2021/3/3 QP 习题课

Part I

1. de Broglie wave : $\lambda = h/p$ $E = \frac{1}{2}mv^2$

   (粒子)

2. 不确定性原理

$$\Delta x \cdot \Delta p \geq \hbar/2 \qquad \Delta E \cdot \Delta t \geq \hbar/2$$

3. Schrödinger equation

① time-dependent

$$i\hbar \frac{\partial}{\partial t}\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right)\psi$$

$$\hat{H} = \underline{-\frac{\hbar^2}{2m}\nabla^2} + \underline{V(\vec{r},t)}$$

② time-independent $(V = V(x))$

$$\psi(\vec{r},t) = \varphi(\vec{r})\cdot f(t) = e^{-iEt/\hbar}\,\underline{\underline{\varphi(\vec{r})}}$$

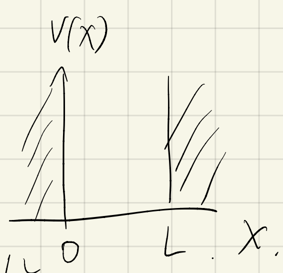
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\varphi(\vec{r}) = E\varphi(\vec{r})$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

4. particle-in-a-box

(1) 1D

$$V(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{other} \end{cases}$$



$$\varphi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \qquad E_n = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, 3, \cdots$$

※ $V(x) = \begin{cases} 0 & -L/2 \leq x \leq L/2 \\ \infty & \text{other} \end{cases}$

$$\varphi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}(x + L/2)\right)$$

**. 自由粒子. $L \to \infty$.

$$\psi(x) = A' e^{ikx} + B' e^{-ikx}. \qquad k = \sqrt{2mE}/\hbar.$$

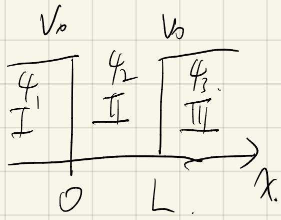
$x \to \pm\infty$. $\psi(x)$ 有限 $\Rightarrow E \geq 0$. & 连续!

$\psi(x)$ 不平方可积.

(2) 3D.

5. 有限深势阱.

$$\begin{cases} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi = E\psi. & (0 \leq x \leq L). \quad k_1 = \sqrt{2mE}/\hbar \\ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi = (E - V_0)\psi. & (\text{others}). \quad k_2 = \sqrt{2m(E-V_0)}/\hbar \end{cases}$$



$$\psi_1(x) = Ae^{ik_2x} + Be^{-ik_2x}$$
$$\psi_2(x) = Ce^{ik_1x} + De^{-ik_1x}$$
$$\psi_3(x) = Fe^{ik_2x} + Ge^{-ik_2x}$$

$\psi_1(0) = \psi_2(0)$

$\psi_1'(0) = \psi_2'(0)$

$\psi_2(L) = \psi_3(L)$

$\psi_2'(L) = \psi_3'(L)$

边界条件 & $x \to \pm\infty$. $\psi(x)$有限 & 归一化.

求解 波函数系数.

$E < V_0$

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx} \qquad k = \sqrt{2mE}/\hbar$$
$$\psi_2(x) = Ce^{k'x} + De^{-k'x} \qquad k' = \sqrt{2m(V_0 - E)}/\hbar.$$
$$\psi_3(x) = A'e^{ikx}$$

$$T = \frac{|A'|^2}{|A|^2}.$$

6. 一维谐振子.

频率. 圆频率.

$V(x) = \frac{1}{2}kx^2 \qquad \nu = \frac{1}{2\pi}\sqrt{k/m} \qquad \omega = 2\pi\nu = \sqrt{k/m}$

$E_n = h\nu(n+\frac{1}{2}) = \hbar\omega(n+\frac{1}{2}). \qquad n = 0, 1, 2, \cdots$

$\psi_n(x) = (2^n \cdot n!)\left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} H_n(\alpha^{1/2}x). \qquad \alpha = 2\pi\nu m/\hbar = \omega m/\hbar$

H_n 厄米多项式.

* $\int_{-\infty}^{\infty} \psi_n^* \psi_{n'} dx = \delta_{nn'}$ 正交归一

**. 递推关系.

$\xi H_n(\xi) = \frac{1}{2}[H_{n+1}(\xi) + nH_{n-1}(\xi)]$. 微扰中常用.

$$\frac{d H_n(\xi)}{d\xi} = 2n H_{n-1}(\xi).$$

7. Operators.

(1). $\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x) \cdot x \cdot \psi(x) dx = \langle \psi | \hat{x} | \psi \rangle$.

