# PY 452 - Problem Set 6 Solutions

**#1** $\psi(x) = A e^{-bx^2}$ , $A = \left(\frac{2b}{\pi}\right)^{1/4}$

a) $V = \alpha|x| \Rightarrow \langle V \rangle = 2\alpha A^2 \int_0^\infty x e^{-2bx^2} dx = \frac{\alpha}{\sqrt{2b\pi}}$

[7.5]

$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{\alpha}{\sqrt{2\pi b}}$ , $\frac{\partial \langle H \rangle}{\partial b} = 0 \Rightarrow b = \left(\frac{m\alpha}{\sqrt{2\pi}\hbar^2}\right)^{2/3}$

$\hookrightarrow \langle H \rangle_{min} = \frac{\hbar^2}{2m}\left(\frac{m\alpha}{\sqrt{2\pi}\hbar^2}\right)^{2/3} + \frac{\alpha}{\sqrt{2\pi}}\left(\frac{\sqrt{2\pi}\hbar^2}{m\alpha}\right)^{1/3} = \boxed{\frac{3}{2}\left(\frac{\alpha^2\hbar^2}{2\pi m}\right)^{1/3}}$

b) $V = \alpha x^4 \Rightarrow \langle V \rangle = 2\alpha A^2 \int_0^\infty x^4 e^{-2bx^2} = \frac{3\alpha}{16b^2}$

$\hookrightarrow \langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{3\alpha}{16b^2}$ , $\frac{\partial \langle H \rangle}{\partial b} = 0 \Rightarrow b = \left(\frac{3\alpha m}{4\hbar^2}\right)^{1/3}$

$\hookrightarrow \langle H \rangle_{min} = \frac{\hbar^2}{2m}\left(\frac{3\alpha m}{4\hbar^2}\right)^{1/3} + \frac{3\alpha}{16}\left(\frac{4\hbar^2}{3\alpha m}\right)^{2/3} = \boxed{\frac{3}{4}\left(\frac{3\alpha\hbar^4}{4m^2}\right)^{1/3}}$

c) $V = \alpha x^n$ with $n$ even $\Rightarrow \langle V \rangle = 2\alpha A^2 \int_0^\infty x^n e^{-2bx^2} dx$

$\hookrightarrow \langle V \rangle = \frac{\alpha\,\Gamma\left(\frac{n}{2}+1\right)}{\sqrt{\pi}\,(2b)^{n/2}}$ , so $\langle V \rangle \to \infty$ as $n \to \infty$.

Not surprising since we are trying to use a gaussian trial function on an infinite square well. Consider $V(x)$ as $n \to \infty$.

$$V(x) = \begin{cases} 0 & |x|<1 \\ \alpha & |x|=1 \\ \infty & |x|>1 \end{cases}$$

Precisely infinite square well.

Since integral does not converge, variational method with this trial function fails

#2 $\psi(r) = Ae^{-(Br)^\nu}$

First, we normalize this trial function to find A.

$$1 = \iiint |\psi|^2 dV = 4\pi A^2 \int_0^\infty e^{-2(Br)^\nu} r^2 dr \text{, let } u = 2(Br)^\nu$$

$du = 2B^\nu \nu r^{\nu-1} dr$, $r = \left(\frac{u}{2B^\nu}\right)^{1/\nu}$

$dr = \frac{1}{\nu} \frac{u^{1/\nu - 1}}{(2B^\nu)^{1/\nu}} du$

$$= 4\pi A^2 \int_0^\infty e^{-u} \left(\frac{u}{2B^\nu}\right)^{2/\nu} \left(\frac{1}{\nu}\right)\left(\frac{u^{1/\nu-1}}{(2B^\nu)^{1/\nu}}\right) du$$

$$= \frac{4\pi A^2}{2^{3/\nu}\nu B^3} \int_0^\infty e^{-u} u^{3/\nu - 1} du = \frac{4\pi A^2}{2^{3/\nu}\nu B^3} \Gamma(3/\nu)$$

