QM HW 1

Problem 1

a) The characteristic quantities we have in this problem are $e, \hbar, m$. Energy can be composed by $\frac{e^2}{[L]}$. So we need to find characteristic length scale η, which is

$$\frac{(\hbar/\eta)^2}{m} = \frac{e^2}{\eta}.$$

By solving this, we find out

$$\eta = \frac{\hbar^2}{me^2}.$$

So the ground state energy by dimensional analysis (and uncertainty principle) is

$$\epsilon_0 = \frac{me^4}{\hbar^2}.$$

b) This is a good trial function.

This trial function is exact if we don't have the last term in Hamiltonian. However the last term is some kind of screening effect which makes the potential energy of the system slightly higher. Effectively, the potential well becomes steeper which makes the wave function drops slower as distance becomes larger. The physics behind this is that electrons screen each other from feeling the electric potential generated by the necleus.

The physical meaning of Z is the effective charge of the nucleus.

c) To use variational method, we need

$$\left\langle \hat{H} \right\rangle = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi \mid \psi \rangle}$$

The expectation value of first electron's momentum squared is

$$\begin{aligned}
\langle \psi | \hat{p}_1^2 | \psi \rangle &= (\langle \psi | \hat{p}_1^\dagger)(\hat{p}_1 | \psi \rangle) \\
&= \int |-\mathrm{i}\hbar\psi|^2 \,\mathrm{d}^3 x_1 \,\mathrm{d}^3 x_2 \\
&= \frac{\hbar^2 Z^2}{a_0^2} \int |\psi|^2 \,\mathrm{d}^3 x_1 \,\mathrm{d}^3 x_2 \\
&= \frac{\hbar^2 Z^2}{a_0^2} I^2
\end{aligned}$$

in which i used

$$|-\mathrm{i}\hbar\psi|^2 = \hbar^2 \frac{Z^2}{a_0^2} |\psi|^2$$

\$I\$ is defined as $I = \int e^{-2Zr_2/a_0} \mathrm{d}^3 x_2 = 4\pi \int e^{-2Zr_2/a_0} r^2 \,\mathrm{d}r = \frac{\pi a_0^3}{Z^3}$

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from sympy import *
from sympy import init_printing
a,x,Z = symbols('a,x,Z')


integrate(exp(-2*Z*x/a),x)
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$$\begin{cases} x & \text{for}: 2Z = 0 \\ -\frac{a}{2Z} e^{-\frac{2Z}{a} x} & \text{otherwise} \end{cases}$$

Then the total kinetic energy term is twice of the kinetic energy of one electron.

$$\left\langle \frac{\hat{p}_1^2 + \hat{p}_2^2}{2m} \right\rangle = \frac{\hbar^2 Z^2}{a_0^2 m} I^2$$

The avarage of the third term in Hamiltonian is

$$\begin{aligned} \left\langle \frac{2e^2}{r_1} \right\rangle &= 2e^2 \int \frac{1}{r_1} |\psi|^2 \mathrm{d}^3 x_1 \, \mathrm{d}^3 x_2 \\ &= 2e^2 \int e^{-2Z(r_1+r_2)/a_0} 4\pi r_1 \, \mathrm{d}r_1 \, \mathrm{d}^3 x_2 \\ &= 8\pi e^2 \int e^{-2Zr_2/a_0} \mathrm{d}^3 x_2 \int e^{-2Zr_1/a_0} r_1 \, \mathrm{d}r_1 \\ &= 8\pi e^2 I \int e^{-2Zr_1/a_0} r_1 \, \mathrm{d}r_1 \end{aligned}$$

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integrate(exp(-2*Z*x/a)*x,x)
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$$\begin{cases} \frac{x^2}{2} & \text{for}: 4Z^3 = 0 \\ \frac{e^{-\frac{2Z}{a} x}}{4Z^3} \left(-2Z^2 a x - Z a^2\right) & \text{otherwise} \end{cases}$$

So we have

$$\begin{aligned} \left\langle \frac{2e^2}{r_1} \right\rangle &= 8\pi e^2 I \int e^{-2Zr_1/a_0} r_1 \, \mathrm{d}r_1 \\ &= 2\pi e^2 I \frac{a^2}{Z^2} \end{aligned}$$

