$H\,|n\rangle = E_n\,|n\rangle$ روش وردشی

$E_0 = ?$

$|\psi\rangle$ تابع تست $\sum_n |n\rangle\langle n| = 1$

$$\langle\psi|H|\psi\rangle = \sum_n \langle\psi|\underbrace{H|n\rangle}_{E_n|n\rangle}\langle n|\psi\rangle = \sum_n E_n \langle\psi|n\rangle\langle n|\psi\rangle$$

$$\geq E_0 \sum_n \langle\psi|n\rangle\langle n|\psi\rangle = E_0\langle\psi|\psi\rangle$$

$$E_0 \leq \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \qquad |\psi(\mu)\rangle$$

$$\frac{\langle\psi(\mu)|H|\psi(\mu)\rangle}{\langle\psi(\mu)|\psi(\mu)\rangle} = E(\mu)$$

$$E_0 \leq E(\mu) \qquad \left.\frac{dE(\mu)}{d\mu}\right|_{\mu^*} = 0 \quad \text{کمینه } E(\mu)$$

$Z = 2$ $\qquad E_0 \approx E(\mu^*)$

تابع موج = جزء فضایی × جزء اسپینی

$H = H_1 + H_2 + V_{12}$

$H_i = \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \qquad i = 1,2$

$E^{(0)}_{n_1 n_2} = E_{n_1} + E_{n_2} \qquad E_n = -\frac{Z^2 Ry}{n^2}$

$V_{12} = \frac{e^2}{|\vec r_1 - \vec r_2|}$

$$\left.\begin{aligned}\Delta E^{(1)}_{11} &= \langle 100|\langle 100|V_{12}|100\rangle|100\rangle = 2.5\,Ry\\ E^{(0)}_{11} &= E_1 + E_1 = -4\,Ry \times 2 = -8\,Ry\end{aligned}\right\} \quad -5.5\,Ry = E^{(0)}_{11} + \Delta E^{(1)}_{11}$$

$-5.8\,Ry = E^{\exp}_{11}$

Para He $\quad |100\rangle_{(1)}|100\rangle_{(2)} \qquad |s\,m_s\rangle$ $|00\rangle$

$$\frac{1}{\sqrt2}\Big(|100\rangle_{(1)}|n\ell m\rangle_{(2)} + |n\ell m\rangle|100\rangle\Big)|00\rangle = |s\rangle$$

Ortho He $\quad \frac{1}{\sqrt2}\Big(|100\rangle|n\ell m\rangle - |n\ell m\rangle|100\rangle\Big)|1, m_s\rangle = |t\rangle$

تصحیح انرژی حالت پایه اتم He با استفاده از وردش

$$E_0 \leq E(\tilde Z) = \frac{\langle\psi(\tilde Z)|H|\psi(\tilde Z)\rangle}{\langle\psi(\tilde Z)|\psi(\tilde Z)\rangle}$$

$$|\psi(\tilde Z)\rangle = |100(\tilde Z)\rangle|100(\tilde Z)\rangle$$

$$\langle\vec r|100(\tilde Z)\rangle = \frac{1}{\sqrt\pi}\left(\frac{\tilde Z}{a_0}\right)^{3/2} e^{-\tilde Z r/a_0} = \psi_{100}(\vec r)$$

$$H = \sum_{i=1}^{2}\left(\frac{p_i^2}{2m} - \frac{Ze^2}{r_i}\right) + \frac{e^2}{r_{12}} + \sum_{i=1}^{2}\left(\frac{\tilde Z e^2}{r_i} - \frac{\tilde Z e^2}{r_i}\right)$$

$$H = \sum_{i=1}^{2}\underbrace{\left(\frac{p_i^2}{2m} - \frac{\tilde Z e^2}{r_i}\right)}_{\tilde H_i(\tilde Z)} + \frac{e^2}{r_{12}} - \sum_{i=1}^{2}\frac{(Z-\tilde Z)e^2}{r_i}$$

$$\tilde H_i(\tilde Z)\,|100(\tilde Z)\rangle_i = E_0(\tilde Z)\,|100(\tilde Z)\rangle_i$$

$$E(\tilde Z) = \langle 100(\tilde Z)|\langle 100(\tilde Z)|\,H(\tilde Z)\,|100(\tilde Z)\rangle_{(1)}|100(\tilde Z)\rangle_{(2)}$$

$$\tilde H_1(\tilde Z) + \tilde H_2(\tilde Z) + \frac{e^2}{\quad} - \frac{(Z-\tilde Z)e^2}{\quad} - \frac{(Z-\tilde Z)e^2}{\quad}$$

$$E(\tilde Z) = \langle 100(\tilde Z)|\langle 100(\tilde Z)| \; H(Z) \; |100(\tilde Z)\rangle_{(1)}|100(\tilde Z)\rangle_{(2)}$$

$$\tilde H_1(\tilde Z) + \tilde H_2(\tilde Z) + \frac{e^2}{r_{12}} - \frac{(Z-\tilde Z)e^2}{r_1} - \frac{(Z-\tilde Z)e^2}{r_2}$$

$$= 2E_0(\tilde Z) + \langle 100(\tilde Z)|\langle 100(\tilde Z)| \frac{e^2}{r_{12}} |100(\tilde Z)\rangle |100(\tilde Z)\rangle$$