$\langle p \rangle = \langle \psi(x) | \hat{p_x} | \psi(x) \rangle$ $\hat{p_x} = -i\hbar \frac{\partial}{\partial x}$.

$\langle F(\vec{r}, \vec{p}) \rangle = \langle \psi | \hat{F} | \psi \rangle$.

(2). 方差

$$\sigma_F = \sqrt{\langle F^2 \rangle - \langle F \rangle^2}$$

(3). 性质

①线性. (力学量算符都是线性的)

$\hat{F}(c\psi) = c\hat{F}\psi$. $\hat{F}(\psi_1 + \psi_2) = \hat{F}\psi_1 + \hat{F}\psi_2$.

②厄米性 (力学量算符都是厄米的)

$\langle \psi | \hat{F} | \varphi \rangle = \langle \hat{F}\psi | \varphi \rangle$.

厄米算符的本征值一定是实数.

(4). 本征方程.

$\hat{F} \cdot \psi_n = f_n \cdot \psi_n$. f_n: 本征值. ψ_n: 本征函数.

不同本征值的本征函数 $\perp$.

同一个本征值的不同本征函数 可以 $\perp$化.

完备性. 任意力学量的厄米算符的本征函数集构成完备集 $\{\psi_m\}$.

$$\psi = \sum_m \underset{\sim}{C_m} \psi_m = \sum_m \langle \psi_m | \psi \rangle \psi \qquad \langle \psi_m | \psi \rangle = \int \psi_m^* \psi \, d\tau$$

$\downarrow$

(ψ 与 ψ_m 有相同边界条件. 且 ψ 品优),

(5) 对易

$$[\hat{F}, \hat{G}] = \hat{F}\hat{G} - \hat{G}\hat{F} = 0.$$

$\hat{F}, \hat{G}$ 有共同完备的本征函数系 $\Longleftrightarrow$ $[\hat{F}, \hat{G}] = 0$.

8. 物理量的测量.

(1). 若 A 不显含时间. $\underset{\sim}{d\langle A \rangle / dt = 0}$. $\Leftrightarrow$ $\underset{\sim}{[\hat{A}, \hat{H}] = 0}$

(2). 不确定性原理

$$\Delta F \cdot \Delta G \geq \frac{1}{2} \left| \langle \underline{[\hat{F}, \hat{G}]} \rangle \right|$$

9. 角动量.

(1). $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$ $\qquad [\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0.$

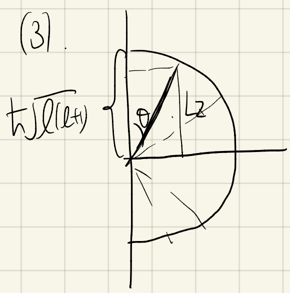
$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$ $\qquad$ 球坐标里 $\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$.

$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$.

(2).
$$\hat{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$$
$$\hat{L}_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$$

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \cdot Y_{lm}^*(\theta, \phi) \, Y_{l'm'}(\theta, \phi) = \delta_{ll'} \delta_{mm'}$$

(3).



$$\cos\theta = \frac{L_z}{L} = \frac{m\hbar}{\sqrt{l(l+1)}\,\hbar} = \frac{m}{\sqrt{l(l+1)}}$$

(4). 阶梯算符.

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \qquad \hat{L}_- = \hat{L}_x - i\hat{L}_y.$$

Part II.

1. H 原子.

(1). SE.

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r} \qquad e' = e/\sqrt{4\pi\varepsilon_0}$$

$$\hat{H}\,\psi(\vec{r}_N, \vec{r}_e) = E\,\psi(\vec{r}_N, \vec{r}_e)$$

(2). 中心力场中的单粒子.

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad \hat{H}\psi(r,\theta,\phi) = E\,\psi(r,\theta,\phi)$$

$$[\hat{H}, \hat{L}^2] = 0. \qquad \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left(-\frac{\hat{L}^2}{\hbar^2}\right).$$

$$\psi(r,\theta,\phi) = R(r)\,Y_{lm}(\theta,\phi)$$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{l(l+1)\hbar^2}{r^2} + V(r)\right]R(r) = E\,R(r)$$

(3). B-O.