$\hookrightarrow A = \left[\frac{2^{3/\nu - 2}\nu B^3}{\pi\Gamma(3/\nu)}\right]^{1/2}$. Now we find $\langle H \rangle = \langle T \rangle + \langle V \rangle$

$$\langle T \rangle = \frac{-\hbar^2}{2m} \iiint \psi \nabla^2 \psi \, dV \text{, } \nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r}\frac{\partial \psi}{\partial r}$$

$$\frac{\partial \psi}{\partial r} = -Ae^{-(Br)^\nu}(\nu B^\nu r^{\nu-1})$$

$$\frac{\partial^2 \psi}{\partial r^2} = Ae^{-(Br)^\nu}\left(-\nu(\nu-1)B^\nu r^{\nu-2} + \nu^2 B^{2\nu} r^{2\nu-2}\right)$$

$$\hookrightarrow \langle T \rangle = \frac{-\hbar^2}{2m} 4\pi A^2 \int_0^\infty e^{-2(Br)^\nu}\left(\nu^2 B^{2\nu} r^{2\nu-2} - \nu(\nu+1)B^\nu r^{\nu-2}\right) r^2 dr \text{, } u = 2(Br)^\nu$$

$$= \frac{\hbar^2}{2m} 4\pi A^2 \int_0^\infty e^{-u}\left(\frac{\nu(\nu+1)}{2} u - \frac{\nu^2}{4} u^2\right) \frac{1}{\nu} \frac{u^{1/\nu - 1}}{(2B)^{3/\nu}} du$$

$$= \frac{\hbar^2 B^2}{m} \frac{\nu(\nu+1)\Gamma(1/\nu + 1)}{\Gamma(3/\nu)} 2^{2/\nu - 3} \quad \text{(plugged in for A)}$$

$$\langle V \rangle = -4\pi A^2 \int_0^\infty \frac{e^2}{r} e^{-2(Br)^\nu} r^2 dr = -4\pi e^2 A^2 \int_0^\infty e^{-u} \frac{u^{1/\nu}}{(2B^\nu)^{1/\nu}} \frac{1}{\nu} \frac{u^{1/\nu - 1}}{(2B^\nu)^{1/\nu}} du$$

$$= \frac{-4\pi e^2 A^2}{\nu (2B^\nu)^{2/\nu}} \int_0^\infty e^{-u} u^{2/\nu - 1} du = \frac{-4\pi e^2 A^2}{\nu (2B^\nu)^{2/\nu}} \Gamma(2/\nu) = \frac{-e^2 B \cdot 2^{1/\nu} \Gamma(2/\nu)}{\Gamma(3/\nu)}$$

$$\hookrightarrow \langle H \rangle = \frac{\hbar^2 B^2}{m} \left( \frac{\nu(\nu+1) 2^{2/\nu - 3} \Gamma(1/\nu + 1)}{\Gamma(3/\nu)} \right) - e^2 B \left( 2^{1/\nu} \frac{\Gamma(2/\nu)}{\Gamma(3/\nu)} \right)$$

$$\frac{\partial \langle H \rangle}{\partial B} = 0 \Rightarrow B = \frac{me^2}{\hbar^2} \frac{2^{1/\nu} \Gamma(2/\nu) / \Gamma(3/\nu)}{2 \left( \frac{\nu(\nu+1) 2^{2/\nu - 3} \Gamma(1/\nu + 1)}{\Gamma(3/\nu)} \right)} = \frac{me^2}{\hbar^2} \frac{2^{2 - 1/\nu} \Gamma(2/\nu)}{\nu(\nu+1) \Gamma(1/\nu + 1)}$$

$$\hookrightarrow \langle H \rangle_{min} = \frac{me^4}{\hbar^2} \left( \frac{2 \Gamma(2/\nu)^2}{\nu(\nu+1)\Gamma(1/\nu+1)\Gamma(3/\nu)} - \frac{4 \Gamma(2/\nu)^2}{\nu(\nu+1)\Gamma(1/\nu+1)\Gamma(3/\nu)} \right)$$

$$= \frac{-me^4}{\hbar^2} \left( \frac{2}{\nu+1} \frac{\Gamma(2/\nu)^2}{\Gamma(1/\nu)\Gamma(3/\nu)} \right) = \boxed{\frac{-e^2}{a_0} \left( \frac{2}{\nu+1} \right) \left( \frac{\Gamma(2/\nu)^2}{\Gamma(1/\nu)\Gamma(3/\nu)} \right)}$$