$$- \langle 100(\tilde Z)|\langle 100(\tilde Z)| \sum_i \frac{(Z-\tilde Z)e^2}{r_i} |100\rangle|100\rangle$$

$$E(\tilde Z) = 2E_0(\tilde Z) + \frac{5}{8}\frac{\tilde Z e^2}{a_0} - 2\times(Z-\tilde Z)e^2\frac{\tilde Z}{a_0}$$

$$\begin{cases} E_0 = -1Ry\,\tilde Z^2 \\ \dfrac{e^2}{2a_0} = 1Ry \end{cases}$$

$$E(\tilde Z) = 2Ry\left(\tilde Z^2 - 2Z\tilde Z + \frac{5}{8}\tilde Z\right)$$

$$\frac{dE(\tilde Z)}{d\tilde Z} = 0 \longrightarrow \tilde Z^* = Z - \frac{5}{16} \underset{Z=2}{=} 1.7$$

$E_0 \leqslant E(\tilde Z^*) = -5.78\,Ry$ وردش $E_0 = -5.5\,Ry$:اختلال

$$E_0^{exp} = -5.8\,Ry$$

Para He $\quad |s\rangle = \frac{1}{\sqrt 2}\left(|100\rangle|nlm\rangle + |nlm\rangle|100\rangle\right) \; |00\rangle$

Ortho He $\quad |t\rangle = \frac{1}{\sqrt 2}\left(|100\rangle|nlm\rangle - |nlm\rangle|100\rangle\right) \; |1, m_s\rangle$

$$\Delta E^{Para}_{Ortho} = \langle {}^{s}_{t} | \frac{e^2}{r_{12}} | {}^{s}_{t} \rangle \qquad \begin{matrix}\langle 00|00\rangle = 1 \\ \langle 1m_s|1m_s\rangle = 1\end{matrix}$$

$$= \frac{1}{2}\int d^3r_1\, d^3r_2 \left| \psi_{100}(\vec r_1)\,\psi_{nlm}(\vec r_2) \overset{Para}{\underset{Ortho}{\pm}} \psi_{nlm}(\vec r_1)\,\psi_{100}(\vec r_2)\right|^2 \frac{e^2}{|\vec r_1 - \vec r_2|}$$

$$\Delta E = 2\times\frac{1}{2}\int d^3r_1\, d^3r_2\, |\psi_{100}(\vec r_1)|^2\, |\psi_{nlm}(\vec r_2)|^2 \frac{e^2}{r_{12}} \quad ✓ \qquad 0 = \left[J_z, \frac{e^2}{|\vec r_1 - \vec r_2|}\right]$$

$$\pm\, 2 \times \frac{1}{2}\int d^3r_1\, d^3r_2\, \psi^*_{100}(\vec r_1)\,\psi^*_{nlm}(\vec r_2)\;\psi_{nlm}(\vec r_1)\,\psi_{100}(\vec r_2)\,\frac{e^2}{r_{12}} \quad ✓$$

$$\Delta E^{(1)\,Para}_{\;\;Ortho} = J_{nl} \pm K_{nl} \rightarrow$$ برهمکنش تبادلی (اصل طرد پائولی)

$$J_{nl} > 0 \qquad K_{nl} > 0 \quad ✓$$

$$\vec S_i = \frac{\hbar}{2}\vec\sigma_i \qquad \Delta E^{(1)}_{nl} = J_{nl} - \frac{1}{2}\left(1 + \vec\sigma_1\cdot\vec\sigma_2\right) K_{nl}$$ اری

$$\langle s, m_s | \frac{1}{2}\left(1 + \vec\sigma_1\cdot\vec\sigma_2\right) | s, m_s\rangle \qquad \begin{matrix} s=0 & m_s = 0 & |00\rangle \to + \\ s=1 & m_s = \pm1, 0 & |1, m_s\rangle \to - \end{matrix}$$

$$\vec\sigma_1\cdot\vec\sigma_2 = \frac{4}{\hbar^2}\,\vec S_1\cdot\vec S_2 = 2\left(s(s+1) - \frac{3}{2}\right)$$

$$\vec S_1\cdot\vec S_2 = \frac{1}{2}\left(\vec S^2 - \vec S_1^2 - \vec S_2^2\right)$$

$$\langle s, m_s | \frac{1}{2}\left(\vec S^2 - \vec S_1^2 - \vec S_2^2\right) | s, m_s\rangle = \frac{\hbar^2}{2}\left(s(s+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\times 2\right)$$

$$= \frac{\hbar^2}{2}\left(s(s+1) - \frac{3}{2}\right)$$

$$\langle s, m_s | \frac{1}{2}\left(1 + \vec\sigma_1\vec\sigma_2\right) | s, m_s\rangle = \frac{1}{2}\left[1 + 2\left(s(s+1) - \frac{3}{2}\right)\right]$$

$$S=0 \qquad \frac{1}{2}\left(1+(-3)\right) = -1$$

$$S=1 \qquad \frac{1}{2}\left(1+1\right) = +1$$

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

$s=0 \quad J_{nl}+K_{nl}$

$s=1 \quad J_{nl}-K_{nl}$