(4). $\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{l(l+1)\hbar^2}{r^2} - \frac{Ze'}{r}\right]R = ER.$

$$E_n = -\frac{Z^2}{2n^2}\left(\frac{e'^2}{a}\right). \qquad R_{nl}.$$

$$* \int_0^\infty R_{nl}^* R_{n'l'}\, r^2\, dr = \delta_{nn'}\delta_{ll'} \quad ✗$$

$$\int_0^\infty R_{nl}^* R_{n'l}\, r^2\, dr = \delta_{nn'}. \quad ✓$$

$$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi).$$

$$E_n = -\frac{Z^2}{2n^2}\left(\frac{e'^2}{a}\right) = -\frac{Z^2}{2n^2}(27.2\,\text{eV}) \qquad \frac{e'^2}{a} = 27.2\,\text{eV}.$$

$(n = 1, 2, 3, \cdots;\ l = 0, \cdots, n-1;\ ;\ m = -l, \cdots, +l).$

简并度 n^2.

(5). node. $\left.\begin{array}{l} R_{nl}: n-l-1. \\ Y_{lm}: l \end{array}\right\} \Rightarrow n-1$ 个 nodes. for $R_{nl}Y_{lm}$.

指数项 $e^{-Zr/na}$ → 给出 n

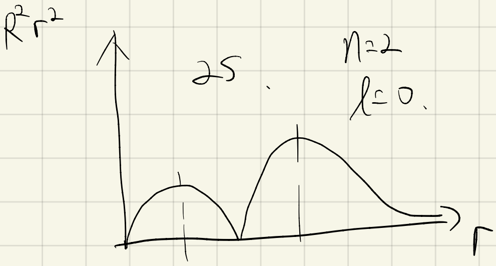
R_{nl} 有 $(n-l-1)$ 个节点 $\Rightarrow l = n-(n-l-1)-1$

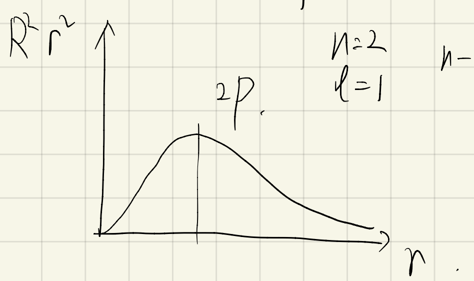
(不包含原点的零点)

R_{nl}

(6). 径向分布函数 $R_{nl}^2 \cdot r^2$

$R_{nl}^2 r^2$ 取得最大值时 r_m. $r=r_m$ 出现概率最高. 极值数 $n-l$.





$n-l=1$

(7). 实波函数

$e^{\pm im\phi}$

$\psi_{2p_x} = \frac{1}{\sqrt{2}}(\psi_{2p_1}+\psi_{2p_{-1}}) \propto \sin\theta\cos\phi$

$\psi_{2p_y} = \frac{1}{\sqrt{2}i}(\psi_{2p_1}-\psi_{2p_{-1}}) \propto \sin\theta\sin\phi$

$\Rightarrow$ 还是 $\hat{H}$ 和 $\hat{L}^2$ 的本征函数，不再是 $\hat{L}_z$ 的本征函数.

$\psi_{2p_z} = \psi_{2p_0} \propto \cos\theta$

2. 变分法

(1) 变分原理

对于任意的满足边界条件 体系粒子坐标的 品优函数 ϕ. 一定有

$$\frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} = \frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \geq E_0$$

$E_\lambda = \langle\phi_\lambda|\hat{H}|\phi_\lambda\rangle / \langle\phi_\lambda|\phi_\lambda\rangle \Rightarrow \frac{\partial E_\lambda}{\partial\lambda}\Big|_{\lambda=\lambda^*}=0 \Rightarrow E(\lambda^*)$

(2). 线性变分法

$\phi = \sum_j c_j f_j$ $\{f_j\}$ 为一组已知基函数.

$$E=\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}\qquad \langle\phi|\hat{H}|\phi\rangle=\sum_{j,k}c_j c_k H_{jk}$$

$$\langle\phi|\phi\rangle=\sum_{j,k}c_j c_k S_{jk}.$$

变分 $\partial \bar{E}/\partial c_i=0$

$$\sum_{j=1}^{n}c_j(H_{ij}-\bar{E}^{*}S_{ij})=0.$$

$$|H_{n\times n}-E\,S_{n\times n}|=0.\qquad \begin{vmatrix} H_{11}-ES_{11} & \cdots & H_{1n}-ES_{1n}\\ \vdots & \ddots & \vdots \\ H_{n1}-ES_{n1} & \cdots & H_{nn}-ES_{nn}\end{vmatrix}=0.$$

解得 $E_1\le E_2\le\cdots\le E_n$　把 E_i 代入原方程求解 $\{c_j\}$.

