§ 8 变分法

§ 8.1 量子力学的变分原理

能量 $E[\psi] = \dfrac{\langle\psi|\hat{E}|\psi\rangle}{\langle\psi|\psi\rangle}$，基态能量 E_0

$$E[\psi] \geq E_0$$

$$E[\psi] = \frac{\sum_n E_n |\langle n|\psi\rangle|^2}{\sum_n |\langle n|\psi\rangle|^2} \geq \frac{\sum_n E_0 |\langle n|\psi\rangle|}{\sum_n |\langle n|\psi\rangle|^2}$$

Ritz方法：$|\psi\rangle = \sum_i \alpha_i |i\rangle$

$$\frac{\partial E}{\partial \alpha_i} = 0$$

例：用变分法求解一维谐振子的基态。

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

$$\langle x|\psi\rangle = A e^{-bx^2}$$

$$E(b) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\hbar^2}{2m} b + \frac{m\omega^2}{8b}$$

$$\frac{\partial E(b)}{\partial b} = 0 \rightarrow b = \frac{m\omega}{2\hbar}, \quad E_0 \approx \frac{1}{2}\hbar\omega$$

$$\langle x|\psi\rangle = \left(\frac{2b}{\pi}\right)^{1/4} e^{-\frac{m\omega}{2\hbar}x^2}$$

§ 8.2 氦原子

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2} - \frac{1}{|r_1 - r_2|}\right)$$

忽略电子的相互作用：

基态：$\phi_0(\hat{r}_1, \hat{r}_2) = \psi_{100}(\hat{r}_1)\psi_{100}(\hat{r}_2)$

代回计算能量，

$$\langle \hat{H} \rangle = 2Z^2 E_1 + \frac{e^2}{4\pi\varepsilon_0}\int \phi_0^2(\hat{r}_1, \hat{r}_2)\frac{1}{|\hat{r}_1 - \hat{r}_2|} d^3r_1 d^3r_2$$

$$\frac{1}{|\hat{r}_1 - \hat{r}_2|} = \frac{1}{\sqrt{\hat{r}_1^2 + \hat{r}_2^2 - 2\hat{r}_1\hat{r}_2\cos\gamma}} = \begin{cases} \sum_l \frac{r_1^l}{r_2^{l+1}} P_l(\cos\gamma) & 0 \le r_1 \le r_2 \\ \sum_l \frac{r_2^l}{r_1^{l+1}} P_l(\cos\gamma) & r_1 > r_2 \end{cases}$$

$$\int_{-1}^{1} P_m(x) P_n(x)\, dx = \frac{1}{2n+1}\delta_{mn}, \quad P_0(x) = 1$$

$$\int \phi_0^2(\hat{r}_1, \hat{r}_2)\frac{1}{|\hat{r}_1 - \hat{r}_2|} d^3r_1 d^3r_2$$

$=$

$= \frac{5Z}{8a}$

考虑屏蔽效应，假设1个电子屏蔽后的核电荷为$Z-\eta$