Lecture Wednesday 5 September 2007

Topics Helium part 3: Ground State; Independent electrons; (Variational Method next)

Bound states – energies – and Helium; Classically unstable

In classical physics bound "states" are never periodic, never stable!

Poincaré:

Wavefunction for 2 independent electrons

Ground state of hydrogenlike each one

$$\varphi_{1s}^{(Z)}(\vec{r}_1) \quad \varphi_{1s}^{(Z)}(\vec{r}_2) \qquad 1s \quad n=1 \quad l=0$$

$$\underbrace{H = T_1 + V_1 + T_2 + V_2}_{\text{SPIN Must BE SINGLET}} + \cancel{\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}$$

$$H\left(\varphi_{1s}(\vec{r}_1)\cdot\varphi_{1s}(\vec{r}_2)\right) \longrightarrow ?$$

Independent particles - energies

$$(T_1 + V_1 + T_2 + V_2)\,\varphi_a(1)\,\varphi_b(2)$$

$$\underbrace{\varphi_b(2)(T_1 + V_1)\varphi_a(1)}_{\text{hydrogen-like}} + \varphi_a(1)\overbrace{(T_2 + V_2)\varphi_b(2)}^{\text{hydrogen-like}}$$

$\frac{d^2}{dx^2}$ type

Thus independent electron assumption leads to 2-hydrogen like Schrö'd. eq.

$E_a\varphi_a(1)$ $\qquad$ $E_b\varphi_b(2)$

$$H_0\varphi_a(1)\varphi_b(2) = (E_a + E_b)\,\varphi_a(1)\varphi_b(2)$$

is the H with neglected $\cancel{\frac{e^2}{|\vec{r}_1 - \vec{r}_2|}}$

The energies are then $\left(\frac{Z^2}{n_a^2} + \frac{Z^2}{n_b^2}\right) E_{1s}(\text{hydrogen})$

Experiment etc ....

Two-electron systems in units of eV

	H^-	He	Li^+	Be^{++}	$B^{(3+)}$	$C^{(4+)}$
Z	1	2	3	4	5	6
Ion.pot.[au]	0,757	24,60	75,62	153,95	259,49	392,22
2.Ion.pot	13,600	54,40	122,40	217,60	340,00	489,60
EXP.BindEner	-14,357	-79,00	-198,02	-371,55	-599,49	-881,82
$2\,E_{1s}$	-27,200	-108,80	-244,80	-435,20	-680,00	-979,20
$2\,E_{1s}$ + 5/8 Z	-10,200	-74,80	-193,80	-367,20	-595,00	-877,20
Variational	-12,856	-77,46	-196,46	-369,86	-597,66	-879,86
EXP.BindEner	-14,357	-79,00	-198,02	-371,55	-599,49	-881,82

Ion.pot. Ionization potential: The energy to remove the first electron

2.Ion.pot Second Ionization potential: The energy to remove the second electron

Evaluate expectation value – What is expectation value ?

Example – age distribution – average value of age

$$\left(T_1 + V_1 + T_2 + V_2 + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\right) \varphi_a(1)\,\varphi_b(2)$$

Expectation value:

Wavefunction independent;

But CORRECT FULL ENERGY

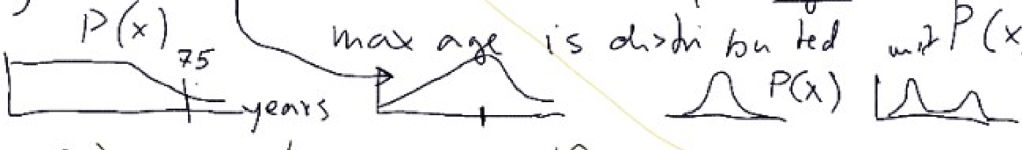
$$\int \varphi_a^*(1)\,\varphi_b^*(2)\left[T_1 + V_1 + T_2 + V_2 + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}\right] \varphi_a(1)\,\varphi_b(2)\; d1\, d2$$

$$\int P(x)\, x\, dx$$

(average value)

expectation for age

max age is distributed with $P(x)$



Our $P(x)$ is $|\varphi_a(r_1)\,\varphi_b(r_2)|^2$

$-(E_a + E_b)$

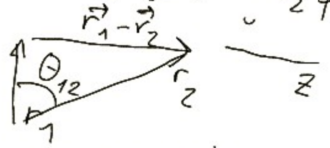
Generally for any two states a,b - but we specify a->1s b->1s; Multipole expansion

$$\int d^3r_1\, d^3r_2\, |\varphi_a(r_1)|^2 |\varphi_b(r_2)|^2 \frac{e^2}{|\vec{r}_1-\vec{r}_2|} \Big\}\ \text{all mixed}$$

$$\varphi_{nlm}(\vec{r}) = R_{nl}(r)\, Y_{lm}(\hat{r}) \quad \text{angular variables } \vartheta_r, \varphi_r$$

$$d^3r_1 = \underbrace{r_1^2 dr_1}_{\text{only } r} \cdot \sin\vartheta_1\, d\vartheta_1\, d\varphi_1 \quad \text{only angles}$$

$$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta_{12}}} \quad \text{expres } \theta_{12} \text{ in } \vartheta_1\varphi_1,\ \vartheta_2\varphi_2$$



