量子力学期末

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1 Recall

薛定谔方程

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle \tag{1}$$

海森堡运动方程

$$i\hbar\frac{d}{dt}A(t) = [A(t), H], \quad A(t) = U^\dagger(t)AU(t), U(t) = e^{-iHt/\hbar} \tag{2}$$

概率密度, 概率流

$$\rho = |\psi|^2, \quad \boldsymbol{j} = -\frac{i\hbar}{2m}[\psi^*(\nabla\psi) - (\nabla\psi^*)\psi] = \frac{\hbar}{m}\Im(\psi^*\nabla\psi) \tag{3}$$

电磁场中的正则动量

$$\boldsymbol{p} \to \boldsymbol{p} - \frac{q\boldsymbol{A}}{c}, \quad V_e = q\phi \tag{4}$$

不确定度关系

$$\langle(\Delta A)^2\rangle\langle(\Delta B)^2\rangle \geq \frac{1}{4}|\langle[A,B]\rangle|^2 \tag{5}$$

5 个基本原理

- 描写微观系统状态的数学量是希尔伯特空间中的矢量. 相差一个复数因子的两个矢量描写同一个状态.

- 描写微观系统物理量的是希尔伯特空间中的厄米算符; 物理量所能取的值, 是相应算符的本征值; 物理量 A 在状态 $|\psi\rangle$ 中取各值 a_i 的概率, 与态矢量 $|\psi\rangle$ 按 A 的归一化本征矢量 $\{|a_i\rangle\}$ 的展开式中 $|a_i\rangle$ 的系数的复平方成正比

$$|\psi\rangle = \sum_i |a_i\rangle c_i, \quad c_i = \langle a_i|\psi\rangle \tag{6}$$

- 微观系统中每个粒子的直角坐标系下的位置算符 $X_i(i=1,2,3)$ 与相应的正则动量算符 P_j 有下列对易关系

$$[X_i, X_j] = [P_i, P_j] = 0, \quad [X_i, P_j] = i\hbar\delta_{ij} \tag{7}$$

- 微观系统的状态 $|\psi(t)\rangle$ 随时间变化的规律是薛定谔方程

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle \tag{8}$$

- 描写全同粒子系统的态矢量, 对于任意一对粒子的对调, 是对称的或者反对称的, 服从前者的称为波色子, 服从后者的称为费米子.

2 自旋

2.1 自旋态, 自旋算符

可分离变量出自旋态

$$\psi(r, s_z) = \phi(r)\chi(s_z), \quad \chi(s_z) = (a, b)^T \tag{9}$$

自旋算符

$$\boldsymbol{s} = \frac{\hbar}{2}\boldsymbol{\sigma} \tag{10}$$

其中 σ 是 Pauli 算符, 在 $\uparrow,\downarrow$ 表象下

$$[\sigma_i,\sigma_j]=2i\epsilon_{ijk}\sigma_k,\quad \sigma_\alpha^2=1,\quad \sigma_\alpha\sigma_\beta=-\sigma_\beta\sigma_\alpha, \tag{11}$$

$$\sigma_x=\begin{pmatrix}0&1\\1&0\end{pmatrix},\sigma_y=\begin{pmatrix}0&-i\\i&0\end{pmatrix},\sigma_z=\begin{pmatrix}1&0\\0&-1\end{pmatrix} \tag{12}$$

更进一步

$$\boldsymbol{\sigma}^\dagger=\boldsymbol{\sigma},\quad \sigma_\alpha\sigma_\beta=\delta_{\alpha\beta}+i\sum_\gamma\epsilon_{\alpha\beta\gamma}\sigma_\gamma \tag{13}$$

定义

$$\sigma_\pm=\frac{1}{2}(\sigma_x\pm i\sigma_y),\quad \sigma_+=\begin{pmatrix}0&1\\0&0\end{pmatrix},\sigma_-=\begin{pmatrix}0&0\\1&0\end{pmatrix} \tag{14}$$