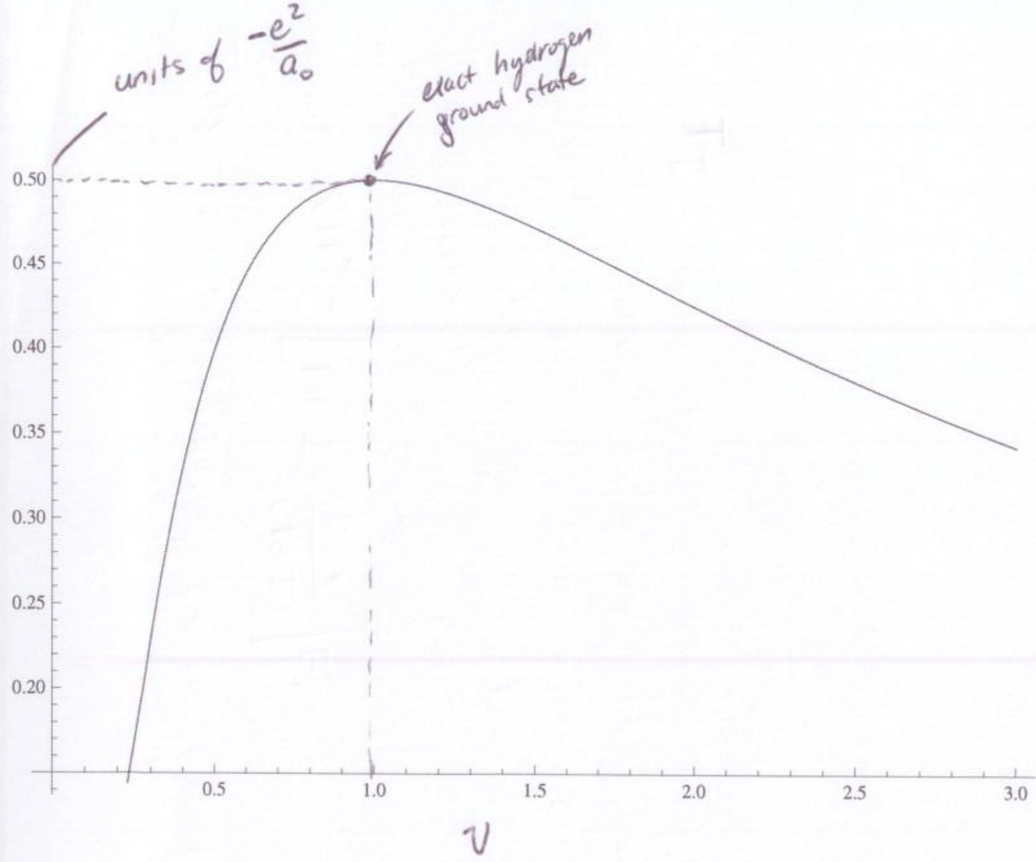
at $\nu = 1$, we have $\langle H \rangle_{min} = \frac{-e^2}{2a_0}$ which is the exact hydrogen ground state energy. Plot is attached, produced by mathematica.

# $\boxed{\#3}$

In 7.38, the cross term has a negative sign instead of positive. Propogating this change through the calculation leads to a negative sign on the overlap term ($I$) in 7.43. Also the exchange integral ($X$) in 7.44 changes sign. Thus the calculated electron energy is

$$\langle H \rangle = \left[ 1 + 2 \frac{(D - X)}{(1 - I)} \right] E_1$$

Thus the total energy as in (7.51) is


units of $-\frac{e^2}{a_0}$
exact hydrogen ground state
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.5
1.0
1.5
2.0
2.5
3.0
$\nu$

$$F(x) = \frac{E_{tot}}{-E_1} = \frac{2a}{R} - 1 - 2\,\frac{(D-X)}{(1-I)}$$ with $I$ from (7.42) and $X$ from (7.48) and $x \equiv R/a$

$$\hookrightarrow F(x) = -1 + \frac{2}{x}\left[\frac{(1+x)e^{-2x} + (\frac{2}{3}x^2-1)e^{-x}}{1-(1+x+x^2/3)e^{-x}}\right]$$

$\hookrightarrow$


Since the energy here is always greater than the separated energy, so there is no evidence of bonding in this case.

