PHY 491 – HW2- Solutions

Problem 1

1. Calculate the ground state energy of a hydrogen atom using the variational principle. Assume that the variational form for the wave function is a Gaussian of the form $Ne^{-\left(\frac{r}{\alpha}\right)^2}$, where N is the normalization constant and α is a variational parameter. How does this variational energy compare with the exact ground state energy?

We will need these integrals:

$$\int_0^\infty xe^{-x^2}\,dx = \frac{1}{2};\ \int_0^\infty x^2e^{-x^2}\,dx = \frac{\sqrt{\pi}}{4};\ \int_0^\infty x^4e^{-x^2}\,dx = \frac{3\sqrt{\pi}}{8}$$

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

$$\psi = Ne^{-\left(\frac{r}{\alpha}\right)^2};\qquad \langle\psi|\psi\rangle = 4\pi N^2\int_0^\infty e^{-2\left(\frac{r}{\alpha}\right)^2}r^2dr$$

Change variable: $x = \sqrt{2}\frac{r}{\alpha}$

$$\langle\psi|\psi\rangle = 4\pi N^2\left(\frac{\alpha}{\sqrt{2}}\right)^3\int_0^\infty e^{-x^2}x^2dx = 4\pi N^2\frac{\alpha^3}{8\sqrt{2}}\sqrt{\pi}$$

$$\langle\psi|T|\psi\rangle = -\frac{1}{2}\int\psi^*\nabla^2\psi\,d\vec{r} = -\frac{1}{2}4\pi N^2\int_0^\infty r^2\,dr\,e^{-\left(\frac{r}{\alpha}\right)^2}\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\right]e^{-\left(\frac{r}{\alpha}\right)^2} = \frac{4\pi}{\alpha^2}N^2\int_0^\infty\left(3r^2 - 2r^4/\alpha^2\right.$$

Again change variable to x:

$$= \frac{12\pi N^2}{\alpha^2}\left(\frac{\alpha}{\sqrt{2}}\right)^3\int_0^\infty x^2e^{-x^2}dx - \frac{8\pi N^2}{\alpha^4}\left(\frac{\alpha}{\sqrt{2}}\right)^5\int_0^\infty x^4e^{-x^2}dx = 4\pi N^2\alpha\frac{6\sqrt{\pi}}{32\sqrt{2}}$$

Thus we have

$$\frac{\langle\psi|T|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{3}{2\alpha^2}$$

Similarly

$$\langle\psi|V|\psi\rangle = -4\pi N^2\int_0^\infty r^2e^{-2\left(\frac{r}{\alpha}\right)^2}\frac{1}{r}dr = -4\pi N^2\left(\frac{\alpha}{\sqrt{2}}\right)^2\int_0^\infty xe^{-x^2}\,dx = -4\pi N^2\left(\frac{\alpha^2}{4}\right)$$

Therefore

$$\frac{\langle\psi|V|\psi\rangle}{\langle\psi|\psi\rangle} = -\frac{1}{\alpha}\sqrt{\frac{8}{\pi}}$$

Putting all together the trial energy (variational energy) is given by

$$E(\alpha) = \frac{3}{2\alpha^2} - \sqrt{\frac{8}{\pi}}\frac{1}{\alpha}$$

Minimizing the trial energy with respect to the variable α , we get

$$\alpha_{min} = 3\sqrt{\frac{\pi}{8}}; and$$

$$E_{min} = \frac{4}{3\pi} - \frac{8}{3\pi} = -\frac{4}{3\pi} = -0.4244 Hartree = -11.54\ eV$$

This is about 2 eV higher than the exact energy. Not bad!

Problem 2

$$2\langle T\rangle = \langle \vec{r}.\nabla V\rangle = \left\langle r\frac{e^2}{r^2}\right\rangle = -\langle V\rangle$$

$$\langle T\rangle_n + \langle V\rangle_n = +\frac{1}{2}\langle V\rangle_n = E_n;\ for\ the\ n^{th}\ energy\ level$$

$$-\frac{1}{2}\left\langle\frac{e^2}{r}\right\rangle_n = -\frac{me^4}{2\hbar^2 n^2}$$

$$\left\langle\frac{1}{r}\right\rangle_n = \frac{me^2}{\hbar^2 n^2} = \frac{1}{an^2};\ a = \frac{\hbar^2}{me^2}$$

Problem 3

$$\left\langle\psi_{nlm}\left|\frac{1}{r}\right|\psi_{nlm}\right\rangle = \frac{1}{n^2 a}$$

I worked this out in the class using $e^2 = \lambda$ as a parameter and Feynmann-Hellman Theorem. Please check.

$$\left\langle\psi_{nlm}\left|\frac{1}{r^2}\right|\psi_{nlm}\right\rangle = \frac{1}{(l+\frac{1}{2})n^3 a^2}$$

After separating the radial and angular parts, the effective Hamiltonian for the hydrogen atom can be written as

$$H = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} - \frac{l(l+1)}{r^2}\right] - \frac{e^2}{r} \equiv H(l)$$

Hellman Feynman theorem gives

$$\left\langle \psi_{nl} \left| \frac{\partial H(l)}{\partial l} \right| \psi_{nl} \right\rangle = \frac{\partial E_{nl}}{\partial l}$$

$$\frac{\hbar^2}{2m}(2l+1)\left\langle \frac{1}{r^2} \right\rangle_{nl} = -\frac{\partial}{\partial l}\left[\frac{me^4}{2\hbar^2 n^2}\right] = -\frac{\partial}{\partial l}\left[\frac{me^4}{2\hbar^2 (j_{\max} + l + 1)^2}\right]$$

$$= \left[\frac{me^4}{\hbar^2 (j_{\max} + l + 1)^3}\right] = \frac{me^4}{\hbar^2 n^3}$$

$$\left\langle \frac{1}{r^2} \right\rangle_{nl} = \frac{1}{(l+1/2)n^3 a^2}$$