HW #6 Chem 1410 Fall 2000

7-8. $$\hat{H} = -\frac{\hbar^2}{2\mu r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{k}{2}r^2$$

Consider the trial function $e^{-\alpha r^2}$

$$\langle E \rangle = \frac{-\frac{\hbar^2}{2\mu}\int_0^\infty \left(-6\alpha r^2 + 4\alpha^2 r^4\right) e^{-2\alpha r^2}\, dr + \frac{k}{2}\int_0^\infty r^4 e^{-2\alpha r^2}\, dr}{\int_0^\infty r^2 e^{-2\alpha r^2}\, dr}$$

$$\langle E \rangle = \frac{\frac{6\hbar^2\alpha}{2\mu}\int_0^\infty r^2 e^{-2\alpha r^2}\, dr - \frac{4\alpha^2\hbar^2}{2\mu}\int_0^\infty r^4 e^{-2\alpha r^2}\, dr + \frac{k}{2}\int_0^\infty r^4 e^{-2\alpha r^2}\, dr}{\int_0^\infty r^2 e^{-2\alpha r^2}\, dr}$$

$$\int_0^\infty r^2 e^{-2\alpha r^2}\, dr = \frac{1}{2}\sqrt{\frac{\pi}{2\alpha}}\,\frac{1}{4\alpha}$$

$$\int_0^\infty r^4 e^{-2\alpha r^2}\, dr = \frac{1}{2}\sqrt{\frac{\pi}{2\alpha}}\,\frac{3}{16\alpha^2}$$

$$\langle E \rangle = \frac{\frac{6\hbar^2\alpha}{2\mu}\frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}} - \frac{4\alpha^2\hbar^2}{2\mu}\frac{3}{32\alpha^2}\sqrt{\frac{\pi}{2\alpha}} + \frac{k}{2}\frac{3}{32\alpha^2}\sqrt{\frac{\pi}{2\alpha}}}{\frac{1}{8\alpha}\sqrt{\frac{\pi}{2\alpha}}}$$

$$= \frac{\frac{3}{8}\frac{\hbar^2}{\mu} - \frac{3\hbar^2}{16\mu} + \frac{3k}{64\alpha^2}}{1/8\alpha} = \frac{3\hbar^2\alpha}{\mu} - \frac{3}{2}\frac{\hbar^2\alpha}{\mu} + \frac{3k}{8\alpha}$$

$$= \frac{3}{2}\frac{\hbar^2\alpha}{\mu} + \frac{3}{8}\frac{k}{\alpha} \longrightarrow \frac{dE}{d\alpha} = \frac{3}{2}\frac{\hbar^2}{\mu} - \frac{3k}{8\alpha^2} = 0$$

$$\Rightarrow \alpha_{opt} = \frac{\sqrt{\mu k}}{2\hbar}$$

$$E_{opt} = \frac{3}{2}\frac{\hbar^2}{\mu}\frac{\sqrt{\mu k}}{2\hbar} + \frac{3}{8}k\frac{2\hbar}{\sqrt{\mu k}} = \frac{3}{4}\hbar\sqrt{\frac{k}{\mu}} + \frac{3}{4}\hbar\sqrt{\frac{k}{\mu}}$$

$$E_{opt} = \frac{3}{2}\hbar\sqrt{\frac{k}{\mu}}$$

This is the exact energy for this problem.
This happens because our trial function is of the form of the exact wave function.

Now consider the trial function $e^{-\alpha r}$

$$\langle E\rangle = \frac{-\frac{\hbar^2}{2\mu}\int_0^\infty e^{-\alpha r}(-2\alpha r + \alpha^2 r^2)e^{\alpha r}\,dr + \frac{k}{2}\int_0^\infty r^4 e^{-2\alpha r}\,dr}{\int_0^\infty r^2 e^{-2\alpha r}\,dr}$$

$$= \frac{\frac{2\hbar^2\alpha}{2\mu}\int_0^\infty r e^{-2\alpha r}\,dr - \frac{\hbar^2\alpha^2}{2\mu}\int_0^\infty r^2 e^{-2\alpha r}\,dr + \frac{k}{2}\int_0^\infty r^4 e^{-2\alpha r}\,dr}{\int_0^\infty r^2 e^{-2\alpha r}\,dr}$$

$$= \frac{\frac{\hbar^2\alpha}{\mu}\frac{1}{(2\alpha)^2} - \frac{\hbar^2\alpha^2}{2\mu}\frac{2}{(2\alpha)^3} + \frac{k}{2}\frac{4!}{(2\alpha)^5}}{\frac{2}{(2\alpha)^3}}$$

$$= \frac{\hbar^2\alpha}{\mu}\frac{2\alpha}{2} - \frac{\hbar^2\alpha^2}{2\mu} + \frac{k}{4}\frac{4\cdot 6}{(2\alpha)^2} = \frac{\hbar^2\alpha^2}{2\mu} + \frac{3}{2}\frac{k}{\alpha^2}$$

$$\frac{\partial E}{\partial\alpha} = 0 = \frac{\hbar^2\alpha}{\mu} - \frac{3}{2}\cdot\frac{2k}{\alpha^3} \Rightarrow \alpha^4_{opt} = \frac{3k\mu}{\hbar^2}$$

$$\alpha^2_{opt} = \frac{\sqrt{3k\mu}}{\hbar}$$

$$E_{opt} = \frac{\hbar^2}{2\mu}\frac{\sqrt{3k\mu}}{\hbar} + \frac{3k\hbar}{2\sqrt{3k\mu}} = \sqrt{3}\,\hbar\sqrt{\frac{k}{\mu}} \leftarrow \text{about 15\% too large}$$

7-16. Consider a one-dimensional oscillator with the potential $V = \frac{1}{2}kx^2 + \frac{\gamma}{6}x^3 + \frac{\delta}{24}x^4$.

