Quantum Mechanics 2

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Helium

First Approximation

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Helium Atom

Let us consider the Helium atom. The radial Hamiltonian for $l = 0$ is

$$H = -\frac{\hbar^2}{2mr_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2mr_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

The first two terms comprise the Hamiltonian for the first electron, the next two terms for the second electron, and the last term is the interaction between the two electrons, with their distance being $r_{12} = |\vec{r}_2 - \vec{r}_1|$.

First Approximation

For our first approximation, let us choose the direct product of two hydrogen ground states as our trial function

$$\tilde{\psi} = e^{-Z(r_1+r_2)/a}$$

with a being the Bohr radius.

Using the Gamma function

$$\Gamma(z) = \int_0^\infty t^{z-1}\, e^{-t} dt$$

we have

$$\langle\tilde{\psi}|\tilde{\psi}\rangle = \int_0^\infty e^{-2Zr_1/a}\, r_1^2 dr_1 \int_0^\infty e^{-2Zr_2/a}\, r_2^2 dr_2 \int d\Omega_1 d\Omega_2 = \left[4\pi \left(\frac{a}{2Z}\right)^3 \Gamma(3)\right]^2$$

$$= 4(4\pi)^2 \left(\frac{a}{2Z}\right)^6$$

First Approximation

We may split the Hamiltonian into three parts

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

where

$$H_1 = -\frac{\hbar^2}{2mr_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}, \quad H_2 = -\frac{\hbar^2}{2mr_2^2}\frac{\partial}{\partial r_2}\left(r_2^2\frac{\partial}{\partial r_2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$

and

$$H_{12} = \frac{e^2}{4\pi\varepsilon_0 r_{12}},$$

First Approximation

Now,

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial e^{-\alpha r}}{\partial r}\right)=\frac{\partial}{\partial r}(-\alpha r^2 e^{-\alpha r})=\alpha^2 r^2 e^{-\alpha r}-2\alpha r e^{-\alpha r}$$

Hence,

$$\int_0^\infty\left[-\frac{\hbar^2}{2mr^2}e^{-\alpha r}\frac{\partial}{\partial r}\left(r^2\frac{\partial e^{-\alpha r}}{\partial r}\right)-\frac{Ze^2}{4\pi\varepsilon_0 r}e^{-2\alpha r}\right]r^2\,dr$$

$$=\int_0^\infty\left[-\frac{\hbar^2\alpha^2}{2m}+\frac{\hbar^2\alpha}{mr}-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]e^{-2\alpha r}r^2\,dr$$

$$=-\frac{\hbar^2\alpha^2}{2m}\frac{\Gamma(3)}{(2\alpha)^3}+\frac{\hbar^2\alpha}{m}\frac{\Gamma(2)}{(2\alpha)^2}-\frac{Ze^2}{4\pi\varepsilon_0}\frac{\Gamma(2)}{(2\alpha)^2}=-\frac{\hbar^2}{8m\alpha}+\frac{\hbar^2}{4m\alpha}-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{(2\alpha)^2}$$

$$=\frac{\hbar^2}{8m\alpha}-\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{(2\alpha)^2}$$

First Approximation

Then

$\langle\tilde{\psi}|H_1|\tilde{\psi}\rangle$

$$= \int_0^\infty e^{-Zr_1/a}\left[-\frac{\hbar^2}{2mr_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\right]e^{-Zr_1/a}r_1^2\,dr_1\int_0^\infty e^{-2Zr_2/a}\,r_2^2 dr_2\int d\Omega_1 d\Omega_2$$

$$= \left[\frac{\hbar^2}{4m}\frac{a}{2Z} - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{a}{2Z}\right)^2\right]2(4\pi)^2\left(\frac{a}{2Z}\right)^3$$

and

$$\frac{\langle\tilde{\psi}|H_1|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\hbar^2}{2m}\left(\frac{Z}{a}\right)^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{Z}{a}$$

From [Hydrogen 4], we have

$$\frac{e^2}{4\pi\varepsilon_0} = \frac{\hbar^2}{ma}$$

Thus,

$$\frac{\langle\tilde{\psi}|H_1|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\hbar^2}{2m}\left(\frac{Z}{a}\right)^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{Z}{a} = -\frac{Z^2e^2}{8\pi\varepsilon_0 a}$$

First Approximation

Similiarly,

$$\frac{\langle\tilde{\psi}|H_2|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\hbar^2}{2m}\left(\frac{Z}{a}\right)^2 - \frac{Ze^2}{4\pi\varepsilon_0}\frac{Z}{a} = -\frac{Z^2e^2}{8\pi\varepsilon_0 a}$$