2.2 角动量本征态

总角动量 j, 轨道角动量 l, 自旋角动量 s, 可取 $(H,\boldsymbol{l}^2,\boldsymbol{j}^2,j_z)$

$$\boldsymbol{j}=\boldsymbol{l}+\boldsymbol{s},\quad \boldsymbol{j}^2=j_\alpha\cdot j_\alpha,\quad [\boldsymbol{j},\boldsymbol{s}\cdot\boldsymbol{j}]=0,\quad [\boldsymbol{j}^2,j_\alpha]=0, \tag{15}$$

$$\boldsymbol{j}^2\phi=j(j+1)\hbar^2\phi\ (j=l\pm\frac{1}{2}),\quad \boldsymbol{l}^2\phi=l(l+1)\hbar^2\phi, \tag{16}$$

$$j_z\phi=m_j\hbar\phi=(m+\frac{1}{2})\hbar\phi \tag{17}$$

$$\phi_{ljm_j}=\frac{1}{\sqrt{2l+1}}\begin{pmatrix}\sqrt{l+m+1}Y_{lm}\\\sqrt{l-m}Y_{l,m+1}\end{pmatrix} \tag{18}$$

$$=\frac{1}{\sqrt{2j}}\begin{pmatrix}\sqrt{j+m_j}Y_{j-\frac{1}{2},m_j-\frac{1}{2}}\\\sqrt{j-m_j}Y_{j-\frac{1}{2},m_j+\frac{1}{2}}\end{pmatrix}\ (j=l+\frac{1}{2}) \tag{19}$$

$$\phi_{ljm_j}=\frac{1}{\sqrt{2l+1}}\begin{pmatrix}-\sqrt{l-m}Y_{lm}\\\sqrt{l+m+1}Y_{l,m+1}\end{pmatrix} \tag{20}$$

$$=\frac{1}{\sqrt{2j+2}}\begin{pmatrix}-\sqrt{j-m_j+1}Y_{j+\frac{1}{2},m_j-\frac{1}{2}}\\\sqrt{j+m_j+1}Y_{j+\frac{1}{2},m_j+\frac{1}{2}}\end{pmatrix}\ (j=l-\frac{1}{2},l\neq 0) \tag{21}$$

$$\phi_{0\frac{1}{2}\frac{1}{2}}=\frac{1}{\sqrt{4\pi}}(1,0)^T,\quad \phi_{0\frac{1}{2}-\frac{1}{2}}=\frac{1}{\sqrt{4\pi}}(0,1)^T \tag{22}$$

结论

$$(\boldsymbol{s}\cdot\boldsymbol{l})\phi_{ljm_j} = \begin{cases} \frac{\hbar^2}{2} l\phi_{ljm_j}, & j = l+\frac{1}{2} \\ -\frac{\hbar^2}{2}(l+1)\phi_{ljm_j}, & j = l-\frac{1}{2}\ (l\neq 0) \end{cases} \tag{23}$$

$$\langle\sigma_z\rangle = \begin{cases} m_j/j, & j = l+\frac{1}{2} \\ -m_j/(j+1), & j = l-\frac{1}{2}\ (l\neq 0) \end{cases} \tag{24}$$

2.3 反常 Zeeman 效应

原子精细结构 $\Rightarrow\ E_{nlj=l+\frac{1}{2}} > E_{nlj=l-\frac{1}{2}}$
取 $(H, \boldsymbol{l}^2, l_z, s_z)$, 正常 (磁场大, 忽略自旋)

$$E_{nlmm_s} = E_{nl} + \hbar\omega_L(m+2m_s) = E_{nl} + \hbar\omega_L(m\pm 1) \tag{25}$$

反常 (磁场小, 考虑自旋)

$$E_{nljm_j} = E_{nlj} + m_j\hbar\omega_L \tag{26}$$

其中

$$\omega_L = \frac{eB}{2\mu c} \tag{27}$$

2.4 多电子体系

$$\boldsymbol{S} = \boldsymbol{s_1} + \boldsymbol{s_2} \tag{28}$$

非耦合表象. 三重态

$$\chi = \begin{cases} |\uparrow\uparrow\rangle \\ |\downarrow\downarrow\rangle \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \end{cases}, \quad S = 1, M_S = \pm 1, 0 \tag{29}$$

单态

$$\chi = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right), \quad S = 0, M_S = 0 \tag{30}$$

Bell basis, GHZ state, entanglement 见 ppt.

