Phys 402: Applications of Quantum Mechanics

Homework VI (Total 3 problems; due 930am, Thursday, March 10, 2016]
[To receive full credits, please show all necessary steps that lead to your answers.]

1) Prob. 7.3 (Page 298, textbook.)

2) Prob. 7.4 (This is for an excited state. practically variational method rarely used for such a purpose.)

3) Prob. 7.5

4) Use the variational method to obtain the hydrogen atom ground state. Compare with the exact expression on Page 149, Eq. [4.69] and the expression for Bohn radius Eq. [4.72]. Discuss similarities and differences. Hint: You can use a simple exponential function as the trial wave function Instead of the Yukawa form.

5) Further check the ratio between the kinetic energy and potential energy at the variational minimum you have found in 4). Does it satisfy the general relation between the kinetic energy and potential energy implied by Feynman-Hellmann theorem in Prob. 6.32, page 288 ?

Kinetic Energy: $\langle T\rangle = -\frac{\hbar^2}{2m}|A|^2\int_{-\infty}^{\infty}\frac{1}{(x^2+b^2)}\frac{d^2}{dx^2}\left(\frac{1}{(x^2+b^2)}\right)dx.$

But $\frac{d^2}{dx^2}\left(\frac{1}{(x^2+b^2)}\right) = \frac{d}{dx}\left(\frac{-2x}{(x^2+b^2)^2}\right) = \frac{-2}{(x^2+b^2)^2} + 2x\frac{4x}{(x^2+b^2)^3} = \frac{2(3x^2-b^2)}{(x^2+b^2)^3}$, so

$$\langle T\rangle = -\frac{\hbar^2}{2m}\frac{2b^3}{\pi}\int_0^{\infty}\frac{(3x^2-b^2)}{(x^2+b^2)^4}dx = -\frac{4\hbar^2b^3}{\pi m}\left[3\int_0^{\infty}\frac{1}{(x^2+b^2)^3}dx - 4b^2\int_0^{\infty}\frac{1}{(x^2+b^2)^4}dx\right]$$
$$= -\frac{4\hbar^2b^3}{\pi m}\left[3\frac{3\pi}{16b^5} - 4b^2\frac{5\pi}{32b^7}\right] = \frac{\hbar^2}{4mb^2}.$$

Potential Energy: $\langle V\rangle = \frac{1}{2}m\omega^2|A|^2\,2\int_0^{\infty}\frac{x^2}{(x^2+b^2)^2}dx = m\omega^2\frac{2b^3}{\pi}\frac{\pi}{4b} = \frac{1}{2}m\omega^2b^2.$

$$\langle H\rangle = \frac{\hbar^2}{4mb^2} + \frac{1}{2}m\omega^2b^2. \quad \frac{\partial\langle H\rangle}{\partial b} = -\frac{\hbar^2}{2mb^3} + m\omega^2 b = 0 \Longrightarrow b^4 = \frac{\hbar^2}{2m^2\omega^2} \Longrightarrow b^2 = \frac{1}{\sqrt{2}}\frac{\hbar}{m\omega}.$$

$$\langle H\rangle_{\min} = \frac{\hbar^2}{4m}\frac{\sqrt{2}m\omega}{\hbar} + \frac{1}{2}m\omega^2\frac{1}{\sqrt{2}}\frac{\hbar}{m\omega} = \hbar\omega\left(\frac{\sqrt{2}}{4} + \frac{1}{2\sqrt{2}}\right) = \boxed{\frac{\sqrt{2}}{2}\hbar\omega} = 0.707\,\hbar\omega > \frac{1}{2}\hbar\omega. \ \checkmark$$