General method (multipole expansion of Coulomb term)

$$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \sum_{L=0}^{\infty}\sum_{M=-L}^{L} \frac{4\pi}{2L+1}\left(\frac{r_<^L}{r_>^{L+1}}\right) Y_{LM}(\vartheta_1\varphi_1)\, Y_{LM}(\vartheta_2\varphi_2)$$

How to perform the 6-dim integration: two angular (4 dimensions) using Y – spherical harmonics

$$\int d^3r_1\, d^3r_2\, |\varphi_a(r_1)|^2 |\varphi_b(r_2)|^2 \frac{e^2}{|\vec{r}_1-\vec{r}_2|} \Big\}\ \text{all mixed}$$

$$\varphi_{nlm}(\vec{r}) = R_{nl}(r)\, Y_{lm}(\hat{r}) \quad \text{angular variables } \vartheta_r, \varphi_r$$

$$d^3r_1 = \underbrace{r_1^2 dr_1}_{\text{only } r} \cdot \sin\vartheta_1\, d\vartheta_1\, d\varphi_1 \quad \text{only angles}$$

$$\varphi_{1s} \rightarrow C e^{-\frac{Zr}{a_0}} \cdot Y_{00}(\vartheta,\varphi) \qquad Y_{00} = \frac{1}{\sqrt{4\pi}} \ \text{constant}$$

$$\int Y^*_{lm}(\vartheta,\varphi)\, Y_{l'm'}(\vartheta,\varphi)\, d\Omega = \delta_{l,l'}\,\delta_{mm'} \qquad \delta_{ab} = \begin{cases} 0 & a=b \\ 1 & \text{other} \end{cases}$$

$$\int Y_{lm}\, d\Omega = 0 \ \text{ for } l \neq 0 \text{ because } \sqrt{4\pi}\int Y_{lm} Y^*_{00} \rightarrow 0$$

Orthogonality of spherical harmonics

Gives that the integral of one Y is zero (unless L=0....)

The evaluation reduces to a two-dimensional integral over r_1 and r_2 (with $r_>$)

$$\iiiint\!\!\iint R Y_{00}^* R Y_{00}^* \left(\sum \frac{4\pi}{2L+1} \left(\frac{r_<^L}{r_>^{L+1}} \right) Y_{LM}^*(1)\, Y_{LM}(2) \right) R\, Y_{00}(1)\, R\, Y_{00}(2)$$

for general LM the angular integrals GIVE ZERO! $\quad Y_{00} = \frac{1}{\sqrt{4\pi}}$

only $L=0$ $M=0$ can contribute

all angular integrations combined with give 1

$$\boxed{\int r_1^2 dr_1\, r_2^2 dr_2\, \frac{1}{r_>} R^2 R^2}$$

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{L=0} \sum_{M=-L} \frac{4\pi}{2L+1} \left(\frac{r_<^L}{r_>^{L+1}} \right) Y_{LM}^*(\vartheta_1 \varphi_1)\, Y_{LM}(\vartheta_2 \varphi_2)$$

We must evaluate the integrals

$$R_{1,0}(r) = 2 \cdot \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot e^{-\frac{Z \cdot r}{a_0}} = R_{1,0}^*(r)$$

$$\int_0^\infty \int_0^\infty r_1^2 \cdot r_2^2 \cdot R_{1,0}(r_1)^2 \cdot R_{1,0}(r_2)^2 \frac{e^2}{r_>} dr_1 dr_2$$
$$= \int_0^\infty \int_0^\infty 2^4 \left(\frac{Z}{a_0}\right)^6 e^{-\frac{2Z}{a_0}(r_1+r_2)} r_1^2 \cdot r_2^2 \frac{e^2}{r_>} dr_1 dr_2$$
$$= 2^4 \left(\frac{Z}{a_0}\right)^6 \cdot e^2 \int_0^\infty \int_0^\infty e^{-\frac{2Z}{a_0}(r_1+r_2)} r_1^2 \cdot r_2^2 \frac{1}{r_>} dr_1 dr_2$$

The $r_>$ must be replaced .... which leads to two integrations

$$\int_0^\infty \left(\int_0^{r_1} e^{-r_1-r_2} r_1 r_2^2 dr_2 \right) dr_1 + \int_0^\infty \left(\int_{r_1}^\infty e^{-r_1-r_2} r_1^2 r_2 dr_2 \right) dr_1$$
$$= \int_0^\infty r_1 e^{-r_1} \underbrace{\int_0^{r_1} r_2^2 e^{-r_2} dr_2}_{intB} dr_1 + \int_0^\infty r_1^2 e^{-r_1} \underbrace{\int_{r_1}^\infty e^{-r_2} r_2 dr_2}_{intC} dr_1$$

And the result is .....

$\langle \quad | V12 | \quad \rangle \quad \to \quad \displaystyle\int_0^\infty \int_0^\infty \ldots = \frac{5}{8} \frac{Z e^2}{a_0}$

And the result is .....

$\langle \quad | \text{ V12 } | \quad \rangle$ ->
$$\int_0^\infty \int_0^\infty \ldots = \frac{5}{8}\frac{Ze^2}{a_0}$$

The multipole expansion we used:

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{LM} \frac{4\pi}{2L+1} \frac{r_<^L}{r_>^{L+1}} Y_{LM}^\star(\hat{r}_1) Y_{LM}(\hat{r}_2)$$

$$r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\vec{r}_1| < |\vec{r}_2|$$
$$r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\vec{r}_1| > |\vec{r}_2|$$