3 代数解法

3.1 产生湮灭算符, 升降算符

谐振子

$$a = \sqrt{\frac{m\omega}{2\hbar}}(x + \frac{ip}{m\omega}), \quad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(x - \frac{ip}{m\omega}) \tag{31}$$

$$N = a^\dagger a, \quad [a, a^\dagger] = 1, [N, a] = -a, [N, a^\dagger] = a^\dagger, \quad H = \hbar(N + \frac{1}{2}) \tag{32}$$

$$a|n\rangle = \sqrt{n}|n-1\rangle, \quad a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \quad |n\rangle = \frac{(a^\dagger)^n}{\sqrt{n!}}|0\rangle \tag{33}$$

$$a^\dagger = \frac{1}{\sqrt{2}}\left(\alpha x - \frac{1}{\alpha}\frac{d}{dx}\right), \quad \alpha = \sqrt{\frac{m\omega}{\hbar}} \tag{34}$$

$$\psi_n(x) = \frac{1}{\sqrt{n!}}\left(\frac{\alpha^2}{\pi}\right)^{1/4}\left(\alpha x - \frac{1}{\alpha}\frac{d}{dx}\right)^n e^{-\alpha^2 x^2/2} \tag{35}$$

角动量 $(\boldsymbol{j}^2, j_z, \boldsymbol{j}_1^2, \boldsymbol{j}_2^2) \to |jm\rangle$

$$j_\pm = j_x \pm i j_y, \quad [j_z, j_\pm] = \pm\hbar j_\pm, [j_+, j_-] = 2\hbar j_z, \tag{36}$$

$$\{j_+, j_-\} = 2(\boldsymbol{j}^2 - j_z^2), \quad j_\pm j_\mp = \boldsymbol{j}^2 - j_z^2 \pm \hbar j_z, \tag{37}$$

$$\boldsymbol{j}^2|jm\rangle = j(j+1)|jm\rangle, \quad j_z|jm\rangle = m|jm\rangle, \tag{38}$$

$$j_+ |jm\rangle = \sqrt{(j-m)(j+m+1)}\, |jm+1\rangle\,, \tag{39}$$

$$j_- |jm\rangle = \sqrt{(j+m)(j-m+1)}\, |jm-1\rangle \tag{40}$$

$$\langle jm+1| j_+ |jm\rangle = \sqrt{(j-m)(j+m+1)}, \tag{41}$$

$$\langle jm-1| j_- |jm\rangle = \sqrt{(j+m)(j-m+1)} \tag{42}$$

$$\langle jm+1| j_x |jm\rangle = \frac{1}{2}\sqrt{(j-m)(j+m+1)}, \tag{43}$$

$$\langle jm-1| j_x |jm\rangle = \frac{1}{2}\sqrt{(j+m)(j-m+1)} \tag{44}$$

$$\langle jm+1| j_y |jm\rangle = -\frac{1}{2}\sqrt{(j-m)(j+m+1)}, \tag{45}$$

$$\langle jm-1| j_y |jm\rangle = \frac{1}{2}\sqrt{(j+m)(j-m+1)} \tag{46}$$

3.2 C-G 系数

设 $j = j_1 + j_2$, $(\boldsymbol{j_1}^2, j_{1z}, \boldsymbol{j_2}^2, j_{2z}) \to |j_1 m_1 j_2 m_2\rangle$

$$|jm\rangle = \sum_{m_1, m_2} \langle j_1 m_1 j_2 m_2 | jm\rangle\, |j_1 m_1 j_2 m_2\rangle \tag{47}$$