What remains to be evaluated is the electron-electron interaction term. To carry this out, we first note that

$$\frac{1}{r_{12}} = \frac{1}{|\vec{r}_2 - \vec{r}_1|} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1r_2\cos\gamma}} = \sum_{l=0}^{\infty}\frac{r_<^l}{r_>^{l+1}}P_l(\cos\gamma)$$

where the Legendre Polynomial can be expressed as sum of spherical harmonics products using the Addition Theorem

$$P_l(\cos\gamma) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}^*(\theta_1,\varphi_1)Y_{lm}(\theta_2,\varphi_2)$$

First Approximation

With these,

$$\langle\tilde{\psi}|H_{12}|\tilde{\psi}\rangle = \int e^{-2Z(r_1+r_2)/a}\frac{e^2}{4\pi\varepsilon_0 r_{12}} r_1^2\, dr_1 r_2^2 dr_2 d\Omega_1 d\Omega_2$$

$$= \frac{e^2}{4\pi\varepsilon_0}\int e^{-2Z(r_1+r_2)/a}\sum_{l=0}^{\infty}\frac{r_<^l}{r_>^{l+1}} r_1^2\, dr_1 r_2^2 dr_2 \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}^*(\theta_1,\varphi_1) Y_{lm}(\theta_2,\varphi_2) d\Omega_1 d\Omega_2$$

The integration over the angles can be carried out through the orthonormalization condition for spherical harmonics

$$\int Y_{lm}^*(\theta,\varphi) Y_{l'm'}(\theta,\varphi)\, d\Omega = \delta_{ll'}\delta_{mm'}$$

and taking note that

$$\sqrt{4\pi} Y_{00} = 1$$

First Approximation

Integrating over the angular part,

$$\sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \int Y_{lm}^*(\theta_1,\varphi_1) Y_{lm}(\theta_2,\varphi_2) d\Omega_1 d\Omega_2$$

$$= \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \int Y_{lm}^*(\theta_1,\varphi_1)\sqrt{4\pi} Y_{00}(\theta_1,\varphi_1) d\Omega_1 \int \sqrt{4\pi} Y_{00}^*(\theta_2,\varphi_2) Y_{lm}(\theta_2,\varphi_2)\, d\Omega_2$$

$$= \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} \frac{(4\pi)^2}{2l+1} \sum_{m=-l}^{l} \int Y_{lm}^*(\theta_1,\varphi_1) Y_{00}(\theta_1,\varphi_1) d\Omega_1 \delta_{l0}\delta_{m0}$$

$$= (4\pi)^2 \frac{1}{r_>} \int Y_{00}^*(\theta_1,\varphi_1) Y_{00}(\theta_1,\varphi_1) d\Omega_1 = \frac{(4\pi)^2}{r_>}$$

Hence,

$$\langle\tilde{\psi}|H_{12}|\tilde{\psi}\rangle = \frac{e^2}{4\pi\varepsilon_0}(4\pi)^2 \int e^{-2Z(r_1+r_2)/a} \frac{1}{r_>} r_1^2 dr_1 r_2^2 dr_2$$

First Approximation

The integral over r_1 can be split into the region where $r_1 < r_2$, and then $r_2 < r_1$

$$\int e^{-2Z(r_1+r_2)/a} \frac{1}{r_>} r_1^2 dr_1 r_2^2 dr_2$$

$$= \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a} \left[\int_0^{r_2} r_1^2 dr_1 \frac{1}{r_2} e^{-2Zr_1/a} + \int_{r_2}^\infty r_1^2 dr_1 \frac{1}{r_1} e^{-2Zr_1/a} \right]$$

With the aid of the following formulas

$$\int x e^{bx} dx = \frac{e^{bx}}{b}\left[x - \frac{1}{b}\right]$$

$$\int x^2 e^{bx} dx = \frac{e^{bx}}{b}\left[x^2 - \frac{2x}{b} + \frac{2}{b^2}\right]$$

First Approximation

We have

$$\int_0^{r_2} r_1^2 dr_1 \frac{1}{r_2} e^{-2Zr_1/a} = \frac{1}{r_2} \frac{e^{-2Zr_1/a}}{(-2Z/a)} \left[r_1^2 - \frac{2r_1}{(-2Z/a)} + \frac{2}{(-2Z/a)^2} \right] \Bigg|_0^{r_2}$$

$$= -\frac{1}{r_2} \frac{a}{2Z} e^{-2Zr_2/a} \left[r_2^2 + \frac{ar_2}{Z} + \frac{a^2}{2Z^2} \right] + \frac{1}{r_2} \frac{a^3}{4Z^3}$$

and

$$\int_{r_2}^{\infty} r_1^2 dr_1 \frac{1}{r_1} e^{-2Zr_1/a} = \frac{e^{-2Zr_1/a}}{(-2Z/a)} \left[r_1 - \frac{1}{(-2Z/a)} \right] \Bigg|_{r_2}^{\infty} = \frac{a}{2Z} e^{-2Zr_2/a} \left[r_2 + \frac{a}{2Z} \right]$$

