Quantum Mechanics 2
Spring 2019

Homework 3 Problems

1. Griffiths 8.6

   (a) Use the variational principle to prove that the first order non-degenerate perturbation theory always overestimates the ground state energy.

   Solution: First order perturbation theory says that the ground state energy is approximately equal to:

   $$\langle \psi_0^{(0)} | H_0 + H' | \psi_0^{(0)} \rangle \tag{1}$$

   However, we know that for any state $|\psi\rangle$ whatsoever, $E_g \leq \langle \psi | H | \psi \rangle$. Furthermore, if $\psi_0^{\text{true}} \neq \psi_0^{(0)}$, which it generally does not, then the inequality is strict.

   (b) Based on part (a), you would expect that the second-order correction to the ground state is always negative. Confirm that this is indeed the case by examining equation:

   $$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} \tag{2}$$

   Solution: Since $E_0^{(0)}$ is the ground state of the unperturbed system, it holds that $E_0^{(0)} < E_m^{(0)}, \forall m \neq 0$ (a.k.a $E_0^{(0)} - E_m^{(0)} < 0$). It follows immediately from this that the second order correction (2) is negative for $n = 0$.

2. (Griffiths 8.5) Using a trial function of your own devising, obtain an upper-bound on the ground state energy for the potential:

   $$V(x) = \{ \begin{array}{cc} mgx & 0 < x \\ \infty & x \leq 0 \end{array} \tag{3}$$

   and compare it with the exact answer $E_g = 2.338(\frac{mg^2\hbar^2}{2})^{\frac{1}{3}}$.

Solution: For a trial function, I will choose a Gaussian times a linear function. It is important that the trial wavefunction be zero at $x = 0$ as demanded by the potential being infinite at that point and beyond. To make my life easier, I would first like to extract the relevant length scale for the problem using dimensional analysis so that I can make my variational parameter dimensionless. The only dimensionful parameters of the problem are $\hbar, m,$ and g. The quantity with units of length I can construct out of these parameters is:

$$l = \Big(\frac{\hbar^2}{m^2 g}\Big)^{\frac{1}{3}} \tag{4}$$

Therefore, I choose my trial wavefunction to be:

$$\psi_\alpha(x) = Axe^{-(\frac{x}{\alpha l})^2} \tag{5}$$

Needless to say, because of the potential, the wavefunction is zero for $x < 0$. We determine A by properly normalizing the wavefunction:

$$\int_0^\infty \psi_\alpha(x)^2 = 1 \Rightarrow A = \Big(\frac{128}{\pi}\Big)^{\frac{1}{4}}(\alpha l)^{-\frac{3}{2}} \tag{6}$$

Next, we calculate the expectation value of the energy for our trial wavefunction:

$$\langle\psi_\alpha|H|\psi_\alpha\rangle = \int_0^\infty \psi_\alpha(x)\Big(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + mgx\Big)\psi_\alpha(x) \tag{7}$$

First, we can notice that taking the second derivative of our wavefunction, we get:

$$\psi_\alpha^{''}(x) = \frac{2}{(\alpha l)^2}\Big[2\Big(\frac{x}{\alpha l}\Big)^2 - 3\Big]\psi_\alpha \tag{8}$$

Therefore, our energy is:

$$E_\alpha = \int_0^\infty \Big(-\frac{\hbar^2}{m} \frac{1}{(\alpha l)^2} \Big[2\Big(\frac{x}{\alpha l}\Big)^2 - 3 \Big] + mgx \Big) \psi_\alpha(x)^2 \tag{9}$$

We need to compute 3 integrals: $\int_0^\infty \frac{x^2}{(\alpha l)^2} \psi_\alpha^2 dx$, $\int_0^\infty x \psi_\alpha^2 dx$, and $\psi_\alpha^2 dx$. The last one is just 1 because we already normalized our wavefunction. Therefore, let us compute the first two. The first one is:

$$\begin{aligned} \int_0^\infty \frac{x^2}{(\alpha l)^2} \psi_\alpha^2 dx &= \int_0^\infty \frac{x^4}{(\alpha l)^2} A^2 e^{-2(\frac{x}{\alpha l})^2} dx \\ &= \frac{3}{4} \int_0^\infty A^2 x^2 e^{-2(\frac{x}{\alpha l})^2} = \frac{3}{4} \end{aligned} \tag{10}$$