3. 微扰论.

$\hat{H}=\hat{H}_0+\hat{H}'$　$H'\ll H_0$.　$\hat{H}_0$的本征函数$\{\psi_n^{(0)}\}$和$\{E_n^{(0)}\}$.

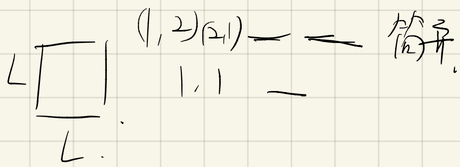
(1). 非简并态

$$E_n^{(1)}=H'_{nn}\qquad E_n^{(2)}=\sum_{m\neq n}\frac{|H'_{mn}|^2}{E_n-E_m}.$$

$$\psi_n^{(1)}=\sum_{m\neq n}\frac{H'_{mn}}{E_n-E_m}\psi_m^{(0)}.$$

(2). 简并态.

$$\begin{vmatrix} H'_{11}-E_n^{(1)} & H'_{12} & \cdots & H'_{1n}\\ H'_{21} & H'_{22}-E_n^{(1)} & & H'_{2n}\\ \vdots & & \ddots & \vdots\\ H'_{n1} & \cdots & & H'_{nn}-E_n^{(1)}\end{vmatrix}=0.$$



4. He原子基态.

(1). 变分法

先考　有效核电荷数 ζ.

$$\underline{\phi_\zeta}=\frac{1}{\pi}\left(\frac{\zeta}{a_0}\right)^3 e^{-\zeta r_1/a_0}\,e^{-\zeta r_2/a_0}.$$

$E(\zeta)=\langle\phi_\zeta|\hat{H}|\phi_\zeta\rangle$　$\zeta=Z-5/16$ 时E有极小值.

$$E(f) = \langle \phi_f | \hat{H} | \phi_f \rangle / \underbrace{\langle \phi_f | \phi_f \rangle}$$

(2). 微扰论

$$\hat{H}_0 = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze'^2}{r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze'^2}{r_1}\right)$$

$$\hat{H}' = \frac{e'^2}{r_{12}}$$

$$\hat{H}_0:\quad \psi^{(0)} = \psi_{n,l,m}(\vec{r}_1)\,\psi_{n'l'm'}(\vec{r}_2)$$

基态 $\psi^{(0)}_{1s} = 1s(1)1s(2)$ $\qquad E^{(0)}_{1s} = -2\cdot\dfrac{Z^2e'^2}{2a_0}$

$$E^{(1)} = H'_{00} = \langle 1s(1)\,1s(2) | \frac{e'^2}{r_{12}} | 1s(1)\,1s(2)\rangle = \frac{5}{8}Z\left(\frac{e'^2}{a_0}\right)$$

5. 自旋与Pauli原理

(1). $S = \frac{1}{2}$ $\qquad m_s = \pm\frac{1}{2}$

(2). 氢原子 (忽略自旋对 $\hat{H}$ 的影响)

$[\hat{H}, \hat{S}^2] = 0 \qquad [\hat{H}, \hat{S}_z] = 0 \qquad$ 简并 $2n^2$

$\psi_{n,l,m} \longrightarrow \psi_{nlm}(r,\theta,\phi)\cdot\eta(m_s)$

$\eta(m_s) = \alpha$ or β or $c_1\alpha + c_2\beta$

(3). 全同性原理

(4). 交换算符 $\hat{P}_{ij}$

$\hat{P}_{ij}\,\psi(\cdots, q_i, \cdots q_j, \cdots) = C\cdot\psi(\cdots q_j, \cdots, q_i, \cdots) \qquad |C| = 1$

$\hat{P}_{ij}\psi = +\psi$ 交换对称

$\hat{P}_{ij}\psi = -\psi$ 交换反对称

(5). Pauli 原理

多电子体系波函数必须交换反对称!

