Quantum Assignment 2

1. Make contour plots of the real 2p and 3d orbitals of the helium atom, in the x-z plane (set $y = 0$). You can use any platform you wish. If you wish to use a spreadsheet, you can do low-tech contours by making a (managable) grid of x and z values, evaluating the wavefunction (normalized to the interval, -10 to 10) to one digit. [20 marks + 5 bonus marks for 3D surfaces - by any means]

2. Excited hydrogen atoms emit light via spontaneous emission. These transitions are induced by zero point energy density of the electromagnetic field. The rate of spontaneous emission from higher level, j', to a lower level, j, is given by

$$\text{rate} = \frac{\omega_{j'j}^3 |\mu_{j'j}|^2}{3\pi\epsilon_0\hbar c^3} = \frac{4\alpha\omega_{j'j}^3 \left(|\langle\psi_{j'}|x\psi_j\rangle|^2 + |\langle\psi_{j'}|y\psi_j\rangle|^2 + |\langle\psi_{j'}|z\psi_j\rangle|^2 \right)}{3c^2}$$

where

$$\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c} = 7.29735 \times 10^{-3}$$

is the fine structure constant, and

$$\omega_{j'j} = \frac{E_{j'} - E_j}{\hbar}$$

is the angular frequency of the transition.

(a) What are the selection rules for atomic spontaneous emission? How do they arise from the above rate expression? [10 marks]

(b) Determine the lifetimes (in ns) of the three 2p states ($m_\ell = 0, \pm 1$) using the above formula. [15 marks]

(c) Why is the measured lifetime of the 2s state larger than the 2p lifetimes by a factor of about 10^8? [5 marks]

3. The Coulomb and exchange integrals determine the effect of electron repulsion on the excited states of helium. For example, for the $1s^1 2s^1$ electron configuration, we have

$$J_{1s,2s} = \int \frac{(1s)^2(\mathbf{x}_1)(2s)^2(\mathbf{x}_2)}{r_{12}}\, d\mathbf{x}_1 d\mathbf{x}_2$$

and

$$K_{1s,2s} = \int \frac{(1s)(\mathbf{x}_1)(2s)(\mathbf{x}_1)(1s)(\mathbf{x}_2)(2s)(\mathbf{x}_2)}{r_{12}}\, d\mathbf{x}_1 d\mathbf{x}_2.$$

These are six dimensional integrals. However, they are simplified via the Laplace expansion of $1/r_{12}$,

$$\frac{1}{r_{12}} = \frac{1}{\|\mathbf{x}_1 - \mathbf{x}_2\|} = \sum_{\ell=0}^{\infty} \frac{4\pi}{2\ell+1} \sum_{m_\ell=-\ell}^{\ell} (-1)^{m_\ell} \frac{r_<^\ell}{r_>^{\ell+1}} Y^*_{\ell,m_\ell}(\theta_1,\phi_1) Y_{\ell,m_\ell}(\theta_2,\phi_2).$$

Substituting this expression into the above matrix elements allows the electron 1 and 2 integrals to be evaluated independently. Moreover, the radial and angular integrals are also separated. Finally, the resulting angular matrix elements - here, of the form, $\langle Y_{0,0}|Y_{\ell,m_\ell}Y_{0,0}\rangle$, can be evaluated analytically. First, only the $m_\ell = 0$ term is non-zero. This is because the ϕ integral is otherwise zero. Next, since $Y_{0,0}(\theta,\phi)$ is real and

$$Y^2_{0,0}(\theta,\phi) == (4\pi)^{-1} = (4\pi)^{-1/2} Y_{0,0}(\theta,\phi),$$

the above matrix element reduces to

$$\langle Y_{0,0}|Y_{\ell,0}Y_{0,0}\rangle = (4\pi)^{-1/2}\langle Y_{0,0}|Y_{\ell,0}\rangle$$
$$= \begin{cases} (4\pi)^{-1/2} & \ell = 0 \\ 0 & \text{otherwise} \end{cases}$$

Thus,

$$J_{1s,2s} = 4\pi \int_0^\infty \int_0^\infty \frac{1}{r_>} R^2_{1,0}(r_1) R^2_{2,0}(r_2) r_1^2 r_2^2 dr_1 dr_2 \quad \underbrace{(4\pi)^{-1/2}}_{\text{from } \theta_1,\phi_1 \text{ integration}} \quad \underbrace{(4\pi)^{-1/2}}_{\text{from } \theta_2,\phi_2 \text{ integration}}$$
$$= \int_0^\infty \int_0^\infty \frac{1}{r_>} R^2_{1,0}(r_1) R^2_{2,0}(r_2) r_1^2 r_2^2 dr_1 dr_2$$

and

$$K_{1s,2s} = \int_0^\infty \int_0^\infty \frac{1}{r_>} R_{1,0}(r_1) R_{2,0}(r_1) R_{1,0}(r_2) R_{2,0}(r_2) r_1^2 r_2^2 dr_1 dr_2.$$

(a) Compute $J_{1s,2s}$ and $K_{1s,2s}$ numerically. You can use a spreadsheet to compute the integrand on a 2D grid (cutoff the grid when the integrand gets really small - i.e., at large r_1 and r_2). The double integral is formed by summing the columns, then summing the row of column sums. [15 marks]

(b) Compute $J_{1s,2p}$ and $K_{1s,2p}$ and show that the $1s^1 2s^1$ triplet state has lower energy than the $1s^1 2p^1$ triplet state (in this first order perturbation theory approximation). [15 marks]

It is sufficient to consider only the $2p_0$ orbital (the z orbital), since the calculation is easier, and the electron repulsion integral must be the same for the other orbitals. Here, you need to evaluate angular matrix elements of the form, $\langle Y_{0,0}|Y_{\ell,m_\ell}Y_{0,0}\rangle$, $\langle Y_{1,0}|Y_{\ell,m_\ell}Y_{1,0}\rangle$ and $\langle Y_{0,0}|Y_{\ell,m_\ell}Y_{1,0}\rangle$. Since $Y_{1,0}(\theta,\phi)$ is real, and

$$Y_{1,0}(\theta,\phi) = \left(\frac{4\pi}{3}\right)^{-1/2} \cos\theta,$$

$$Y^2_{1,0}(\theta,\phi) = \left(\frac{4\pi}{3}\right)^{-1} \cos^2\theta.$$

$\cos^2\theta$ can be written as a combination of $Y_{0,0}(\theta,\phi)$ and $Y_{2,0}(\theta,\phi)$. Also,

$$Y_{0,0}(\theta,\phi) Y_{1,0}(\theta,\phi) = (4\pi)^{-1/2} Y_{1,0}(\theta,\phi).$$