其中 $\langle j_1 m_1 j_2 m_2 | jm\rangle$ 称为 Clebsch-Gordan (CG) 系数

$$\sum_{m_1} \langle j_1 m_1 j_2 m - m_1 | j' m\rangle \langle j_1 m_1 j_2 m_2 | jm\rangle = \delta_{jj'} \tag{48}$$

$$\sum_{jm} \langle j_1 m_1 j_2 m - m_1 | jm\rangle \langle j_1 m_1' j_2 m - m_1' | jm\rangle = \delta_{m_1 m_1'} \tag{49}$$

$$j = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2| \tag{50}$$

更进一步

- 性质 (三角形法则): 1. $m = m_1 + m_2 \Leftrightarrow \langle j_1 m_1 j_2 m_2 | jm\rangle \neq 0$.

  2. $|j_1 - j_2| \leq j \leq j_1 + j_2 \Leftrightarrow \langle j_1 m_1 j_2 m_2 | jm\rangle \neq 0$

- 相位规定: 1. $\langle j_1 m_1 j_2 m_2 | jm\rangle \in \mathbb{R}$

  2. $\langle j_1 m_1 = j_1 j_2 m_2 = j - j_2 | jm = j\rangle \geq 0$

4 微扰论

4.1 非简并

$H = H_0 + H'$. 1 级

$$|\psi_k\rangle = |\psi_k^{(0)}\rangle + \sum_{n\neq k} \frac{H'_{nk}}{E_k^{(0)} - E_n^{(0)}} |\psi_n^{(0)}\rangle, E_k = E_k^{(0)} + H'_{kk} \tag{51}$$

2 级

$$E_k^{(2)} = \langle\psi_k^{(0)}| H' |\psi_k^{(1)}\rangle \tag{52}$$

$$E_k = E_k^{(0)} + H'_{kk} + \sum_{n\neq k} \frac{|H'_{nk}|^2}{E_k^{(0)} - E_n^{(0)}}, \quad \left|\frac{H'_{nk}}{E_k^{(0)} - E_n^{(0)}}\right| \ll 1 \tag{53}$$

3 级

$$E_k^{(3)} = \langle\psi_k^{(1)}| H' - E^{(1)} |\psi_k^{(1)}\rangle \tag{54}$$

$$= \sum_{n\neq k}\sum_{m\neq k} \frac{H'_{kn}H'_{nm}H'_{mk}}{(E_k^{(0)} - E_n^{(0)})(E_k^0 - E_m^{(0)})} \tag{55}$$

$$- H'_{kk} \sum_{n\neq k} \frac{H'_{kn}H'_{nk}}{(E_k^{(0)} - E_n^{(0)})^2} \tag{56}$$

4.2 简并

$$det|H' - E^{(1)}| = 0 \Rightarrow E_{k\alpha}^{(1)}, \alpha = 1, \ldots, f_k \tag{57}$$

$$|\phi_{k\alpha}^{(0)}\rangle = \sum_{\mu}^{f_k} a_{\alpha\mu} |\psi_{k\mu}^{(0)}\rangle, \quad E_k = E_k^{(0)} + E_{k\alpha}^{(1)} \tag{58}$$

如有部分重根, 则能级简尚未完全解除. 凡未完全解除简并的能量本征值, 相应的零级波函数仍是不确定的.

Stack effect 见 ppt.

4.3 二能级

$$H_0 |\phi_{1,2}\rangle = E_{1,2} |\phi_{1,2}\rangle , H = H_0 + H' \tag{59}$$

$$E_\pm = \frac{1}{2}\left[(E_1 + E_2) \pm \sqrt{(E_1 - E_2)^2 + 4|H'_{12}|^2}\right] = E_c \pm |H|'_{12}|\sqrt{1 + R^2} \tag{60}$$

$$E_1 = E_c + d, E_2 = E_c - d, R = \frac{d}{|H'_{12}|}, \quad \tan\theta = 1/R, H'_{12} = |H'_{12}|e^{i\gamma} \tag{61}$$

$$|\psi_+\rangle = \cos\frac{\theta}{2} |\phi_1\rangle + \sin\frac{\theta}{2} e^{i\gamma} |\phi_2\rangle , \ |\psi_-\rangle = -\sin\frac{\theta}{2} |\phi_1\rangle + \cos\frac{\theta}{2} e^{i\gamma} |\phi_2\rangle \tag{62}$$

