Chem 532: Second Exam Wednesday, November 9, 2022 (80 pts. possible)

Please budget your time carefully and show all work for partial credit

Assorted physical constants:

$h = 6.62607 \times 10^{-34}$ J s	$m_e = 9.1094 \times 10^{-31}$ kg	$a_o = 5.29177 \times 10^{-11}$ m
$c = 2.99792 \times 10^{8}$ m s^{-1}	$k_B = 1.38065 \times 10^{-23}$ J K^{-1}	$R = 1.09737 \times 10^{5}$ cm^{-1}
1 nm = 10^{-9} m	$e = 1.60218 \times 10^{-19}$ C	$N_A = 6.02214 \times 10^{23}$ mol^{-1}

Assorted relations:

$j_\pm = j_x \pm i j_y$ $j_\pm \left\| j, m_j \right\rangle = \hbar\sqrt{j(j+1) - m_j(m_j \pm 1)}\left\| j, m_j \pm 1 \right\rangle$ $\left[j_x, j_y \right] = i\hbar j_z$ $J^2 = j_1^2 + j_2^2 + 2 j_{1z} j_{2z} + j_{1+} j_{2-} + j_{1-} j_{2+}$ $E_n = -\dfrac{Z^2}{2n^2}$ $\int x \sin^2 ax\, dx = \dfrac{x^2}{4} - \dfrac{x \sin 2ax}{4a} - \dfrac{\cos 2ax}{8a^2}$	$\hat{a} = \dfrac{1}{\sqrt{2}}(Q + iP)$ $\hat{a}^\dagger = \dfrac{1}{\sqrt{2}}(Q - iP)$ $\hat{a}\left\| \psi_v \right\rangle = \sqrt{v}\left\| \psi_{v-1} \right\rangle$ $\hat{a}^\dagger \left\| \psi_v \right\rangle = \sqrt{v+1}\left\| \psi_{v+1} \right\rangle$ $Q = \dfrac{1}{\sqrt{2}}\left(\hat{a} + \hat{a}^\dagger\right)$ $P = \dfrac{i}{\sqrt{2}}\left(\hat{a}^\dagger - \hat{a}\right)$	$Q = \sqrt{\dfrac{m\omega}{\hbar}}\, x$ $P = -i\dfrac{d}{dQ}$ $= \dfrac{1}{\sqrt{m\hbar\omega}}\, p_x$ $H_{SHO} = \hat{a}^\dagger \hat{a} + \dfrac{1}{2} = \hat{a}\hat{a}^\dagger - \dfrac{1}{2}$

(1) (10 pts) Consider a hydrogen-like atom wavefunction and the distance of the electron from the nucleus regardless of angle. Distinguish between the mean radius and the most probable radius. Use words and equations. Please be as specific as possible.

The mean radius is equivalent to the expectation value of $\hat{r}$

$$\langle r \rangle = \langle \psi_n | r | \psi_n \rangle$$

The most probable radius corresponds to a maximum in the radial probability distribution

$$\frac{dP(r)}{dr} = 0 \quad \text{where} \quad P(r) = R_{n\ell}^2 r^2$$

(2) (15 pts) Using raising and lowering operators, what is the average value of ℓ_x^2 in an angular momentum state described by the spherical harmonic $Y_{2,1}$?

$$\ell_x = \frac{1}{2}(\ell_+ + \ell_-)$$

$$\ell_x^2 = \frac{1}{4}(\ell_+\ell_+ + \ell_-\ell_- + \ell_+\ell_- + \ell_-\ell_+)$$

$$\langle Y_{2,1}|\ell_x^2|Y_{2,1}\rangle = \frac{1}{4}\Big[\underbrace{\cancel{\langle Y_{2,1}|\ell_+\ell_+|Y_{2,1}\rangle}}_{0} + \underbrace{\cancel{\langle Y_{2,1}|\ell_-\ell_-|Y_{2,1}\rangle}}_{0}$$

$$+ \langle Y_{2,1}|\ell_+\ell_-|Y_{2,1}\rangle + \langle Y_{2,1}|\ell_-\ell_+|Y_{2,1}\rangle\Big]$$

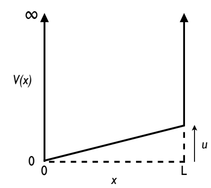
$$= \frac{1}{4}\left\{\langle Y_{2,1}|\ell_+\ell_-|Y_{2,1}\rangle + \langle Y_{2,1}|\ell_-\ell_+|Y_{2,1}\rangle\right\}$$

$$= \frac{1}{4}\left\{\langle Y_{2,1}|\ell_+|Y_{2,0}\rangle \hbar\sqrt{2(2+1)-1(1-1)} + \langle Y_{2,1}|\ell_-|Y_{2,2}\rangle \hbar\sqrt{2(2+1)-1(1+1)}\right\}$$

$$= \frac{1}{4}\left[\hbar\sqrt{6}\,\hbar\sqrt{6-0} + \hbar\sqrt{4}\,\hbar\sqrt{6-2(2-1)}\right]\langle Y_{2,1}|Y_{2,1}\rangle$$

$$= \frac{1}{4}\hbar^2(6+4) = \boxed{\frac{5}{2}\hbar^2}$$

(3) (30 pts) Consider the usual one-dimensional particle in a box of mass m with wavefunctions and energies $\psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)$ and $E_n^{(0)} = \frac{n^2 h^2}{8mL^2}$, respectively, but with a perturbation $H^{(1)} = \frac{u}{L} x$ added as shown below.