Here, we used the fact integration by parts and the normalization of ψ_α. The second integral is:

$$\begin{aligned} \int_0^\infty x \psi_\alpha^2 dx &= \int_0^\infty x^3 A^2 e^{-2(\frac{x}{\alpha l})^2} dx \\ &= A^2 \frac{(\alpha l)^4}{8} = \sqrt{\frac{2}{\pi}} \alpha l \end{aligned} \tag{11}$$

Combining these results, we get that:

$$E_\alpha = \frac{3\hbar^2}{2ml^2} \frac{1}{\alpha^2} + mgl \sqrt{\frac{2}{\pi}} \alpha \tag{12}$$

Now, we would like to find the minimum value of E_α with respect to α. To do so, we differentiate with respect to α and set the result to zero:

$$\frac{dE_\alpha}{d\alpha} = 0 \Rightarrow \alpha = \Big(\frac{9\pi}{2}\Big)^{\frac{1}{6}} \tag{13}$$

Plugging this result back into E_α, we get as our 'prediction' for the ground state energy:

$$E_\alpha = \left(\frac{81}{2\pi}\right)^{\frac{1}{3}} (\frac{mg^2\hbar^2}{2})^{\frac{1}{3}} \approx 2.345(\frac{mg^2\hbar^2}{2})^{\frac{1}{3}} \tag{14}$$

That is remarkably close to the true ground state energy!

3. Calculate the ground state of a hydrogen atom using the variational principle. Assume that the variational wavefunction is a Gaussian of the form $R(r) = Ae^{-(\frac{r}{\alpha})^2}$ where A is for normalization and α is a variational parameter. How does this variational energy compare with the exact ground state energy?

Solution: First, we must properly normalize the wave function:

$$\int_0^\infty 4\pi r^2 R(r)^2 dr = 1 \Rightarrow A = \left(\frac{8}{\pi^3}\right)^{\frac{1}{4}} \alpha^{-\frac{3}{2}} \tag{15}$$

Next, we calculate E_α. Recall that the Hamiltonian for hydrogen is:

$$-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{16}$$

In spherical coordinates, ignoring the angular parts of ∇^2 since our trial function is only dependent on r, we have:

$$HR(r) = \Big[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\Big(r^2\frac{d}{dr}\Big) - \frac{e^2}{4\pi\epsilon_0 r}\Big]R(r) \tag{17}$$

To simplify our life a bit, we can define a new wave function $u(r) = rR(r)$. In term of this function, we have:

$$HR(r) = \frac{1}{r}\Big[-\frac{\hbar^2}{2m}u'' - \frac{e^2}{4\pi\epsilon_0 r}u\Big] \tag{18}$$

Here ' denotes differentiation with respect to r. Therefore, we have:

$$\int_0^\infty 4\pi r^2 R(r) H R(r) dr = 4\pi \int_0^\infty -\frac{\hbar^2}{2m} u u'' - \frac{e^2}{4\pi\epsilon_0 r} u^2 dr \tag{19}$$

To calculate this integral we first need to know u'':

$$u'' = \frac{2}{\alpha^2}\Big(2(\frac{r}{\alpha})^2 - 3\Big)u \tag{20}$$

Plugging this into (19), we get:

$$E_\alpha = 4\pi \int_0^\infty \Big[-\frac{\hbar^2}{2m}\frac{2}{\alpha^2}\Big(2(\frac{r}{\alpha})^2 - 3\Big) - \frac{e^2}{4\pi\epsilon_0 r}\Big] u^2 dr \tag{21}$$