Problem 7.3

$$\psi(x) = \begin{cases} A(x+a/2), & (-a/2 < x < 0), \\ A(a/2-x), & (0 < x < a/2), \\ 0, & (\text{otherwise}). \end{cases}$$

$$1 = |A|^2 2\int_0^{a/2}\left(\frac{a}{2}-x\right)^2 dx = -2|A|^2\frac{1}{3}\left(\frac{a}{2}-x\right)^3\Big|_0^{a/2} = \frac{2}{3}|A|^2\left(\frac{a}{3}\right)^3 = \frac{a^3}{12}|A|^2; \quad A = \sqrt{\frac{12}{a^3}} \quad (\text{as before}).$$

$$\frac{d\psi}{dx} = \begin{cases} A, & (-a/2 < x < 0), \\ -A, & (0 < x < a/2), \\ 0, & (\text{otherwise}). \end{cases} \qquad \frac{d^2\psi}{dx^2} = A\delta\left(x+\frac{a}{2}\right) - 2A\delta(x) + A\delta\left(x-\frac{a}{2}\right).$$

$$\langle T\rangle = -\frac{\hbar^2}{2m}\int\psi\left[A\delta\left(x+\frac{a}{2}\right) - 2A\delta(x) + A\delta\left(x-\frac{a}{2}\right)\right]dx = \frac{\hbar^2}{2m}2A\psi(0) = \frac{\hbar^2}{m}A^2\frac{a}{2}$$
$$= \frac{\hbar^2 a}{2m}\frac{12}{a^3} = 6\frac{\hbar^2}{ma^2} \quad (\text{as before}).$$

$$\langle V\rangle = -\alpha\int|\psi|^2\delta(x)\,dx = -\alpha|\psi(0)|^2 = -\alpha A^2\left(\frac{a}{2}\right)^2 = -3\frac{\alpha}{a}. \quad \langle H\rangle = \langle T\rangle + \langle V\rangle = 6\frac{\hbar^2}{ma^2} - 3\frac{\alpha}{a}.$$

$$\frac{\partial}{\partial a}\langle H\rangle = -12\frac{\hbar^2}{ma^3} + 3\frac{\alpha}{a^2} = 0 \Rightarrow a = 4\frac{\hbar^2}{m\alpha}.$$

$$\langle H\rangle_{\min} = 6\frac{\hbar^2}{m}\left(\frac{m\alpha}{4\hbar^2}\right)^2 - 3\alpha\left(\frac{m\alpha}{4\hbar^2}\right) = \frac{m\alpha^2}{\hbar^2}\left(\frac{3}{8}-\frac{3}{4}\right) = \boxed{-\frac{3m\alpha^2}{8\hbar^2}} > -\frac{m\alpha^2}{2\hbar^2}. \ \checkmark$$

Solutions to Set VII

Problem 7.4

(a) Follow the proof in §7.1: $\psi = \sum_{n=1}^{\infty} c_n\psi_n$, where ψ_1 is the ground state. Since $\langle\psi_1|\psi\rangle = 0$, we have: $\sum_{n=1}^{\infty} c_n\langle\psi_1|\psi\rangle = c_1 = 0$; the coefficient of the ground state is zero. So

$$\langle H\rangle = \sum_{n=2}^{\infty} E_n|c_n|^2 \geq E_{\rm fe}\sum_{n=2}^{\infty}|c_n|^2 = E_{\rm fe}, \text{ since } E_n \geq E_{\rm fe} \text{ for all } n \text{ except } 1.$$

(b)

$$1 = |A|^2\int_{-\infty}^{\infty} x^2e^{-2bx^2}dx = |A|^2\, 2\frac{1}{8b}\sqrt{\frac{\pi}{2b}} \Longrightarrow |A|^2 = 4b\sqrt{\frac{2b}{\pi}}.$$

$$\langle T\rangle = -\frac{\hbar^2}{2m}|A|^2\int_{-\infty}^{\infty} xe^{-bx^2}\frac{d^2}{dx^2}\left(xe^{-bx^2}\right)dx$$

$$\frac{d^2}{dx^2}\left(xe^{-bx^2}\right) = \frac{d}{dx}\left(e^{-bx^2} - 2bx^2e^{-bx^2}\right) = -2bxe^{-bx^2} - 4bxe^{-bx^2} + 4b^2x^3e^{-bx^2}$$

