Exam 2, Chem 2430, Answers

1. $\psi_{2s} = \frac{1}{4\sqrt{2\pi}}(2-r)e^{-r/2}$, $\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}} z e^{-r/2}$

(8pts) $\Delta E_{2s} \approx \frac{4\pi}{32\pi}\int_0^\infty \frac{(2-r)^2 r^2 e^{-r} 2e^{-100000r}}{r} dr$

$= \frac{1}{4}\int_0^\infty (2-r)^2 r e^{-100001r} dr \sim 10^{-10}$

(8pts) $\Delta E_{2p_z} = 2/3 \frac{2\pi}{32\pi}\int \frac{r^2 r^2}{r} e^{-100001r} dr \sim 2.5\times 10^{-21}$

(9pts) The energy shifts are very small, but they split the 2s and 2p levels.

This is a crude attempt to account for the finite size of the proton.

(7pts) 2. a) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + \frac{1}{2}kr_1^2 + \frac{1}{2}kr_2^2 + \frac{1}{r_{12}}$

b) For a harmonic oscillator $\psi = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$ in one D.

where $\alpha = m\omega/\hbar$

For 3D $\psi = \left(\frac{\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2/2}$

So the zeroth-order wavefunction is

(7pts) $\psi = \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha r_1^2/2} e^{-\alpha r_2^2/2}$

c) For the delta function perturbation

$\Delta E = \left(\frac{\alpha}{\pi}\right)^3 A\int_0^\infty e^{-\alpha r_1^2} e^{-\alpha r_2^2} \delta(r_1 - r_2) r_1^2 r_2^2 dr_1 dr_2 \, (4\pi)^2$

from angular integration

(11pts) $\Delta E = (4\pi)^2\left(\frac{\alpha}{\pi}\right)^{3} A\int_0^\infty e^{-2\alpha r_1^2} r_1^4 dr_1$

$= (4\pi)^2\left(\frac{\alpha}{\pi}\right)^{3} A \frac{3\sqrt{\frac{\pi}{2}}}{32\alpha^{5/2}} = \frac{3}{2}\sqrt{\frac{\alpha}{2\pi}} A$

3. a) $\Psi = c_1 \phi_1 + c_2 \phi_2$ where

(8) $\phi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(x-5)^2/2}$, $\phi_2 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(x+5)^2/2}$

By symmetry $c_1 = c_2$ for the ground state

(9) b) The potential from the 2x2 matrix eigenvalue problem is $x^2+25 \sqrt{100x^2+4^2}$

So the perturbation is

$x \geq 0: \; x^2+25-\sqrt{100x^2+16}-(x-5)^2$

$x \leq 0: \; x^2+25-\sqrt{100x^2+16}-(x+5)^2$

(8) c) Yes there will be a first order correction due to this perturbation. Among other reasons, the square root term will cause a non-zero 1st order term.

4. $V = \frac{1}{2}kx^2 + \delta x$

(6/6) a) $\partial V/\partial x = kx + \delta$, $x = -\delta/k$

b) $\frac{1}{2}kx^2 + \delta x = \frac{1}{2}k\left(x+\frac{\delta}{k}\right)^2 - \frac{\delta^2}{2k}$ | from completing the square

Since the force constant is not changed, the frequencies are not changed.

Alternatively, one can show (here I set $m=1$, $\hbar=1$)

(6/6) $\psi_0 = e^{-\frac{\sqrt{k}}{2}\left(x+\frac{\delta}{k}\right)^2}$

$\psi_1 = \left(x+\frac{\delta}{k}\right) e^{-\frac{\sqrt{k}}{2}\left(x+\frac{\delta}{k}\right)^2}$

$-\frac{1}{2}\delta^2/2k$, $-\frac{1}{2}\delta^2/2k$

are eigenfunctions of $\hat{H}$, with eigenvalue $\frac{\hbar\omega}{2}$, $\frac{3}{2}\hbar\omega$

(6/6) c) This is explained in the beginning of b) above

(7/7) d) $\langle 0|x|1\rangle$, $\langle 1|x|2\rangle$, $\langle 2|x|3\rangle$, etc.

are all non-zero with this basis set. So the Hamiltonian matrix is of infinite dimension