1. For all spherically symmetric potentials, the discrete spectra of bound states energies have $(2\ell+1)$–fold degeneracy mandated by the $SO(3)$ symmetry — all states $|n_r,\ell,m\rangle$ with the same l and n_r but different m have the same energy $E(n_r,\ell)$. For most potentials, there is no further degeneracy — different combinations of ℓ and n_r give different energies. However, there are two 'accidentally degenerate' exceptions of that rule: the spherically-symmetric harmonic potential $\hat{V}=\frac{1}{2}M\omega^2\hat{r}^2$, and the Coulomb potential $\hat{V}=-e^2Z/\hat{r}$. In both cases the extra degeneracy is not accidental but is due to non-obvious conservation laws leading to unexpected enlargement of the symmetry group from the rotations-only $SO(3)$ to the $SU(3)$ in the harmonic case and to the $SO(3)\times SO(3)\cong SO(4)$ in the Coulomb case.

   The unexpected conservation law in the Coulomb case is the Laplace–Runge–Lenz theorem generalized from classical to quantum mechanics. Classically, we define the Runge–Lenz vector $\mathbf{K}$ as

$$\mathbf{K}\ \stackrel{\rm def}{=}\ \mathbf{p}\times\mathbf{L}\ -\ e^2ZM\,\mathbf{n} \tag{1}$$

   where M is the particle's mass, $\mathbf{L}\stackrel{\rm def}{=}\mathbf{x}\times\mathbf{p}$ is its angular momentum and $\mathbf{n}\stackrel{\rm def}{=}\mathbf{x}/r$ is a unit vector pointing towards the particle. The Laplace–Runge–Lenz theorem states that for Coulomb/Newton potential, $\mathbf{K}$ is a conserved quantity, *i.e.*, does not change with time.

   (a) Prove the classical Laplace–Runge–Lenz theorem.

   (b) Use $\mathbf{K}=\text{const}$ to show that a classical orbit is a conical section of eccentricity $\varepsilon=|\mathbf{K}|/e^2ZM$,

$$r(\phi)\ =\ \frac{\mathbf{L}^2}{e^2ZM\ +\ |\mathbf{K}|\cos\phi} \tag{2}$$

   where ϕ is the angle between the vectors $\mathbf{K}$ and $\mathbf{x}$. For $\varepsilon<1$, the orbit (2) is a closed ellipse whose pericenter lies in the direction pointed by $\mathbf{K}$.
   Hint: prove and use $\mathbf{x}\cdot\mathbf{K}=\mathbf{L}^2-e^2ZMr$.

   In quantum mechanics we define the Runge-Lenz vector operator as

$$\begin{aligned}\hat{\mathbf{K}}\ &\stackrel{\rm def}{=}\ \tfrac{1}{2}\Big(\hat{\mathbf{p}}\times\hat{\mathbf{L}}-\hat{\mathbf{L}}\times\hat{\mathbf{p}}\Big)\ -\ e^2ZM\,\hat{\mathbf{n}}\\ &=\ \hat{\mathbf{p}}\times\hat{\mathbf{L}}\ -\ i\hbar\hat{\mathbf{p}}\ -\ e^2ZM\,\hat{\mathbf{n}}.\end{aligned} \tag{3}$$

(c) Check the Hermiticity of the component operators $\hat{K}_i$ using the top line here as the definition, then check that the bottom line agrees with the top line.

(d) Verify that the Runge–Lenz operator (3) is conserved, *i.e.*, commutes with the Hamiltonian

$$\hat{H} = \frac{1}{2M}\hat{\mathbf{p}}^2 - e^2 Z\,\hat{r}^{-1}. \tag{4}$$

To find out the Lie algebra generated by the conserved operators $\hat{L}^i$ and $\hat{K}^i$, we need their commutation relations

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k\,, \tag{5}$$

$$[\hat{K}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{K}_k\,, \tag{6}$$

$$[\hat{K}_i, \hat{K}_j] = i\hbar\epsilon_{ijk}\hat{L}_k \times (-2M\hat{H}). \tag{7}$$

We know eq. (5) is true, and it is easy to check that the $\hat{\mathbf{K}}$ operator is a vector so its components obey eq. (6).