弱耦合 $R \gg 1$; 强耦合 $R \ll 1, R = 0$

5 量子跃迁

如果初始时刻体系处于若干个能量本征态的叠加, 则称为非定态

5.1 含时微扰

$$H = H_0 + H'(t), U(t) = \mathcal{T} \exp\left(-\frac{i}{\hbar}\int_0^t H(\tau)d\tau\right) \tag{63}$$

$$i\hbar\dot{C}_{k'k} = \sum_n e^{i\omega_{k'n}t} \langle k'| H' |n\rangle C_{nk}, \ \omega_{k'n} = \frac{E_k - E_n}{\hbar}, \quad C_{nk}(0) = \delta_{nk} \tag{64}$$

$$w_{nk} = \frac{d}{dt}P_{nk}(t) = \frac{d}{dt}|C_{nk}(t)|^2 \tag{65}$$

1 级

$$C_{k'k}(t) = C^{(0)}_{k'k} + C^{(1)}_{k'k} = \delta_{k'k} + \frac{1}{i\hbar}\int_0^t e^{i\omega_{k'k}\tau} H'_{k'k} d\tau, \ |P_{k'\neq k}(t)| \ll 1 \tag{66}$$

由于能级一般有简并, 并且简并度不尽相同, 所以不能一般地讲相反的跃迁概率相等.

5.2 突发微扰, 绝热近似

突发 (瞬时但有限大) 微扰并不改变体系的状态

量子绝热定理: 设体系随哈密顿量 $H(t)$ 随时间演化足够缓慢, 初态为 $|\psi(0)\rangle = |m(0)\rangle$, 则 $t = 0$ 时刻体系将保持在 $H(t)$ 的相应的瞬时本征态 $|m(t)\rangle$ 上.

特征时间 $T \approx \frac{1}{\omega_{min}}$, 其中 ω_{min}: 一切初态到一切可能末态的跃迁相应的频率的极小值. 能级接近简并情况下, 量子绝热近似就很差. 能级出现简并, 量子绝热近似完全失效. 成立条件:

$$\left|\frac{\hbar\langle m|n\rangle}{E_m - E_n}\right| \ll 1, \quad \left|\frac{\hbar\langle m|H|n\rangle}{(E_n - E_m)^2}\right| \ll 1 \tag{67}$$

此时

$$|\psi(0)\rangle = |m(0)\rangle, \quad |\psi(t)\rangle = \exp\left[i\left(\alpha_m(t) + \gamma_m(t)\right)\right]|m(t)\rangle \tag{68}$$

$$\alpha_m = -\frac{1}{\hbar}\int_0^t E_m(\tau)d\tau, \quad \gamma_m = i\int_0^t \langle m(\tau)|\left[\frac{\partial}{\partial\tau}|m(\tau)\rangle\right]d\tau \tag{69}$$

5.3 周期微扰, 有限时间的常微扰

周期微扰

$$H'(t) = H'e^{-\omega t}, P_{k'k}(t) = \frac{4|H'_{k'k}|^2}{\hbar^2}\left[\frac{\sin\frac{(\omega_{k'k}-\omega)t}{2}}{\omega_{k'k} - \omega}\right]^2 \tag{70}$$

$$P_{k'k}(t) = \frac{2\pi t}{\hbar^2}|H'_{k'k}|^2\delta(\omega_{k'k} - \omega), \quad (\omega_{k'k} - \omega)t \gg 1 \tag{71}$$

$$w_{k'k} = \frac{2\pi}{\hbar}|H'_{k'k}|^2\delta(E_{k'} - E_k - \hbar\omega) \tag{72}$$