The average of last term in Hamiltonian is

$$
\begin{aligned}
\left\langle \frac{e^2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\beta}} \right\rangle &= \int\int |\psi|^2 \frac{e^2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\beta}} \mathrm{d}^3x_1\,\mathrm{d}^3x_2 \\
&= -e^2 \int\int e^{-2Z(r_1+r_2)/a_0} \frac{1}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\beta}} \mathrm{d}^3x_2\, r_1^2 \mathrm{d}r_1 \mathrm{d}\cos\beta \mathrm{d}\phi \\
&= -2\pi e^2 \int\int e^{-2Z(r_1+r_2)/a_0} \left. \frac{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\beta}}{-r_1r_2} \right|_{\beta=0}^{\beta=\pi} \mathrm{d}^3x_2\, r_1^2 \mathrm{d}r_1 \\
&= -2\pi e^2 \int\int e^{-2Z(r_1+r_2)/a_0} \frac{-r_1-r_2+|r_1-r_2|}{r_1r_2} \mathrm{d}^3x_2\, r_1^2 \mathrm{d}r_1 \\
&= 8\pi^2 e^2 \int\int e^{-2Z(r_1+r_2)/a_0} \frac{-r_1-r_2+|r_1-r_2|}{r_1r_2} r_2^2 \mathrm{d}r_2\, r_1^2 \mathrm{d}r_1 \\
&= 16\pi^2 e^2 \int \mathrm{d}r_1 \left(\int_0^{r_1} e^{-2Z(r_1+r_2)/a_0} r_2^2 r_1 \mathrm{d}r_2 \right. \\
&\quad \left. + \int_{r_1}^{\infty} e^{-2Z(r_1+r_2)/a_0} r_1^2 r_2 \mathrm{d}r_2 \right)
\end{aligned}
$$

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integrate(exp(-2*Z*x/a)*(x**2),x)
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$$
\begin{cases} \frac{x^3}{3} & \text{for}: 4Z^6 = 0 \\ \frac{e^{-\frac{2Z}{a}x}}{4Z^6}\left(-2Z^5 ax^2 - 2Z^4 a^2 x - Z^3 a^3\right) & \text{otherwise} \end{cases}
$$

Now we have

$$
\left\langle \frac{e^2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\beta}} \right\rangle = 16\pi^2 e^2 \int \mathrm{d}r_1 e^{-2Zr_1/a_0} \left(\frac{ar_1\left(a^2 - e^{-\frac{2r_1Z}{a}}\left(a^2+2ar_1Z+2r_1^2Z^2\right)\right)}{4Z^3} + \frac{ar_1^2 e^{-\frac{2r_1Z}{a}}(a+2r_1Z)}{4Z^2} \right)
$$

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integrate(exp(-4*Z*x/a)*(2*Z*x**2+a*x),x)
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$$
\begin{cases} \frac{2Z}{3}x^3 + \frac{ax^2}{2} & \text{for}: 8Z^3 = 0 \\ \frac{e^{-\frac{4Z}{a}x}}{8Z^3}\left(-4Z^3 ax^2 - 4Z^2 a^2 x - Za^3\right) & \text{otherwise} \end{cases}
$$

$$
\left\langle \frac{e^2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\beta}} \right\rangle = \frac{5\pi^2 e^2}{8} \frac{a^5}{Z^5}
$$

With all these results, we can write down the expectation value of Hamiltonian given this trial wave function,

$$
\begin{aligned}
\langle \epsilon \rangle &= \frac{1}{I^2}\left(\frac{\hbar^2 Z^2}{ma^2} I^2 - 4\pi e^2 I \frac{a^2}{Z^2} + \frac{5\pi^2 e^2}{8}\frac{a^5}{Z^5}\right) \\
&= \frac{\hbar^2}{ma^2/Z^2} - \frac{27}{8}\frac{e^2}{a/Z}
\end{aligned}
$$

Now we can do variation on it.

$$
\frac{\mathrm{d}\langle \epsilon \rangle}{\mathrm{d}Z} = 2\frac{\hbar^2}{ma^2} Z - \frac{27}{8}\frac{e^2}{a}
$$

Set $\langle \epsilon \rangle = 0$, we get

$$
Z = \frac{27}{16}\frac{me^2 a}{\hbar^2}
$$

Insert this result into energy expectation value, we get

$$
\epsilon_0 = -\frac{me^4}{\hbar^2}\left(\frac{27}{16}\right)^2
$$

Ground state energy should be no larger than this because the trial wave function consists of ground state and possibly higher energy level states.