Lecture Thursday 6. September 2007

Topics Helium atom part 4: Ground State; Variational Methods

Scaling – how to transform to dimensionless

$$\int \mathcal{R}\left(\frac{r_2}{a}\right)^2 \frac{1}{\frac{r_{12}}{a}} \mathcal{R}\left(\frac{r_1}{a}\right)^2 d^3r_1\, d^3r_2 \qquad e^{-\frac{Z}{a_0}\cdot r} \qquad \boxed{\frac{1}{a}}$$

$$\int |\psi(r_1)|^2 d^3r_1 = 1 \qquad \psi = C \cdot e^{-r/a} \cdot \left(f\left(\frac{r}{a}\right)\right)$$

$$\frac{1}{r_{12}} \longrightarrow \left(\frac{1}{\frac{r_{12}}{a}}\right) \cdot \frac{1}{a}$$

has dimension of $\sqrt{\frac{1}{V}} \approx \left(\frac{1}{a^3}\right)^{\frac{1}{2}}$

Integral $= \frac{1}{a} \cdot$ Integral (in atomic units)

$$\left\langle \frac{1}{r_{12}} \right\rangle \approx \left(\frac{Z}{a_0}\right) \frac{5}{8}$$

Length scaling

dimensionless

$$\hookrightarrow \frac{Z}{a_0} \cdot I_{\text{dimless}}$$

How do the repulsion, nuclear atraction and kinetic energies change with Z

$$\int \cancel{\mathcal{R}\left(\frac{r_2}{a}\right)^2} \underbrace{\frac{Ze^2}{r_1} \mathcal{R}\left(\frac{r_1}{a}\right)^2}\, d^3r_1\, \cancel{d^3r_2} \qquad e^{-\frac{Z}{a_0}\cdot r} \qquad \boxed{\frac{1}{a}}$$

$$\left\langle \frac{Z}{r_1} \right\rangle \quad \text{Potential} \qquad {}^{-r/a} \cdot \left(f\left(\frac{r}{a}\right)\right)$$

$$\hookrightarrow \frac{Z^2}{a_0} \cdot I_{\text{dimless}} \qquad \frac{\hbar^2}{m a_0^2} = \frac{e^2}{a_0}$$

$$\frac{\hbar^2}{2m} \int \cancel{\mathcal{R}\left(\frac{r_2}{a}\right)^2} \underbrace{\frac{d^2}{dr_1^2} \mathcal{R}\left(\frac{r_1}{a}\right)^2}\, d^3r_1\, \cancel{d^3r_2} \qquad e^{-\frac{Z}{a_0}\cdot r} \qquad \boxed{\frac{1}{a}}$$

$$\frac{Z^2}{a_0^2}$$

Kinetic Scale as Z^2

Variational methods

Variationalmethods, first time

$$\langle \psi(\alpha) | H | \psi(\alpha) \rangle \longrightarrow \mathcal{H}(\alpha)$$

function of parameter α

In helium → phys idea → screening

Z – screen

effective Z

(for example)

General on variational method; Expansion – analogy to vector spaces

$$\underline{\underline{\psi(\vec r)}} = \underline{\underline{\sum_i}} c_i \varphi_i(\vec r)$$

φ_i are $\boxed{H \varphi_i = E_i \varphi_i}$

Solutions of H form a <u>complete set</u>

Vectors in 3-dim space

$\vec R = \underbrace{x\vec e_x + y\vec e_y + z\vec e_z}_{\text{Generalizations}}$ (ANY) Linear "spaces" of functions

All things we can do with coordinates

we can generalize to "functions"

3dim space ... 3 base vectors

Functional space ... ∞ base functions

→ ANY $\psi(\vec r) = \sum^{\infty} c_i \varphi_i$ (c_i components)

General proof; Expansion in eigenstates; Complete set of basis functins;

$$\underline{\underline{\psi(\vec{r})}} = \underline{\underline{\sum_i}} c_i \varphi_i(\vec{r})$$

φ_i are $\boxed{H\varphi_i = E_i \varphi_i}$

$$\int \varphi_i^*(\vec{r}) \varphi_i(\vec{r})\, d^3r = 1$$

$$\int \varphi_i^*(\vec{r}) \varphi_j(\vec{r})\, d^3r = 0 \quad \text{for } i \neq j \qquad \delta_{ij}$$

$$\mathcal{H}(\alpha) = \int \psi_\alpha^*(r\ldots)\, H\, \psi_\alpha(\ldots)\, d\ldots\ldots$$

$$\mathcal{H}(\alpha) = \sum_i \sum_j \int c_i^* \varphi_i^* H c_j \varphi_j\, d^3r\ldots$$