(6). Slater 行列式

$$\psi_n(1,2,\cdots,N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_{i_1}(1) & \psi_{i_1}(2) & \cdots & \psi_{i_1}(N) \\ \vdots & \ddots & & \vdots \\ \psi_{i_N}(1) & \psi_{i_N}(2) & \cdots & \psi_{i_N}(N) \end{vmatrix}$$

(7). He原子基态、

基态、 $\psi^{(0)} = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 1s(1)\beta(1) & 1s(2)\beta(2) \end{vmatrix}$

激发态.

$\frac{\uparrow}{\uparrow}\,\begin{matrix}2s\\1s\end{matrix}$ $\quad \psi^{(0)} = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) \end{vmatrix}$

$$\langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle = \underbrace{e'^2 \int \frac{1s^2(1)\, 2s^2(2)}{r_{12}} d\vec{r}_1 d\vec{r}_2}_{J_{1s2s}} - \underbrace{e'^2 \int \frac{1s(1)2s(1)1s(2)2s(2)}{r_{12}} d\vec{r}_1 d\vec{r}_2}_{K_{1s2s}}$$

$\frac{\downarrow}{\uparrow}\,\begin{matrix}2s\\1s\end{matrix}$ $\quad \psi^{(0)} = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) \\ 2s(1)\beta(1) & 2s(2)\beta(2) \end{vmatrix}$

$$\langle \psi^{(0)} | \hat{H}' | \psi^{(0)} \rangle = J_{1s2s} - 0.$$

6. 多电子原子 HF.

$$\hat{H} \overset{\text{BO}}{=} \sum_i \hat{H}_i^0 + \sum_{i<j} \frac{e'^2}{r_{ij}}.$$

(1). Hartree 方法. (不考虑自旋).

① 单电子(轨道)近似 ② BO 近似 ③ 中心力场 ④ 非相对论近似.

$$\psi^{(0)} = S_1(r_1,\theta_1,\phi_1)\, S_2(r_2,\theta_2,\phi_2)\cdots S_n(r_n,\theta_n,\phi_2)$$

$$E = \sum_{i=1}^{n} \underset{\sim}{\epsilon_i} + \frac{1}{2}\sum_i \sum_{j\neq i} J_{ij}$$

(2). HF方法 (考虑)

σ轨道: $E_\sigma = \epsilon_\sigma^0 + \sum_u (J_{u\sigma} - K_{u\sigma})$.

$E_{tot} = \sum_\sigma \epsilon_\sigma^0 + \frac{1}{2}\sum_u\sum_\sigma (J_{u\sigma} - K_{u\sigma})$.

(3). 原子光谱项及支项

$^{2S+1}L_J$ $L = l_1 + l_2$. $S = s_1 + s_2$. $J = |L-S|, \dots, L+S$

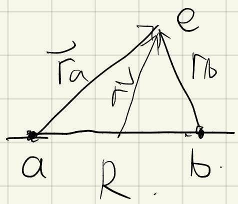
L	0	1	2	3.	4
符号.	S	P	D	F	G

(4) Hund规则

S↑, E↓ ; S相同, L↑ E↓.

光谱支项. 若小于半满 J↑ E↓. 大于半满 J↓ E↓.

7. 双原子分子.



(1). H_2^+.

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_a^2 + \nabla_b^2) - \frac{\hbar^2}{2m}\nabla_e^2 - \frac{Ze'^2}{r_a} - \frac{Ze'^2}{r_b} + \frac{Z^2e'^2}{R}.$$

BOA.

$$\begin{cases} \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze'^2}{r_a} - \frac{Ze'^2}{r_b} + \frac{Z'e'^2}{R}. \\ \hat{H}\psi = E\psi \end{cases}$$

轴对称近似, 与φ无关

$[\hat{H}, \hat{L}_z] = 0$

$\psi = f(r,\theta)\, e^{im\phi}$ $(m = 0, \pm1, \pm2)$

$$\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}(-m^2)\right] f(r,\theta) = E\, f(r,\theta).$$

$E = E(m^2)$. $m \neq 0$ $\pm m$ 双重简并.

(2). 用 $\lambda=|m|$ 表征 从 0.