(a) What is the full Hamiltonian for the perturbed system? Be as explicit as possible.

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{u}{L}x$$

(b) What is the correction to the unperturbed ground state energy to 1st-order in perturbation theory, $E_1^{(1)}$?

$$E_1^{(1)} = \langle \psi_1^{(0)} | \tfrac{u}{L}x | \psi_1^{(0)} \rangle$$

$$= \frac{2u}{L^2}\int_0^L x \sin^2\left(\tfrac{\pi}{L}x\right) dx = \frac{2u}{L^2}\int_0^L x \sin^2 ax \, dx$$

$$= \frac{2u}{L^2}\left[\frac{x^2}{4} - \frac{x \sin 2ax}{4a} - \frac{\cos 2ax}{8a^2}\right]_0^L$$

$$= \frac{2u}{L^2}\left[\frac{L^2}{4} - \frac{L \sin 2aL}{4a} - \frac{\cos 2aL}{8a^2} + \frac{1}{8a^2}\right]$$

$$= \frac{2u}{L^2}\left[\frac{L^2}{4} - \frac{L \overbrace{\sin 2\pi}^{0}}{4\pi/L} - \frac{\overbrace{\cos 2\pi}^{1}}{8\pi^2/L^2} + \frac{1}{8\pi^2/L^2}\right]$$

$$= \boxed{\frac{u}{2}}$$

(c) Now consider the linear variation method with the trial function $\phi = c_1\psi_1^{(0)} + c_2\psi_2^{(0)}$. Using what you know about the form of the secular determinant and other fundamental definitions, show that the secular determinant can be expressed in terms of $E_i^{(0)}$, $E_i^{(1)}$, E, and $\left\langle \psi_1^{(0)} \middle| H^{(1)} \middle| \psi_2^{(0)} \right\rangle$, where i = 1, 2. Explicitly show your logic. Do not solve the resulting equation.

$$\begin{vmatrix} H_{11}-E & H_{12} \\ H_{12} & H_{22}-E \end{vmatrix} = 0$$

$$S_{11} = S_{22} = 1$$
$$S_{12} = S_{21} = 0$$

where $H_{11} = \langle \psi_1^{(0)} | H | \psi_1^{(0)} \rangle = \langle \psi_1^{(0)} | H^{(0)} + H^{(1)} | \psi_1^{(0)} \rangle$

$= E_1^{(0)} + E_1^{(1)}$

$H_{22} = \langle \psi_2^{(0)} | H^{(0)} + H^{(1)} | \psi_2^{(0)} \rangle = E_2^{(0)} + E_2^{(1)}$

$H_{12} = \langle \psi_1^{(0)} | H^{(0)} + H^{(1)} | \psi_2^{(0)} \rangle = \langle \psi_1^{(0)} | H^{(1)} | \psi_2^{(0)} \rangle$

So:

$$\begin{vmatrix} E_1^{(0)} + E_1^{(1)} - E & \langle \psi_1^{(0)} | H^{(1)} | \psi_2^{(0)} \rangle \\ \langle \psi_1^{(0)} | H^{(1)} | \psi_2^{(0)} & E_2^{(0)} + E_2^{(1)} - E \end{vmatrix} = 0$$

(4) (25 pts) Consider the 1s2s excited state of the He atom. In class we used degenerate 1st-order perturbation theory with the two Hartree product wavefunctions $\psi_1^{(0)} = 1s(1)2s(2)$ and $\psi_2^{(0)} = 2s(1)1s(2)$ as a basis set. The perturbation is of course $1/r_{12}$ in atomic units.

(a) Write the equation involving the secular determinant and explicitly relate the perturbation integrals $H_{11}^{(1)}$, $H_{12}^{(1)}$, and $H_{22}^{(1)}$ to the Coulomb and exchange integrals, J_{1s2s} and K_{1s2s}.

$$\begin{vmatrix} H_{11}^{(1)} - E_1^{(1)} & H_{12}^{(1)} \\ H_{12}^{(1)} & H_{22}^{(1)} - E_1^{(1)} \end{vmatrix} = 0$$

$$H_{11}^{(1)} = \left\langle 1s(1)2s(2) \right| \frac{1}{r_{12}} \left| 1s(1)2s(2) \right\rangle = J_{1s2s}$$

$$H_{22}^{(1)} = \left\langle 2s(1)1s(2) \right| \frac{1}{r_{12}} \left| 2s(1)1s(2) \right\rangle = J_{2s1s} = J_{1s2s}$$

$$H_{12}^{(1)} = \left\langle 1s(1)2s(2) \right| \frac{1}{r_{12}} \left| 2s(1)1s(2) \right\rangle = K_{1s2s}$$

(b) With a resulting 1st-order correction to the ground state energy equal to $J_{1s2s} - K_{1s2s}$, what is the normalized zeroth-order wavefunction corresponding to the ground state? Please show your work.

Secular eqn: $\left(J_{1s2s} - E_1^{(1)}\right) c_1 + K_{1s2s} c_2 = 0$

$$\left[J_{1s2s} - \left(J_{1s2s} - K_{1s2s}\right)\right] c_1 + K_{1s2s} c_2 = 0$$

$$\therefore \; c_1 = -c_2$$

normalization: $c_1^2 + c_2^2 = 1$ since $\langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = \delta_{ij}$

$$\therefore \; c_1 = \frac{1}{\sqrt{2}}$$

$$\psi = \frac{1}{\sqrt{2}} \left[1s(1)2s(2) - 2s(1)1s(2) \right]$$