I keep ψ_α $\int \psi_\alpha^*()\psi_\alpha = 1$

$$\int c_i^* c_j E_j\, \varphi_i^* \varphi_j\, d\ldots$$

$$\mathcal{H}(\alpha) = \sum_i |c_i^\alpha|^2 E_i \qquad \text{All } E_i > E_{GS} \qquad \sum_i |c_i^\alpha|^2 = 1$$

$$> \sum_i |c_i^\alpha|^2 \cdot E_{GS}$$

The Ground state is smallest in energy

I keep ψ_α $\int \psi_\alpha^*()\psi_\alpha = 1$

$$\int c_i^* c_j E_j\, \varphi_i^* \varphi_j\, d\ldots$$

$$\mathcal{H}(\alpha) = \sum_i |c_i^\alpha|^2 E_i \qquad \text{All } E_i > E_{GS} \qquad \sum_i |c_i^\alpha|^2 = 1$$

$$> \sum_i |c_i^\alpha|^2 \cdot E_{GS}$$

for any ψ_α

$$\mathcal{H}(\alpha) \geq E_{GS} \quad \text{allways}$$

except when $\psi_\alpha = \varphi_{GS}$

The closer to $\varphi_{GS} \rightarrow$ closer to $\underline{\underline{E_{GS}}}$

I thus need to look for a minimum in α

$\psi(\alpha) = \frac{C(\alpha)}{x^2+\alpha^2}$

$\varphi(\alpha) = C_\alpha e^{-\alpha x}$

Apply this to our expectation value of z (lower case z variable)

$$H = \underbrace{T_1 + T_2}_{\frac{\hbar^2}{2m}\nabla^2} + \underbrace{V_1 + V_2}_{\frac{Ze^2}{r_1}} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \quad \underbrace{z\frac{5}{8}\,\text{au}}$$

Z^2 scaling

$\psi\left(\frac{Z}{a}\cdot r\right)$ but for effective z $\psi\left(\frac{z}{a}\cdot r\right)$

$zZ\cdot$ au $\quad \frac{5}{8}z \quad z$ eff.

$$\psi\left(\tfrac{z}{a}\cdots\right) \left| \frac{\hbar^2}{2m}\nabla_1^2 + \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \right| \psi\left(\tfrac{z}{a}\right)$$

$$\mathcal{H}(z) = \frac{1}{2}z^2 + \frac{1}{2}z^2 - zZ - zZ + \frac{5}{8}z$$

$$\mathcal{H} = z^2 - 2zZ + \frac{5}{8}z$$

$$0 = \frac{d\mathcal{H}(z)}{dz} = 2z - 2Z + \frac{5}{8} \qquad \boxed{z = Z - \frac{5}{16}}$$

Here we evaluate the actual H(z) with z=Z - 5/16

$$\mathcal{H}(z) = z^2 - 2zZ + \frac{5}{8}z$$

$$z = Z - \frac{1}{2}\frac{5}{8}$$

$$Z^2 - \frac{5}{8}Z + \left(\frac{1}{2}\frac{5}{8}\right)^2 - 2ZZ$$

Variational result

$$\boxed{-Z^2 - \frac{1}{4}\left(\frac{5}{8}\right)^2 + \frac{5}{8}Z} \text{ a.u. } [27.2\,\text{eV}] \qquad + \frac{5}{8}Z + \frac{5}{8}Z - \frac{1}{2}\left(\frac{5}{8}\right)^2$$

$$\psi\left(\tfrac{z}{a}\cdots\right) \left| \frac{\hbar^2}{2m}\nabla_1^2 + \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|r_1 - r_2|} \right| \psi\left(\tfrac{z}{a}\right)$$

$$\mathcal{H}(z) = \frac{1}{2}z^2 + \frac{1}{2}z^2 - zZ - zZ + \frac{5}{8}z$$

$$\mathcal{H} = z^2 - 2zZ + \frac{5}{8}z$$

$$0 = \frac{d\mathcal{H}(z)}{dz} = 2z - 2Z + \frac{5}{8} \qquad \boxed{z = Z - \frac{5}{16}}$$

How to make variation more efficient

Other variational methods

$\longrightarrow$ with correlation

$$\Psi(r_1, r_2) = \phi_Z(r_1)\,\phi_Z(r_2)$$

Hylleraas functions

$$\Psi(r_1 r_2) = f(r_1)\cdot f(r_2)\cdot g(r_{12})$$

$s = r_1 + r_2$

$t = r_1 - r_2$

$u = r_{12} = |\vec{r}_1 - \vec{r}_2|$

$$\phi(s, t, u) \equiv \Psi(\vec{r}_1, \vec{r}_2) \equiv e^{-ks} \sum_{l,m,n}^{N} c_{l,2m,n}\, s^l t^{2m} u^n$$

$$\frac{\partial \mathcal{H}(k, \{c\})}{\partial k} = 0$$

$$\frac{\partial \mathcal{H}}{\partial c_{001}} = 0 = \frac{\partial \mathcal{H}}{\partial c_{010}} = \frac{\partial \mathcal{H}}{\partial c_{100}} = \ldots$$