Take $\psi = c_0\psi_0 + c_2\psi_2$ as the trial function where ψ_0 and ψ_2 are eigenfunctions of the Harmonic oscillator problem.

$$H_{00} = E_0 + \langle \psi_0 | \frac{\gamma x^3}{6} + \frac{\delta}{24}x^4 | \psi_0 \rangle$$

$$= E_0 + \frac{\delta}{24}\langle \psi_0 | x^4 | \psi_0 \rangle$$

$$H_{22} = E_2 + \langle \psi_2 | \frac{\gamma x^3}{6} + \frac{\delta}{24}x^4 | \psi_2 \rangle$$

$$= E_2 + \frac{\delta}{24}\langle \psi_2 | x^4 | \psi_2 \rangle$$

$$H_{02} = \langle \psi_0 | \underbrace{-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2}_{E_2} + \frac{\gamma x^3}{6} + \frac{\delta}{24}x^4 | \psi_2 \rangle$$

$$= \frac{\delta}{24}\langle \psi_0 | x^4 | \psi_2 \rangle$$

The integrals over x^3 are zero by the properties of even/odd functions.

E_0 and E_2 are the energies of the $v=0$ and $v=2$ levels of the Harmonic oscillator.

Why wasn't ψ_1 included in the trial function? The answer in the solutions manual is wrong. ψ_1 should actually have been included since $\langle \psi_0 | x^3 | \psi_1 \rangle \neq 0$

$$\langle \psi_0 | x^4 | \psi_0 \rangle = \sqrt{\frac{\alpha}{\pi}} \int_{-\infty}^{\infty} x^4 e^{-\alpha x^2} dx = \frac{3}{4\alpha^2}$$

$$\langle \psi_0 | x^4 | \psi_2 \rangle = \sqrt{\frac{\alpha}{2\pi}} \int_{0}^{\infty} (2\alpha x^6 - x^4) e^{-\alpha x^2} dx = \frac{3}{\sqrt{2}\,\alpha^2}$$

$$\langle \psi_2 | x^4 | \psi_2 \rangle = \left(\frac{\alpha}{4\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 (4\alpha^2 x^4 - 4\alpha x^2 + 1) e^{-\alpha x^2} dx = \frac{39}{4\alpha^2}$$

$$H_{00} = \frac{\hbar\omega}{2} + \frac{\delta}{24}\left(\frac{3}{4\alpha^2}\right)$$

$$H_{22} = \frac{3\hbar\omega}{2} + \frac{\delta}{24}\left(\frac{39}{4\alpha^2}\right)$$

$$H_{02} = \frac{\delta}{24} \frac{3}{\sqrt{2}\,\alpha^2}$$

$$\begin{vmatrix} H_{00} - E & H_{02} \\ H_{20} & H_{22} - E \end{vmatrix} = 0 \Rightarrow E = \frac{H_{00} + H_{22}}{2} \pm \frac{1}{2}\sqrt{(H_{00} - H_{22})^2 + 4 H_{02}^2}$$

$$E = \frac{3\hbar\omega}{2} \pm \frac{1}{2}\sqrt{\left(2\hbar\omega + \frac{\delta}{24}\cdot\frac{36}{4\alpha^2}\right)^2 + 4\frac{\delta^2}{(24)^2}\frac{9}{2\alpha^4}}$$

$$E = \frac{3\hbar\omega}{2} \pm \frac{1}{2}\sqrt{\left(2\hbar\omega + \frac{3}{8}\frac{\delta}{\alpha^2}\right) + \frac{\delta^2}{32\alpha^4}}$$

$$E = \frac{3\hbar\omega}{2} \pm \frac{1}{2}\sqrt{4\hbar^2\omega^2 + \frac{12}{8}\hbar\omega\frac{\delta}{\alpha^2} + \frac{9}{64}\frac{\delta^2}{\alpha^4} + \frac{\delta^2}{32\alpha^4}}$$

$$E = \frac{3\hbar\omega}{2} \pm \frac{1}{2}\sqrt{(2\hbar\omega)^2 + \frac{3}{2}\hbar\omega\frac{\delta}{\alpha^2} + \frac{11}{64}\frac{\delta^2}{\alpha^4}}$$

The ground state corresponds to the - sign.

7-23 H atom in an electric field.

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} + e\mathcal{E}r\cos\theta$$

$$E^{(1)} = \langle \psi_0 | e\mathcal{E}r\cos\theta | \psi_0 \rangle$$

$$= \frac{e\mathcal{E}}{\pi a_0^3}\int_0^\infty r^3 e^{-2r/a_0} dr \int_0^{2\pi} 1\, d\phi \int_0^\pi \sin\theta\cos\theta\, d\theta$$

$$\int_0^\pi \sin\theta\cos\theta\, d\theta = \left.\frac{\sin^2\theta}{2}\right|_0^\pi = 0$$

So there is no first-order correction of the energy of the H atom due to the presence of the electric field.