omega_x \cdot \frac{1}{2} + \hbar\omega_y \cdot \frac{1}{2} + \hbar\omega_z \cdot \frac{1}{2}$$

$$E_1 = \hbar\omega_x \cdot \frac{1}{2} + \hbar\omega_y \cdot \frac{1}{2} + \hbar\omega_z \cdot \frac{3}{2}$$

z방향으로의 spring 운동이 제일 쉽다.

$$
\begin{aligned}
\left(C_V\right)_{\text{vib}} &= \frac{\partial \overline{E}}{\partial T} N_0 \\
&= N_0 k_B \left(\frac{\hbar\omega_z}{k_B T}\right)^2 e^{-\frac{\hbar\omega_z}{k_B T}}
\end{aligned}
$$

매우 높은 온도에서나