PHY 491: Atomic, Molecular, and Condensed Matter Physics
Michigan State University, Fall Semester 2012

Solve by: Wednesday, September 12, 2012

Homework 2 – Solution

2.1. Calculate the ground state energy of a hydrogen atom using the variational principle. Assume that the variational 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?

You will need these integrals:

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

Solution:

$$E(\alpha) = \frac{<\psi(\alpha)|H|\psi(\alpha)>}{<\psi(\alpha)|\psi(\alpha)>} = \text{ min.}$$

Use

$$\psi = Ne^{-\left(\frac{r}{\alpha}\right)^2} \quad \text{and} \quad <\psi|\psi>= 4\pi N^2 \int_0^\infty e^{-2\left(\frac{r}{\alpha}\right)^2} r^2dr \; .$$

Change variable to $x = \sqrt{2}\frac{r}{\alpha}$ to get for the denominator

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

In the numerator, we consider the kinetic and the potential part separately. For the kinetic part, we get

$$\begin{aligned} <\psi(\alpha)|T|\psi(\alpha)> &= -\frac{1}{2}\int \psi^* \nabla^2 \psi d\vec{r} \\ &= -\frac{1}{2}4\pi N^2 \int_0^\infty r^2dre^{-\left(\frac{r}{\alpha}\right)^2}\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\right]e^{-\left(\frac{r}{\alpha}\right)^2} \\ &= -\frac{4\pi}{\alpha^2}N^2 \int_0^\infty \left(3r^2 - \frac{2r^4}{\alpha^2}\right)e^{-2\left(\frac{r}{\alpha}\right)^2}dr \; . \end{aligned}$$

Change the variable again to $x = \sqrt{2}\frac{r}{\alpha}$ to obtain

$$\begin{aligned} <\psi(\alpha)|T|\psi(\alpha)> &= \frac{12\pi N^2}{\alpha^2}\left(\frac{\alpha}{\sqrt{2}}\right)^3 \int_0^\infty x^2e^{-x^2}dx - \frac{8\pi N^2}{\alpha^4}\left(\frac{\alpha}{\sqrt{2}}\right)^5 \int_0^\infty x^4e^{-x^2}dx \\ &= 4\pi N^2\alpha\frac{6\sqrt{\pi}}{32\sqrt{2}} \; . \end{aligned}$$

Consequently,

$$\frac{<\psi(\alpha)|T|\psi(\alpha)>}{<\psi(\alpha)|\psi(\alpha)>} = \frac{3}{2\alpha^2} \; .$$

Similarly,

$$\begin{aligned} < \psi(\alpha)|V|\psi(\alpha) > &= -4\pi N^2 \int_0^\infty r^2 e^{-2\left(\frac{r}{\alpha}\right)^2} \frac{1}{r} dr \\ &= -4\pi N^2 \left(\frac{\alpha}{\sqrt{2}}\right)^2 \int_0^\infty x e^{-x^2} dx \\ &= -4\pi N^2 \left(\frac{\alpha^2}{4}\right) . \end{aligned}$$

Thus,

$$\frac{< \psi(\alpha)|V|\psi(\alpha) >}{< \psi(\alpha)|\psi(\alpha) >} = -\frac{1}{\alpha}\sqrt{\frac{8}{\pi}} .$$

Combining all our results, the trial energy (variational energy) is

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

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

$$a_{min} = 3\sqrt{\frac{\pi}{8}}$$

and

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

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

2.2. Use the virial theorem which states that $2 < T > = < \vec{r} \cdot \vec{\nabla} V >$and show that for the hydrogen atom

$$< \psi_{nlm}|\frac{1}{r}|\psi_{nlm} > = \frac{1}{n^2 a_B} .$$

Solution:

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

For the n^{th} energy level,

$$\begin{aligned} E_n &= < T >_n + < V >_n = +\frac{1}{2} < V >_n \\ &= -\frac{1}{2}\left\langle \frac{e^2}{r} \right\rangle_n = -\frac{me^4}{2\hbar^2 n^2} . \end{aligned}$$

Substituting

$$a_B = \frac{\hbar^2}{me^2}$$

we get

$$< \psi_{nlm}|\frac{1}{r}|\psi_{nlm} > = \left\langle \frac{1}{r} \right\rangle_n = \frac{1}{n^2 a_B} .$$

2.3. Use the Hellmann-Feynman theorem, which states that

$$\frac{\partial E_n}{\partial \lambda} =< \psi_n|\frac{\partial H}{\partial \lambda}|\psi_n >$$

to show that for a hydrogen atom

$$< \psi_{nlm}|\frac{1}{r}|\psi_{nlm} >= \frac{1}{n^2 a_B} \; ,$$
$$< \psi_{nlm}|\frac{1}{r^2}|\psi_{nlm} >= \frac{1}{(l+\frac{1}{2})n^3 a_B^2} \; .$$

Solution:

$$< \psi_{nlm}|\frac{1}{r}|\psi_{nlm} >= \frac{1}{n^2 a_B}$$

has been worked out in Class using the Hellmann-Feynman theorem and $e^2 = \lambda$ as a parameter. So we only need to prove

$$< \psi_{nlm}|\frac{1}{r^2}|\psi_{nlm} >= \frac{1}{(l+\frac{1}{2})n^3 a_B^2} \; .$$

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

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

The Hellmann-Feynman theorem gives

$$\begin{aligned}
< \psi_{nl}|\frac{\partial H(l)}{\partial l}|\psi_{nl} > &= \frac{\partial E_{nl}}{\partial l} \; , \\
\frac{\hbar^2}{2m}(2l+1)\left\langle\frac{1}{r^2}\right\rangle_{nl} &= -\frac{\partial}{\partial l}\left[\frac{me^4}{2\hbar^2 n^2}\right] = -\frac{\partial}{\partial l}\left[\frac{me^4}{2\hbar^2(j_{max}+l+1)^2}\right] \\
&= \left[\frac{me^4}{\hbar^2(j_{max}+l+1)^3}\right] = \frac{me^4}{\hbar^2 n^3} \; .
\end{aligned}$$

$$< \psi_{nlm}|\frac{1}{r^2}|\psi_{nlm} >= \left\langle\frac{1}{r^2}\right\rangle_{nl} = \frac{1}{(l+\frac{1}{2})n^3 a_B^2} \; .$$

2.4. Using the first order perturbation results for $E_{mv}^{(1)}$, where mv denotes mass-velocity, and for $E_{so}^{(1)}$, where so denotes spin-orbit, show that

$$E_{mv}^{(1)} + E_{so}^{(1)} = E_{fs}^{(1)} = \frac{(E_n^0)^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) \; ,$$

where fs denotes fine structure and j is the total angular momentum containing orbital angular momentum plus spin.

Solution:

$$
\begin{aligned}
E^{(1)}_{mv} &= -\frac{(E^0_n)^2}{2mc^2}\left[\frac{4n}{l+\frac{1}{2}} - 3\right] \\
E^{(1)}_{so} &= -\frac{(E^0_n)^2}{mc^2} n \left[\frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+\frac{1}{2})(l+1)}\right] .
\end{aligned}
$$

Adding the two expressions we obtain $E^{(1)}_{fs}$. Since $s = 1/2$, we have $j = l + 1/2$ or $j = l - 1/2$. This means that $l = j - 1/2$ or $l = j + 1/2$. Eliminate l from the above equation for each value of l. Do the algebra and you will get the answer in terms of j.