λ	0	1	2	3	4
符号	σ	π	δ	ϕ	γ

$$\underbrace{\pi \quad \delta \quad \phi \quad \gamma}_{\text{双重简并}}$$

(3). LCAO-MO 近似.

$$\psi = c_1 1s_a + c_2 1s_b$$

$$\begin{vmatrix} H_{aa}-ES_{aa} & H_{ab}-ES_{ab} \\ H_{ba}-ES_{ba} & H_{bb}-ES_{bb} \end{vmatrix} = 0$$

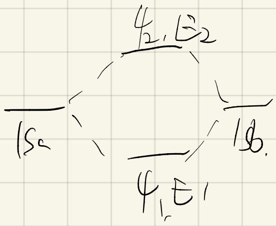
$H_{aa}=H_{bb}=\alpha$ $\quad H_{ab}=H_{ba}=\beta$

$S_{aa}=S_{bb}=1$ $\quad S_{ab}=S_{ba}=S$

$$\Rightarrow \begin{cases} E_1=\dfrac{\alpha+\beta}{1+S} \\ E_2=\dfrac{\alpha-\beta}{1-S} \end{cases}$$

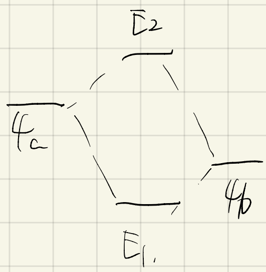
$\psi_1 = \dfrac{1}{\sqrt{2+2S}}(1s_a+1s_b)$ 成键

$\psi_2 = \dfrac{1}{\sqrt{2-2S}}(1s_a-1s_b)$ 反键



(4). $S_{ab}=S_{ba}=0$, $\quad H_{aa}\neq H_{bb}$

$$\begin{vmatrix} \alpha_a-E & \beta \\ \beta & \alpha_b-E \end{vmatrix} = 0 \xrightarrow{\alpha_a>\alpha_b} \begin{cases} E_1=\alpha_b-h \\ E_2=\alpha_a+h \end{cases}$$



$$\begin{cases} \psi_1 = (h\varphi_a+|\beta|\varphi_b)/\sqrt{h^2+\beta^2} \\ \psi_2 = (|\beta|\varphi_a-h\varphi_b)/\sqrt{h^2+\beta^2} \end{cases}$$

$$h=\frac{\sqrt{(\alpha_a-\alpha_b)^2+4\beta}-(\alpha_a-\alpha_b)}{2}$$

$h\uparrow$ 成键越强.

(5). 双原子分子轨道

① BO近似 LCAO-MO近似 轨道近似 非相对论近似.

② 成键三原则

a. 对称性匹配 b. 能量近似 c. 最大重叠.

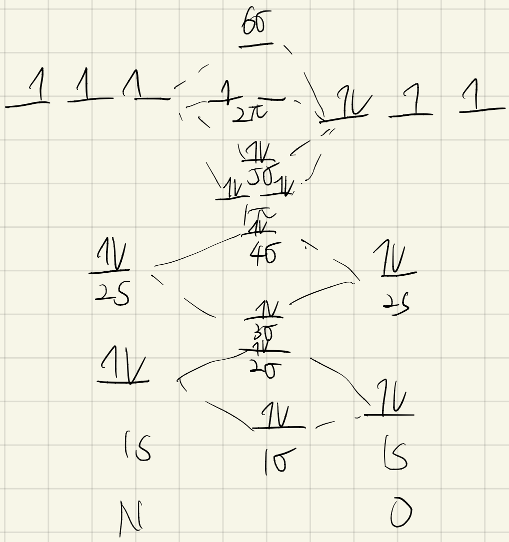
③ 电子排布

同核 $H_2 \sim N_2$ $1\sigma_g$ $1\sigma_u$ $2\sigma_g$ $2\sigma_u$ $1\pi_u$ $3\sigma_g$ $1\pi_g$ $3\sigma_u$.

$O_2 - F_2$ $1\sigma_g$ $1\sigma_u$ $2\sigma_g$ $2\sigma_u$ $3\sigma_g$ $1\pi_u$ $1\pi_g$ $3\sigma_u$

键级 $P = \frac{n - n^*}{2}$.

异核 NO. 1σ 2σ 3σ 4σ 1π 5σ 2π 6σ.



$P = \frac{6-1}{2} = 2.5$.

CO : N_2.