$$\langle T\rangle = -\frac{\hbar^2}{2m}4b\sqrt{\frac{2b}{\pi}}\,2\int_0^{\infty}\left(-6bx^2 + 4b^2x^4\right)e^{-2bx^2}dx = -\frac{2\hbar^2b}{m}\sqrt{\frac{2b}{\pi}}\,2\left[-6b\frac{1}{8b}\sqrt{\frac{\pi}{2b}} + 4b^2\frac{3}{32b^2}\sqrt{\frac{\pi}{2b}}\right]$$

$$= -\frac{4\hbar^2b}{m}\left(-\frac{3}{4} + \frac{3}{8}\right) = \frac{3\hbar^2b}{2m}.$$

$$\langle V\rangle = \frac{1}{2}m\omega^2|A|^2\int_{-\infty}^{\infty} x^2e^{-2bx^2}x^2dx = \frac{1}{2}m\omega^2 4b\sqrt{\frac{2b}{\pi}}\,2\frac{3}{32b^2}\sqrt{\frac{\pi}{2b}} = \frac{3m\omega^2}{8b}.$$

$$\langle H\rangle = \frac{3\hbar^2b}{2m} + \frac{3m\omega}{8b};\quad \frac{\partial\langle H\rangle}{\partial b} = \frac{3\hbar^2}{2m} - \frac{3m\omega^2}{8b^2} = 0 \Longrightarrow b^2 = \frac{m^2\omega^2}{4\hbar^2} \Longrightarrow b = \frac{m\omega}{2\hbar}.$$

$$\langle H\rangle_{\rm min} = \frac{3\hbar^2}{2m}\frac{m\omega}{2\hbar} + \frac{3m\omega^2}{8}\frac{2\hbar}{m\omega} = \hbar\omega\left(\frac{3}{4} + \frac{3}{4}\right) = \boxed{\frac{3}{2}\hbar\omega.}$$

This is *exact*, since the trial wave function is in the form of the true first excited state.

Problem 7.5

(a) Use the unperturbed ground state $(\psi_{\rm gs}^0)$ as the trial wave function. The variational principle says $\langle\psi_{\rm gs}^0|H|\psi_{\rm gs}^0\rangle \geq E_{\rm gs}^0$. But $H = H^0 + H'$, so $\langle\psi_{\rm gs}^0|H|\psi_{\rm gs}^0\rangle = \langle\psi_{\rm gs}^0|H^0|\psi_{\rm gs}^0\rangle + \langle\psi_{\rm gs}^0|H'|\psi_{\rm gs}^0\rangle$. But $\langle\psi_{\rm gs}^0|H^0|\psi_{\rm gs}^0\rangle = E_{\rm gs}^0$ (the unperturbed ground state energy), and $\langle\psi_{\rm gs}^0|H'|\psi_{\rm gs}^0\rangle$ is precisely the first order correction to the ground state energy (Eq. 6.9), so $E_{\rm gs}^0 + E_{\rm gs}^1 \geq E_{\rm gs}$. QED

(b) The second order correction $(E_{\rm gs}^2)$ is $E_{\rm gs}^2 = \sum_{m\neq{\rm gs}}\frac{|\langle\psi_m^0|H'|\psi_{\rm gs}\rangle|^2}{E_{\rm gs}^0 - E_m^0}$. But the numerator is clearly *positive*, and the denominator is always negative (since $E_{\rm gs}^0 < E_m^0$ for all m), so $E_{\rm gs}^2$ is *negative*.

Solution.

Prob. 4.

$$\psi_\lambda(r) = N e^{-\frac{r}{\lambda}}$$

$$1 = \int |\psi_\lambda(r)|^2 dV = \int |\psi_\lambda(r)|^2 \underbrace{4\pi r^2 dr}_{dV} = N^2 \pi \lambda^3$$

or $N = \frac{1}{\sqrt{\pi\lambda^3}}$

$\vec{\nabla}_{\vec{r}} \cdot \vec{\nabla}_{\vec{r}}$ $\quad \vec{\nabla}$ - gradient operator

$$\langle T \rangle = \frac{1}{2} \int \psi_\lambda^*(r) \left(-\frac{\partial}{\partial \vec{r}} \cdot \frac{\partial}{\partial \vec{r}} \psi_\lambda(r) \right) dV$$

