1. a) In the infrared spectrum of $H^{79}Br$, there is an intense line at 2630 cm^{-1}. Calculated the force constant of $H^{79}Br$ and the period of vibration of $H^{79}Br$.

   b) The force constant of $^{79}Br^{79}Br$ is 240 N $\cdot m^{-1}$. Calculated the fundamental vibrational frequency and zero-point energy of $^{79}Br^{79}Br$

   c) Calculate the average z component of angular momentum, $\langle L_z \rangle$, for an electron in a ring of constant potential when it has the wavefunction:

$$i)\ \psi(\phi) = \sqrt{\frac{1}{\pi}} \sin 3\phi$$

and

$$ii)\ \psi(\phi) = \sqrt{\frac{1}{2\pi}} \mathbf{e}^{-3i\phi}.$$

2. The Earth (mass $\cong 6 \times 10^{24}$ kg) rotates about the sun (at an average distance of r $\cong 1.5 \times 10^{11}$ m) once per year (one year $= 10\pi$ million seconds).

   a) What is the Earth's angular momentum with respect to the sun in units of $\hbar$?

   b) What is the smallest principle quantum number n that allows the electron in a hydrogen atom to have this value of angular momentum?

   c) How large is such an atom? Use $\langle \hat{r} \rangle$ for the H atom in the $1s$ state to express this size.

3. The five $l = 2$ spherical harmonic functions are:

$$Y_{2,0}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}\left(2\cos^2\theta - \sin^2\theta\right)$$

$$Y_{2,\pm1}(\theta,\phi) = \mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\cos\theta\sin\theta\mathbf{e}^{\pm i\phi}$$

$$Y_{2,\pm2}(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\mathbf{e}^{\pm 2i\phi}$$

   a) Prove that these functions are eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ with appropriate eigenvalues.

   b) Write $Y_{2,0}(\theta,\phi)$ in terms of $\frac{x}{r}$, $\frac{y}{r}$, and $\frac{z}{r}$.

   c) Use superposition to relate $Y_{2,1}$ and $Y_{2,-1}$ to real functions of $\frac{x}{r}$, $\frac{y}{r}$, and $\frac{z}{r}$. *Hint: Remember that* $\boldsymbol{e}^{\pm i\phi} = \cos\phi \pm i \sin\phi$

d) Show that the smplitude,

$$\psi(\theta,\phi) = \frac{1}{\sqrt{2}}[Y_{1,0}(\theta,\phi)+Y_{2,0}(\theta,\phi)]$$

is an eigenfunction of $\hat{L}_z$ but not $\hat{L}^2$. $Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$.

4. In class you were shown that not only are the $2l+1$ m states of each l degenerate for the hydrogen atom, but there is an additional degeneracy for each n from the fact that $0 \leq l \leq n-1$.

a) Given that under parity

$$\hat{P}Y_{lm}(\theta,\phi) = (-1)^{-l}Y_{lm}(\theta,\phi),$$

what is the first n for which a superposition of two different l states of even parity can be constructed? What are the values of l?

b) The same question as in a), but for the case of odd parity.

5. This is a subtle question. When (in physical space, a.k.a. position representation) an eigenfunction of some Hamiltonian, $\hat{H}$, is $\psi_s(\vec{r})$ with a corresponding eigenvalue E_s (i.e. $\hat{H}\psi_s(\vec{r}) = E_s\psi_s(\vec{r})$), then we know that

$$E_s = \int \psi_s^*(\vec{r})\hat{H}\psi_s(\vec{r})d^3r,$$

where here we assume that $\psi_s(\vec{r})$ is normalized. Now, the amazing thing about the hydrogen atom (or any tow-body coulomb interaction) is that the $2s$ and $2p$ states are degenerate. Suppose instead of having a coulomb interaction that the relative interaction in atomic units is actually

$$V'(\rho) = \frac{-\mathbf{e}^{-\gamma\rho}}{\rho},$$

where $\gamma << 1$.

a) Show that the new relative Hamiltonian, $\hat{H}'$, may be written as,

$$\hat{H}' = \hat{H} + \left(\frac{-\mathbf{e}^{-\gamma\rho}}{\rho} + \frac{1}{\rho}\right),$$

where $\hat{H}$ is the hydrogen atom Hamiltonian.

b) Assume that γ is so small that the eigenfunctions of the hydrogen atom Hamiltonian $\hat{H}$ are also eigenfunctions of $\hat{H}'$. Show that no matter how small γ is, the energies of the $2s$ and $2p_z$ are no longer degenerate. Are the three $2p$ states still degenerate?

Extra credit: Suppose instead of a regular Coulomb interaction that the potential was given by $\frac{-1}{\rho^{1+\varepsilon}}$, with $\varepsilon << 1$. Show that the $2s$ and $2p_z$ states are not degenerate using the ideas advanced in the previous part of this problem.

6. Starting with the relationship $[\hat{x}, \hat{p}] = i\hbar$ and the definition $\vec{L} = \vec{r} \times \vec{p}$, show that:

$$\begin{aligned} \left[\hat{L}_x, \hat{L}_y\right] &= i\hbar\hat{L}_z \\ &\text{and} \\ \left[\hat{L}_z, \hat{L}^2\right] &= 0 \end{aligned}$$

The following commutator relations may be useful: $[A,BC] = B[A,C] + [A,B]C$ and $[AB,C] = A[B,C] + [A,C]B$.

7. Consider a U atom stripped of all but one electron: U^{91+}.

a) What is the ion's ionization energy in both eV and in atomic units?

b) What is $\langle \hat{r} \rangle$ for the $1s$ state of this ion in both Angstroms and atomic units?

c) For some principle quantum number n^*, U^{91+} will have $\langle \hat{r} \rangle_{n^*s} \geq \langle \hat{r} \rangle_{1s}$ for H. What is the smallest value that $n*$ can be?

d) What does the plot of $\langle \hat{r} \rangle_{1s}$ look like for all the one electron species from H to U^{91+}?

8. Consider two possible spin states:

$$\begin{aligned} \left|\Psi_1\right\rangle &= \left|0\right\rangle \\ \left|\Psi_2\right\rangle &= \sqrt{\frac{1}{4}}\left|0\right\rangle + i\sqrt{\frac{3}{4}}\left|1\right\rangle \end{aligned}$$

a) What is the expectation value of S_z for each of these states? (Expectation value = $\langle S_z \rangle = \left\langle \Psi \middle| S_z \middle| \Psi \right\rangle$)

b) What is $\langle S_x \rangle$ for each of these states?

c) What is $\langle S_y \rangle$ for each of these states?