(e) Verify eq. (7).

For the rest of this problem, let's focus on the subspace of the Hilbert space spanned by the bound states. In terms of the Hamiltonian operator $\hat{H}$, this is the subspace of negative-energy states, so in this subspace $\sqrt{-2M\hat{H}}$ is a well-defined Hermitian operator.

Let's define two vector operators

$$\hat{\mathbf{Q}}_+ = \frac{\hat{\mathbf{L}}}{2} + \frac{\hat{\mathbf{K}}}{2\sqrt{-2M\hat{H}}} \quad\text{and}\quad \hat{\mathbf{Q}}_- = \frac{\hat{\mathbf{L}}}{2} - \frac{\hat{\mathbf{K}}}{2\sqrt{-2M\hat{H}}} \tag{8}$$

in the bound-state subspace. In this subspace the $\hat{Q}^i_\pm$ operators are Hermitian, and their conservation follows from the conservation of $\hat{\mathbf{L}}$, $\hat{\mathbf{K}}$, and $\hat{H}$ itself.

(f) Show that the six operators $\hat{Q}^i_\pm$ obey the following $SO(3) \times SO(3)$ commutation relations:

$$\left[\hat{Q}^i_+, \hat{Q}^j_+\right] = i\hbar\epsilon^{ijk}\hat{Q}^k_+\,, \quad \left[\hat{Q}^i_-, \hat{Q}^j_-\right] = i\hbar\epsilon^{ijk}\hat{Q}^k_-\,, \quad \left[\hat{Q}^i_+, \hat{Q}^j_-\right] = 0. \tag{9}$$

This $SO(3) \times SO(3)$ algebra can be used to describe all bound states as $|q_+, m_+, q_-, m_-\rangle$ —

simultaneous eigenstates of the $\hat{\mathbf{Q}}_\pm^2$ and $\hat{Q}_\pm^z$ operators. However, this description is somewhat redundant:

(g) Verify that $\hat{\mathbf{K}} \cdot \hat{\mathbf{L}} = \hat{\mathbf{L}} \cdot \hat{\mathbf{K}} = 0$ and use this fact to show that all bound states have $\mathbf{Q}_+^2 = \mathbf{Q}_-^2$ and hence $q_+ = q_-$.

Therefore we can label the bound states of the Coulomb potential as $|q, m_+, m_-\rangle$; their energies depend only on q and thus are $(2q+1)^2$–fold degenerate. To compute those energies:

(h) First, show that

$$\hat{\mathbf{K}}^2 \;=\; (e^2 ZM)^2 \;+\; 2M\hat{H}\left(\hat{\mathbf{L}}^2 + \hbar^2\right) \tag{10}$$

(in classical mechanics $\mathbf{K}^2 = (e^2ZM)^2 + 2ME\mathbf{L}^2$).

(i) Second, use (8) and (10) to derive

$$2\hat{\mathbf{Q}}_+^2 \;+\; 2\hat{\mathbf{Q}}_-^2 \;+\; \hbar^2 \;=\; \frac{(e^2ZM)^2}{-2M\hat{H}}\,. \tag{11}$$

(j) And finally use (11) to show that the energy of the $|q, m_+, m_-\rangle$ bound state is

$$E_N \;=\; -\frac{M(e^2Z)^2}{2\hbar^2(2q+1)^2} \;\equiv\; -\frac{M(e^2Z)^2}{2\hbar^2 N^2} \tag{12}$$

where $N \stackrel{\text{def}}{=} 2q+1$ is a positive integer, usually called the *principal quantum number* of the bound state.

(k) Show that for each value of the principal quantum number N, the orbital quantum number ℓ takes all integer values between zero and $N-1$.
Hint: Use $\hat{\mathbf{L}} = \hat{\mathbf{Q}}_+ + \hat{\mathbf{Q}}_-$.

Also, argue that this means that in terms of ℓ and the radial quantum number n_r, $N = l + n_r + 1$, which implies that the spectrum of N consists of *all* positive integers.
Hint: for a fixed n_r, the bound state energy $E(n_r, \ell)$ must srictly increase with ℓ.

2. Going from the sublime to the mundane, this problem is about the Clebbsch–Gordan coefficients $\langle j_1, j_1, j, m | j_1, m_1, j_1, m_2 \rangle$.