$$= -\frac{1}{2} \underbrace{\int \vec{\nabla}_{\vec{r}} \cdot \left(\psi_\lambda^* \vec{\nabla} \psi_\lambda(r) \right) dV} + \frac{1}{2} \int \vec{\nabla}_{\vec{r}} \psi_\lambda^*(\vec{r}) \cdot \vec{\nabla}_{\vec{r}} \psi_\lambda(\vec{r}) dV$$

$$= \underbrace{-\frac{1}{2} \int_{S_\infty} \psi_\lambda^* \vec{\nabla} \psi_\lambda(r) \cdot d\vec{s}}_{= 0} + \frac{1}{2} \int \vec{\nabla}_{\vec{r}} \psi_\lambda^*(\vec{r}) \cdot \vec{\nabla}_{\vec{r}} \psi_\lambda(\vec{r}) dV$$

Surface term at $r = \infty$

so

$$\langle T \rangle = \frac{1}{2} \int \frac{\partial \psi_\lambda^*}{\partial r} \cdot \frac{\partial \psi_\lambda(\vec{r})}{\partial r} dV = \frac{1}{2\lambda^2} N^2 \pi \lambda^3 = \frac{1}{2\lambda^2}$$

$$\langle V \rangle = \int |\psi_\lambda(r)|^2 \left(-\frac{e^2}{4\pi\varepsilon_0 r} \right) dV$$

$$= N^2 \int e^{-\frac{2r}{\lambda}} \left(-\frac{e^2}{4\pi\varepsilon_0 r} \right) \cdot \underbrace{4\pi r^2 dr}_{dV}$$

$$= -\frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{\lambda}$$

$$E_\lambda = \frac{1}{2\lambda^2} - \frac{e^2}{4\pi\varepsilon_0} \frac{1}{\lambda}, \quad \left. \frac{\partial E_\lambda}{\partial \lambda} \right|_{\lambda=\lambda_0} = \left. -\frac{1}{\lambda^3} + \frac{e^2}{4\pi\varepsilon_0} \cdot \frac{1}{\lambda^2} \right|_{\lambda=\lambda_0}$$

$$\lambda_0 = \frac{4\pi\varepsilon_0}{e^2} \cdot \frac{\hbar^2}{m}$$

or $\frac{1}{e^2}$

($\hbar = m$ was set to be 1; but to make the right dimension, put $\hbar, m$ back)

At $\lambda = \lambda_0$,

$$E_\lambda = -\frac{1}{2\lambda_0^2} = -\frac{e^4}{2} \quad \text{if set } \hbar = m = 4\pi\varepsilon_0 = 1$$

$$\text{or } = -\frac{m e^4}{32\pi^2 \varepsilon_0^2 \hbar^2} \quad \text{using conventional units.}$$

Conclusion: $\lambda_0 = \frac{1}{e^2}$ or $\frac{4\pi\varepsilon_0 \hbar^2}{m e^2}$, Bohr Radius in Eq. 4.72

$$E_{\lambda=\lambda_0} = -\frac{m e^4}{32\pi^2 \varepsilon_0 \hbar^2} = -13.6\,\text{eV} \quad \text{same as Eq. 4.69.}$$

5) based on Eq. 4.69, $E \propto e^4 \propto \eta^2$ if $\eta = e^2$.

Set $e^2 = \eta$. Following Feynman-Hellmann theorem,

$$\eta \frac{\partial E}{\partial \eta} = \eta \langle g.s. | \frac{\partial V}{\partial \eta} | g.s. \rangle = \langle g.s. | V | g.s. \rangle = \langle V \rangle$$

Meanwhile. $\eta \frac{\partial E}{\partial \eta} = 2E = 2\langle T \rangle + 2\langle V \rangle$

So $\langle T \rangle = -\frac{1}{2} \langle V \rangle$ for hydrogen eigen states.

At $\lambda = \lambda_0$, indeed one verifies that

$$\langle T \rangle_{\lambda=\lambda_0} = -\frac{1}{2} \langle V \rangle_{\lambda=\lambda_0} \quad \text{satisfies F.H. theorem}$$

However, this breaks down when moving away from $\lambda = \lambda_0$ point.