常微扰

$$H'(t) = H'\left[\theta(t) - \theta(t-T)\right], P_{k'k}(t) = \frac{|H'_{k'k}|^2}{\hbar^2\omega}\left[\frac{\sin\frac{\omega_{k'k}T}{2}}{\omega_{k'k}/2}\right]^2 \tag{73}$$

$$P_{k'k}(t) = \frac{2\pi T}{\hbar^2}|H'_{k'k}|^2\delta(\omega_{k'k}), \quad \omega_{k'k}T \gg 1, t \gg T \tag{74}$$

$$w_{k'k} = \frac{2\pi}{\hbar}|H'_{k'k}|^2\delta(E_{k'} - E_k) \tag{75}$$

Fermi's golden rule

$$w_{k'k} = \frac{2\pi}{\hbar}\langle |H'_{k'k}|^2\rangle \rho(E_{k'})|_{E_{k'}\approx E_k} = \frac{2\pi}{\hbar}|H'_{k'k}|^2\delta(E_{k'}-E_k) \tag{76}$$

5.4 能量时间不确定度关系

激发态 $\Gamma\tau \approx \hbar$

$$\Delta A\cdot\Delta B \geq \frac{1}{2}\langle|[A,B]|\rangle, \frac{dA}{dt} = \frac{[A,H]}{i\hbar} \Rightarrow \Delta E\cdot\Delta t \gtrsim \frac{\hbar}{2} \tag{77}$$

光的吸收、辐射见 ppt.

6 其他近似

6.1 Fermi 气体

$$E_n = \frac{\pi^2\hbar^2 n^2}{2mL^2}, \quad dN = 2\times\frac{1}{8}\times 4\pi n^2 dn, \quad n_{FD} = \frac{1}{e^{\beta(\epsilon-\mu)}+1} \tag{78}$$

$$\Rightarrow N = \int_0^{E_f}\frac{dN}{dE}dE = \frac{k_f^3 L^3}{3\pi^2}, \quad p_f = \hbar k_f = \sqrt{2mE_f} \tag{79}$$

$$\langle E\rangle = \frac{3}{5}E_f, \quad p = \frac{2}{5}\rho E_f \tag{80}$$

6.2 变分法

体系的能量本征值和本征函数, 可以在满足归一化条件下让能量平均值取极值而得到

$$\delta\langle\phi|H|\psi\rangle - \lambda\delta\langle\psi|\psi\rangle = 0 \Leftrightarrow H\psi = \lambda\psi,\ H^*\psi^* = \lambda\psi^* \tag{81}$$

按变分原理求出的 $\langle H\rangle$, 不小于体系的基态能量的严格值. 用变分法计算出的能量与严格值的偏差, 相对于试探波函数本身与严格波函数的偏差, 是二级小.

Ritz 变分法: $\psi(c_1, c_2, \dots)$

$$\sum_i \frac{\partial}{\partial c_i} \langle H \rangle \delta c_i = 0 \tag{82}$$

Hartree 自洽场方法: 平均场近似, 或独立粒子模型. 原子的基态波函数:

$$\psi(\boldsymbol{r}_1, \dots, \boldsymbol{r}_Z) = \phi_{k_1}(\boldsymbol{r}_1) \dots \phi_{k_Z}(\boldsymbol{r}_Z) \tag{83}$$

$$H = \sum_{i=1}^{Z} h_i + \frac{1}{2} \sum_{i \neq j}^{Z} \frac{1}{r_{ij}}, \quad h_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \tag{84}$$

Hartree 方程: 单电子波函数满足的方程

$$\left[h_i + \sum_{i \neq j} \int |\psi_{k_j}(\boldsymbol{r}_j)|^2 \frac{1}{r_{ij}} d\tau_j \right] \phi_{k_i} = \epsilon_i \phi_{k_i} \tag{85}$$

及其复共轭方程. 注意 Hartree 波函数只是部分考虑了交换对称性, 及每个电子的量子态应取得不同.