   Let's start with the states of an electron with a given orbital angular momentum $\ell > 0$ and spin $s = \frac{1}{2}$. In terms of the net angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, these $(2\ell + 1) \times 2$ states form two multiplets with $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$. Specifically, the states with definite j and m_j are

$$\begin{aligned} \left| j = \ell + \tfrac{1}{2}, m_j \right\rangle \ &= \ \sqrt{\frac{\ell + \frac{1}{2} + m_j}{2\ell + 1}} \left| m_\ell = m_j - \tfrac{1}{2}, m_s = +\tfrac{1}{2} \right\rangle \\ &\quad + \sqrt{\frac{\ell + \frac{1}{2} - m_j}{2\ell + 1}} \left| m_\ell = m_j + \tfrac{1}{2}, m_s = -\tfrac{1}{2} \right\rangle, \end{aligned} \tag{13}$$

$$\begin{aligned} \left| j = \ell - \tfrac{1}{2}, m_j \right\rangle \ &= \ \sqrt{\frac{\ell + \frac{1}{2} - m_j}{2\ell + 1}} \left| m_\ell = m_j - \tfrac{1}{2}, m_s = +\tfrac{1}{2} \right\rangle \\ &\quad - \sqrt{\frac{\ell + \frac{1}{2} + m_j}{2\ell + 1}} \left| m_\ell = m_j + \tfrac{1}{2}, m_s = -\tfrac{1}{2} \right\rangle. \end{aligned} \tag{14}$$

   (a) First, argue that

$$\left| j = \ell + \tfrac{1}{2}, m_j = \ell + \tfrac{1}{2} \right\rangle \ = \ \left| m_\ell = +\ell, m_s = +\tfrac{1}{2} \right\rangle. \tag{15}$$

   Then verify eq. (13) for the rest of the $j = \ell + \frac{1}{2}$ states by recursively applying the operator $\hat{J}_- = \hat{L}_- + \hat{S}_-$ to both sides of eq. (13).

   (b) Given eqs. (13) for the $j = \ell + \frac{1}{2}$ states, derive eqs. (14) for the $j = \ell - \frac{1}{2}$ states from the orthogonality condition $\left\langle j = \ell + \frac{1}{2}, m_j | j = \ell - \frac{1}{2}, m_j \right\rangle = 0$ (for the same m_j).

   (c) Verify that eqs. (14) are consistent with the action of the $\hat{J}_- = \hat{L}_- + \hat{S}_-$ operator.

3. Finally, an optional exercise, for extra credit. This problem is also about the Clebbsch–Gordan coefficients.

   Consider a free oxygen atom. In its ground state, 6 out of 8 electrons are paired up, while the 2 un-paired electrons in 2p orbitals have net orbital angular momentum $L = 1$ and net spin $S = 1$, so altogether there are $3 \times 3 = 9$ degenerate states (before we take the spin-orbit coupling into account). In terms of the net angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$, the nine states form a $J = 2$ quintiplet, a $J = 1$ triplet, and a $J = 0$ singlet.

Your task is to spell out states $|J, m_J\rangle$ with definite values of J and m_J as linear combinations of states $|m_L, m_S\rangle$ with definite m_L and m_S.

(a) Start with the $J = 2$ states. First, identify the $|J = 2, m_J = +2\rangle$ state as the only state with $m_J = +2$, and then act recursively with the $\hat{J}_- = \hat{L}_- + \hat{S}_-$ operator to build the rest of the $|J = 2, m_J\rangle$ states.

(b) Next, the $J = 1$ states. Find the $|J = 1, m_J = +1\rangle$ state as the linear combination of only two states with $m_L + m_S = +1$ which is orthogonal to the $|J = 2, m_J = +1\rangle$ state. Then act recursively with the $\hat{J}_- = \hat{L}_- + \hat{S}_-$ operator to build the rest of the $|J = 1, m_J\rangle$ states.

(c) Finally, find the $|J = 0, m_J = 0\rangle$ state as the linear combination of the three states with $m_L + m_S = 0$ which is orthogonal to both $|J = 2, m_J = 0\rangle$ and $|J = 1, m_J = 0\rangle$.