

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

$$\mathbf{K} \stackrel{\text{def}}{=} \mathbf{p} \times \mathbf{L} - e^2 Z M \mathbf{n} \quad (1)$$

where M is the particle’s mass, $\mathbf{L} \stackrel{\text{def}}{=} \mathbf{x} \times \mathbf{p}$ is its angular momentum and $\mathbf{n} \stackrel{\text{def}}{=} \mathbf{x}/r$ 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 $\varepsilon = |\mathbf{K}|/e^2 Z M$,

$$r(\phi) = \frac{\mathbf{L}^2}{e^2 Z M + |\mathbf{K}| \cos \phi} \quad (2)$$

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 $\mathbf{x} \cdot \mathbf{K} = \mathbf{L}^2 - e^2 Z M r$.

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

$$\begin{aligned} \hat{\mathbf{K}} &\stackrel{\text{def}}{=} \frac{1}{2} \left(\hat{\mathbf{p}} \times \hat{\mathbf{L}} - \hat{\mathbf{L}} \times \hat{\mathbf{p}} \right) - e^2 Z M \hat{\mathbf{n}} \\ &= \hat{\mathbf{p}} \times \hat{\mathbf{L}} - i\hbar \hat{\mathbf{p}} - e^2 Z M \hat{\mathbf{n}}. \end{aligned} \quad (3)$$

- (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

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

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

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

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

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

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

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

in the bound-state subspace. In this subspace the \hat{Q}_\pm^i 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}_\pm^i obey the following $SO(3) \times SO(3)$ commutation relations:

$$\left[\hat{Q}_+^i, \hat{Q}_+^j\right] = i\hbar\epsilon^{ijk}\hat{Q}_+^k, \quad \left[\hat{Q}_-^i, \hat{Q}_-^j\right] = i\hbar\epsilon^{ijk}\hat{Q}_-^k, \quad \left[\hat{Q}_+^i, \hat{Q}_-^j\right] = 0. \quad (9)$$

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

$$\hat{\mathbf{K}}^2 = (e^2 Z M)^2 + 2M\hat{H} (\hat{\mathbf{L}}^2 + \hbar^2) \quad (10)$$

(in classical mechanics $\mathbf{K}^2 = (e^2 Z M)^2 + 2MEL^2$).

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

$$2\hat{\mathbf{Q}}_+^2 + 2\hat{\mathbf{Q}}_-^2 + \hbar^2 = \frac{(e^2 Z M)^2}{-2M\hat{H}}. \quad (11)$$

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

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

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 , $N = \ell + n_r + 1$, 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 strictly increase with ℓ .

2. Going from the sublime to the mundane, this problem is about the Clebsch–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

$$|j = \ell + \frac{1}{2}, m_j\rangle = \sqrt{\frac{\ell + \frac{1}{2} + m_j}{2\ell + 1}} |m_\ell = m_j - \frac{1}{2}, m_s = +\frac{1}{2}\rangle + \sqrt{\frac{\ell + \frac{1}{2} - m_j}{2\ell + 1}} |m_\ell = m_j + \frac{1}{2}, m_s = -\frac{1}{2}\rangle, \quad (13)$$

$$|j = \ell - \frac{1}{2}, m_j\rangle = \sqrt{\frac{\ell + \frac{1}{2} - m_j}{2\ell + 1}} |m_\ell = m_j - \frac{1}{2}, m_s = +\frac{1}{2}\rangle - \sqrt{\frac{\ell + \frac{1}{2} + m_j}{2\ell + 1}} |m_\ell = m_j + \frac{1}{2}, m_s = -\frac{1}{2}\rangle. \quad (14)$$

- (a) First, argue that

$$|j = \ell + \frac{1}{2}, m_j = \ell + \frac{1}{2}\rangle = |m_\ell = +\ell, m_s = +\frac{1}{2}\rangle. \quad (15)$$

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 $\langle j = \ell + \frac{1}{2}, m_j | j = \ell - \frac{1}{2}, m_j \rangle = 0$ (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 Clebsch–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 $J = 2$ quintuplet, 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 $|J = 1, m_J = 0\rangle$.