$\boxed{\#4}$ a) $H = H_0 + H' = \begin{pmatrix} E_a & h \\ h & E_b \end{pmatrix}$, $\det(H - \mathbb{1}\lambda) = 0$

$$\hookrightarrow \lambda_\pm = \frac{1}{2}\left[E_a + E_b \pm \sqrt{(E_a-E_b)^2 + 4h^2}\right]$$

b) $E_a^2 = \dfrac{|\langle\psi_b|H'|\psi_a\rangle|^2}{E_a - E_b} = \dfrac{-h^2}{E_b - E_a}$, $E_b^2 = \dfrac{|\langle\psi_a|H'|\psi_b\rangle|^2}{E_b - E_a} = \dfrac{h^2}{E_b - E_a}$

$$\hookrightarrow E_+ = E_b^0 + E_b^1 + E_b^2 \cong \boxed{E_b + \frac{h^2}{E_b - E_a}}$$

$$E_- = E_a^0 + E_a^1 + E_a^2 \cong \boxed{E_a - \frac{h^2}{E_b - E_a}}$$

c) $\langle H \rangle = \langle \cos\theta\, \psi_a + \sin\theta\, \psi_b \,|\, H_0 + H' \,|\, \cos\theta\, \psi_a + \sin\theta\, \psi_b \rangle$

$$= \cos^2\theta \langle \psi_a | H_0 | \psi_a \rangle + \sin^2\theta \langle \psi_b | H_0 | \psi_b \rangle + \sin\theta\cos\theta \langle \psi_b | H' | \psi_a \rangle + \cos\theta\sin\theta \langle \psi_a | H' | \psi_b \rangle$$

$$= E_a \cos^2\theta + E_b \sin^2\theta + 2h\sin\theta\cos\theta$$

Now we minimize with respect to $\theta$.

$\hookrightarrow$ $\dfrac{\partial \langle H \rangle}{\partial \theta} = 0 = (E_b - E_a)\sin 2\theta + 2h\cos 2\theta \Rightarrow \dfrac{\sin 2\theta}{\cos 2\theta} = \dfrac{-2h}{E_b - E_a} \equiv -\epsilon$

$\hookrightarrow$ $\dfrac{\sin 2\theta}{\sqrt{1-\cos^2 2\theta}} = \dfrac{-2h}{E_b - E_a} \Rightarrow \sin 2\theta = \dfrac{\pm\epsilon}{\sqrt{1+\epsilon^2}}$

$\hookrightarrow$ $\cos 2\theta = \dfrac{\mp 1}{\sqrt{1+\epsilon^2}}$, now use $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$

and $\cos^2\theta = \frac{1}{2}(1 + \cos 2\theta) \Rightarrow \cos^2\theta = \frac{1}{2}\left(1 \mp \frac{1}{\sqrt{1+\epsilon^2}}\right)$, $\sin^2\theta = \frac{1}{2}\left(1 \pm \frac{1}{\sqrt{1+\epsilon^2}}\right)$

$\hookrightarrow$ $\langle H \rangle_{min} = \frac{1}{2}\left[E_a + E_b \pm \sqrt{(E_b - E_a)^2 + 4h^2}\right]$ after plugging in and reducing.

d) answers to a and c match exactly. Expanding this for small $h$ yields

$$E_\pm \approx \frac{1}{2}\left(E_a + E_b \pm (E_b - E_a) \pm \frac{2h^2}{(E_b - E_a)}\right), \text{ or}$$

$\boxed{E_+ = E_b + \dfrac{h^2}{E_b - E_a} \quad \text{and} \quad E_- = E_a - \dfrac{h^2}{E_b - E_a}}$, the perterbation results.

Variational principle is so accurate here since our trial wave function is a somewhat general linear combination of the eigenstates.