There are three distinct integral showing up in this expression, namely: $\int_0^\infty 4\pi r^2 u^2 dr$, $\int_0^\infty 4\pi u^2 dr$, and $\int_0^\infty \frac{4\pi}{r} u^2 dr$. The second one just gives 1 because we have normalized our wavefunctions. Therefore, we need only compute the first and third. For the first, we have:

$$\begin{aligned}
\int_0^\infty 4\pi r^2 u^2 dr &= \int_0^\infty 4\pi r^4 A^2 e^{-2(\frac{r}{\alpha})^2} dr \\
&= \int_0^\infty \frac{3\alpha^2}{4} r^2 4\pi A^2 e^{-2(\frac{r}{\alpha})^2} dr \\
&= \int_0^\infty \frac{3\alpha^2}{4} 4\pi u^2 dr \\
&= \frac{3\alpha^2}{4}
\end{aligned} \tag{22}$$

In the second line, we integrated by parts and in the fourth line, we used the normalization condition. Now the other integral we need to compute is:

$$\begin{aligned}
\int_0^\infty \frac{4\pi}{r} u^2 dr &= \int_0^\infty 4\pi r A^2 e^{-2(\frac{r}{\alpha})^2} dr \\
&= 4\pi A^2 \frac{\alpha^2}{4} e^{-2(\frac{r}{\alpha})^2}\Big|_\infty^0 \\
&= \Big(\frac{8}{\pi}\Big)^{\frac{1}{2}} \frac{1}{\alpha}
\end{aligned} \tag{23}$$

Now using these facts, we can compute our expectation value for the energy (21):

$$E_\alpha = \frac{3\hbar^2}{2m\alpha^2} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{8}{\pi}\right)^{\frac{1}{2}}\frac{1}{\alpha} \tag{24}$$

Differentiating with respect to α and setting the result to zero, we get:

$$\alpha = \frac{\hbar^2 4\pi\epsilon_0}{me^2}3\left(\frac{\pi}{8}\right)^{\frac{1}{2}} = \frac{3}{2}\sqrt{\frac{\pi}{2}}a_0 \tag{25}$$

Here, a_0 is the Bohr radius. Plugging this back into E_α, we get:

$$E_\alpha = -\frac{8}{3\pi}\frac{\hbar^2}{2ma_0^2} = \frac{8}{3\pi}E_0 \approx 0.83E_0 \tag{26}$$

where $E_0 = -13.6$ eV is the true ground state energy of hydrogen. Thus, our upperbound for the ground state energy is about -11.54 eV.

4. (Griffiths 8.7) Using $E_g = -79$ eV for the ground state energy of helium, calculate the ionization energy (the energy required to remove just one electron). Hint: First calculate the ground state energy of the helium ion, He^+, with a single electron orbiting the nucleus; then subtract the two energies.

Solution: I guess this problem wanted us to use the variational principle but it is quite unnecessary. The Hamiltonian for the helium ion is obtained by simply making the replacement $e^2 \to 2e^2$. Thus, in every subsequent expression for some measurable quantity of the hydrogen atom where e^2 appears, just replace it with $2e^2$ and you will get the corresponding quantity for the helium ion. In particular, the ground state energy of hydrogen is:

$$E_H = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 = -13.6 \text{ eV} \tag{27}$$

Therefore, the ground state energy of the helium ion will be:

$$E_{He^+} = 4(-13.6 \text{ eV}) = -54.4 \text{ eV} \tag{28}$$

Thus, taking the difference between the ground state energies of helium and the helium ion, we obtain the ionization energy:

$$E_{\text{ionize}} = 24.6 \text{ eV} \tag{29}$$

which is basically the right value.

5. (HW3 Bonus) Why could we use a non-degenerate perturbation theory for the hydrogen atom?

   Answer: The relativistic corrections commute with angular momentum and z-component of angular momentum. Therefore, even though different angular moment eigenstates for the same principle quantum number are degenerate, the "good eigenstates" cannot mix states of different angular quantum numbers (see Griffiths). Therefore, the eigenstates of the non-relativistic approximation are already 'good' eigenstates and we can proceed with non-degenerate perturbation theory.