First Approximation

Hence,

$$\int e^{-2Z(r_1+r_2)/a} \frac{1}{r_>} r_1^2 dr_1 r_2^2 dr_2$$

$$= \int_0^\infty r_2^2 dr_2 e^{-2Zr_2/a} \left[\frac{1}{r_2} \frac{a^3}{4Z^3} - \frac{1}{r_2} \frac{a}{2Z} e^{-\frac{2Zr_2}{a}} \left[r_2^2 + \frac{ar_2}{Z} + \frac{a^2}{2Z^2} \right] + \frac{a}{2Z} e^{-2Zr_2/a} \left[r_2 + \frac{a}{2Z} \right] \right]$$

$$= \frac{a^3}{4Z^3} \int_0^\infty r_2 dr_2 e^{-2Zr_2/a} - \frac{a}{2Z} \int_0^\infty r_2^3 dr_2 e^{-4Zr_2/a} - \frac{a^2}{2Z^2} \int_0^\infty r_2^2 dr_2 e^{-4Zr_2/a}$$

$$- \frac{a^3}{4Z^3} \int_0^\infty r_2 dr_2 e^{-4Zr_2/a} + \frac{a}{2Z} \int_0^\infty r_2^3 dr_2 e^{-4Zr_2/a} + \frac{a^2}{4Z^2} \int_0^\infty r_2^2 dr_2 e^{-4Zr_2/a}$$

The remaining integrals may be evaluated using Gamma functions

$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$$

First Approximation

With

$$\int_0^\infty r_2 dr_2 e^{-2Zr_2/a} = \left(\frac{a}{2Z}\right)^2 \Gamma(2) = \left(\frac{a}{2Z}\right)^2$$

$$\int_0^\infty r_2^2 dr_2 e^{-4Zr_2/a} = \left(\frac{a}{4Z}\right)^3 \Gamma(3) = 2\left(\frac{a}{4Z}\right)^3$$

$$\int_0^\infty r_2 dr_2 e^{-4Zr_2/a} = \left(\frac{a}{4Z}\right)^2 \Gamma(2) = \left(\frac{a}{4Z}\right)^2$$

$\frac{a^3}{4Z^3}$

$-\frac{a^2}{4Z^2}$

$-\frac{a^3}{4Z^3}$

We see that

$$\langle\tilde{\psi}|H_{12}|\tilde{\psi}\rangle = \frac{e^2}{4\pi\varepsilon_0}(4\pi)^2\left[\frac{1}{16}\left(\frac{a}{Z}\right)^5 - \frac{1}{4}\left(\frac{2}{64}\right)\left(\frac{a}{Z}\right)^5 - \frac{1}{4}\left(\frac{1}{16}\right)\left(\frac{a}{Z}\right)^5\right]$$

$$= \frac{e^2}{4\pi\varepsilon_0}(4\pi)^2\left(\frac{a}{Z}\right)^5 \frac{1}{16}\left(1 - \frac{1}{8} - \frac{1}{4}\right) = \frac{5}{4}\frac{e^2}{4\pi\varepsilon_0}(4\pi)^2\left(\frac{a}{2Z}\right)^5$$

First Approximation

and

$$\frac{\langle\tilde{\psi}|H_{12}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{5}{16}\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2Z}{a}\right) = \frac{5Ze^2}{32\pi\varepsilon_0 a}$$

The estimated value of the Helium atom ground state energy is then

$$\bar{H} = \frac{\langle\tilde{\psi}|H|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = \frac{\langle\tilde{\psi}|H_1|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} + \frac{\langle\tilde{\psi}|H_2|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} + \frac{\langle\tilde{\psi}|H_{12}|\tilde{\psi}\rangle}{\langle\tilde{\psi}|\tilde{\psi}\rangle} = -\frac{Z^2e^2}{8\pi\varepsilon_0 a} - \frac{Z^2e^2}{8\pi\varepsilon_0 a} + \frac{5Ze^2}{32\pi\varepsilon_0 a}$$

For $Z = 2$,

$$\bar{H} = -\frac{4e^2}{4\pi\varepsilon_0 a} + \frac{5e^2}{16\pi\varepsilon_0 a} = -\frac{11}{2}\frac{e^2}{8\pi\varepsilon_0 a} = -74.833eV$$

This approximation is 5.24% higher than the experimental value of -78.975 eV