Problem 1: Dipole Matrix Elements in Hydrogen. (15 points)

In the "electric-dipole approximation", the interaction energy between an atomic system and an external electric field can be written as $\hat{H}_{int} = -\hat{\mathbf{d}} \cdot \mathbf{E}$, where $\hat{\mathbf{d}} = -e\hat{\mathbf{x}}$ is the electric dipole operator, $\hat{\mathbf{x}}$ is the observable corresponding to the electron-proton separation, and $\mathbf{E}$ is the electric field (which we treat classically).

(a) Consider the matrix elements between two stationary states of the hydrogen atom:
$$\langle n', l', m' | \hat{H}_{int} | n, l, m \rangle = e \langle n', l', m' | \hat{\mathbf{x}} \cdot \mathbf{E} | n, l, m \rangle$$
Show that parity conservation implies that the matrix element vanishes exactly unless $(-1)^{l'-l} = -1$.

(b) For electric fields pointing along *each* of the Cartesian directions $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ of the relative coordinate vector $\mathbf{x}$, find the matrix elements of between the $1s$ state and the three $2p$ states. Please comment on your results. (*Hint*, use the spherical basis and use the orthogonality of the spherical harmonics).

(c) Now consider an electric field rotating around the z-axis. We can write such a field as
$\mathbf{E}(t) = E_0 \cos\omega t\, \mathbf{e}_x \pm E_0 \sin\omega t\, \mathbf{e}_y = \mathrm{Re}\left[E_0 \left(\mathbf{e}_x \pm i\mathbf{e}_y \right) e^{-i\omega t} \right] = \mp\sqrt{2} E_0 \,\mathrm{Re}\left[\mathbf{e}_\pm e^{-i\omega t} \right]$, where
$\mathbf{e}_\pm \equiv \mp \dfrac{\mathbf{e}_x \pm i\mathbf{e}_y}{\sqrt{2}}$.   Consider, thus, the matrix element $\langle n', l', m' | \hat{\mathbf{x}} \cdot \mathbf{e}_\pm | n, l, m \rangle$ as in part (b) and comment on your results.

The results you have found are examples of the Wigner-Eckart Theorem and dipole selection rules we will study later in the semester.

Problem 2: Matrix Elements in Hydrogen (15 points)

(a) Use direct integration and properties of the Laguerre polynomials to find the mean radius of hydrogen when in the stationary state $|n, l, m\rangle$

$$\langle r \rangle = a_0 \left(\frac{3}{2} n^2 - \frac{l(l+1)}{2} \right).$$

What is the mean radius in the ground state? How does this compare to the peak probability for the electron to be in a radius $r \rightarrow r + dr$?

(b) Using either direct integration or the Feynman-Hellman trick sketched in the lecture notes, show

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{a_0^3} \frac{1}{n^3(l+1/2)l(l+1)} = \frac{1}{l(l+1)} \frac{1}{a_0} \left\langle \frac{1}{r^2} \right\rangle .$$

Problem 4: Spectrum of Multielectron Atoms (10 Points)

Background
We have seen that the spectrum of nonrelativistic hydrogen has an "accidental" degeneracy – states with the same principle quantum number n, but different angular momentum quantum number l are degenerate. This was an artifact of the pure $1/r$ Coulomb potential associated with the electron moving in the field of the proton.

In a multielectron atom things are, of course, more complicated. Each electron moves in the combined attractive field of the nucleus and repulsive field of the other electrons. The Pauli principle must also be accounted for. This many-body problem cannot be solved exactly. One coarse approximation is the "mean-field" approximation, whereby every electron moves in the average field of all the other particles. The mean field is spherically symmetric, and thus, the quantum numbers n and l are still good. This approximation is especially good for alkalis (group IA in the period table) since they have one valence electron around a stable "noble atom-like core". They are thus vaguely hydrogenic if the valence electron does not "penetrate" the core.

Consider the spectrum of Li and Na, two alkali atoms, shown below:
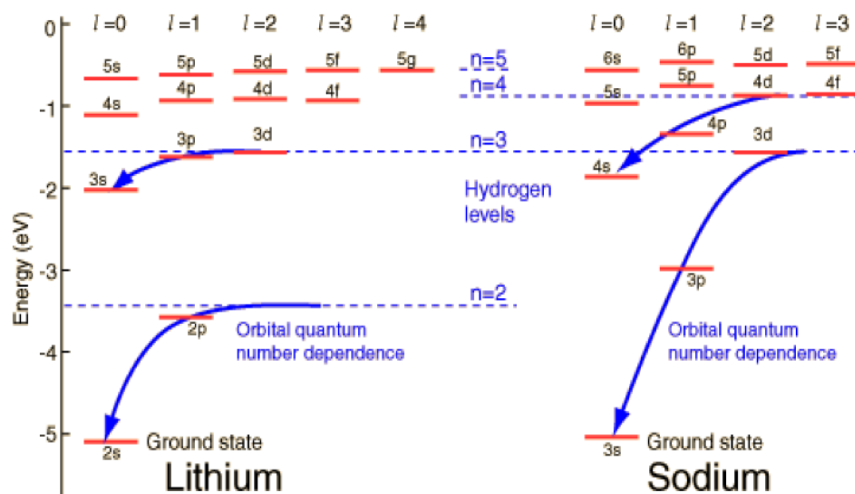
Clearly, states with different l are no longer degenerate.

(a) Using the discussion above and your knowledge of the hydrogenic wave functions, explain the qualitative behavior of these spectra.

(b) Let us take an artificial (but exactly solvable) model of the mean field of the other electrons as having a $1/r^2$ dependence, so that $V(r) = -\dfrac{e^2}{r} + \dfrac{A}{r^2}$. Show that wave functions are hydrogenic in form, and the eignevalues are:

$$E(n_r, l) = -\Re\left[n_r + \frac{1}{2}\left(1 + \sqrt{(2l+1)^2 + 8mA/\hbar^2}\right)\right]^{-2},$$ where $\Re$ is the Rydberg constant.

Sketch an energy level diagram assuming $8mA/\hbar^2 \ll 1$.