PHY215-14: LS and JJ Couplings

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April 22, 2025

1 Pauli Exclusion Principle and the symmetry of the total wavefunction

Regarding the Pauli Exclusion Principle and the symmetry of the total wavefunction for a system of two electrons (fermions), here's a detailed analysis:

1.1 Pauli Exclusion Principle and Antisymmetry Requirement

The Pauli Exclusion Principle states that the total wavefunction of a system of fermions (e.g., electrons) must be antisymmetric under the exchange of any two particles. For two electrons, the total wavefunction is the product of the orbital (spatial) wavefunction (ψ_{orbital}) and the spin wavefunction (ψ_{spin}):

$$\psi_{\text{total}} = \psi_{\text{orbital}} \otimes \psi_{\text{spin}}.$$

For ψ_{total} to be antisymmetric, the product of the symmetries of ψ_{orbital} and ψ_{spin} must be antisymmetric. This means: - If ψ_{orbital} is symmetric (denoted S), then ψ_{spin} must be antisymmetric (denoted A). - If ψ_{orbital} is antisymmetric (A), then ψ_{spin} must be symmetric (S).

1.2 Case of Two Electrons in Different States

Suppose one electron is in the ground state ($|\phi_1\rangle$) and the other is in an excited state ($|\phi_2\rangle$), where $|\phi_1\rangle \neq |\phi_2\rangle$.

Orbital Wavefunction Symmetry The orbital wavefunction for two distinguishable states can be either: - Symmetric:

$$\psi_{\text{orbital}}^{\text{sym}} = \frac{1}{\sqrt{2}} \left(|\phi_1\rangle_1 |\phi_2\rangle_2 + |\phi_2\rangle_1 |\phi_1\rangle_2 \right),$$

- Antisymmetric:

$$\psi_{\text{orbital}}^{\text{asym}} = \frac{1}{\sqrt{2}} \left(|\phi_1\rangle_1 |\phi_2\rangle_2 - |\phi_2\rangle_1 |\phi_1\rangle_2 \right).$$

Spin Wavefunction Symmetry For two electrons, the spin wavefunctions are:
- Symmetric (triplet states, $S = 1$):

$$\chi^{\text{sym}} = \begin{cases} |\uparrow\uparrow\rangle, \\ \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right), \\ |\downarrow\downarrow\rangle. \end{cases}$$

- Antisymmetric (singlet state, $S = 0$):

$$\chi^{\text{asym}} = \frac{1}{\sqrt{2}} \left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right).$$

Allowed Combinations To satisfy the antisymmetry of ψ_{total}:
1. Symmetric orbital + Antisymmetric spin:

$$\psi_{\text{total}} = \psi_{\text{orbital}}^{\text{sym}} \otimes \chi^{\text{asym}} \quad \text{(antisymmetric overall)}.$$

2. Antisymmetric orbital + Symmetric spin:

$$\psi_{\text{total}} = \psi_{\text{orbital}}^{\text{asym}} \otimes \chi^{\text{sym}} \quad \text{(antisymmetric overall)}.$$

Forbidden Combinations - Symmetric orbital + Symmetric spin:
The total wavefunction would be symmetric ($S \otimes S = S$), violating the Pauli principle.
- Antisymmetric orbital + Antisymmetric spin: The total wavefunction would be symmetric ($A \otimes A = S$), also violating the Pauli principle.

1.3 Key Takeaway

Even when electrons occupy different states (ground and excited), the Pauli Exclusion Principle still requires the total wavefunction to be antisymmetric. This means:
- A state with a symmetric spin wavefunction (triplet) must have an antisymmetric orbital wavefunction.
For example, it is possible to have the atomic states of helium as:
$1s^1 2s^1$ with $L = 0$,

If $S = 0$, then $J = 0$, denoted as 1^1S_0.
If $S = 1$, then $J = 1$, denoted as 2^3S_1.
Hence, the lowest excited state is 2^3S_1 and then comes 2^1S_0. Here, $\vec{S} = \vec{S}_1 + \vec{S}_2$, etc.
The ground state is $1s^1 1s^1$ with $L = 0$ and $J = 0$, denoted as 1^1S_0. Note that 1^3S_1 is forbidden.

- A state with both symmetric spin and symmetric orbital wavefunctions is forbidden because it would result in a symmetric total wavefunction, contradicting the antisymmetry requirement for fermions.

Analogy to Identical Particles The requirement arises because electrons are indistinguishable particles: their wavefunctions must not distinguish between them. Antisymmetry ensures that swapping electrons introduces a minus sign, which is characteristic of fermions (via the spin-statistics theorem). This is distinct from bosons (e.g., photons), which require symmetric wavefunctions.

In summary: The total wavefunction must be antisymmetric, and states with symmetric spin and symmetric orbital wavefunctions are not allowed.

2 J-J Coupling in Heavier Atoms

In atomic physics, the dominance of J-J coupling (also known as ”jj coupling”) in heavier atoms arises from the relative strengths of two key interactions: electrostatic repulsion between electrons (which drives LS coupling, or Russell-Saunders coupling) and spin-orbit coupling (which drives jj coupling). Here’s a detailed explanation:

2.1 Two Coupling Schemes: LS vs. JJ

2.1.1 LS Coupling (Russell-Saunders Coupling)

- Applies to light atoms (low atomic number, Z). - Electrons interact primarily via electrostatic repulsion (Coulomb interaction), which is the dominant force. - Orbitals of different electrons first combine to form a total orbital angular momentum

$$\mathbf{L} = \sum \mathbf{l}_i$$

and spins combine to form total spin

$$\mathbf{S} = \sum \mathbf{s}_i$$

- **L** and **S** then couple to form total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

2.1.2 JJ Coupling

- Applies to heavier atoms (high Z). - The spin-orbit interaction (a relativistic effect) becomes stronger than electron-electron repulsion. - For each electron, its orbital angular momentum $\mathbf{l}_i$ and spin $\mathbf{s}_i$ first couple to form a single-electron total angular momentum

$$\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i$$

- These $\mathbf{j}_i$ then combine to form the total angular momentum

$$\mathbf{J} = \sum \mathbf{j}_i$$

2.2 Why Spin-Orbit Coupling Strengthens with Z

The spin-orbit interaction energy is given by:

$$\Delta E_{\text{SO}} \propto \frac{Z^4}{n^3 l(l+1)} \quad \text{(for hydrogen-like atoms)}$$

where n is the principal quantum number and l is the orbital angular momentum quantum number. Key reasons for its increase in heavy atoms:

- **Effective Nuclear Charge (Z_{eff})**: In heavy atoms, inner-shell electrons are tightly bound, and outer electrons experience a large Z_{eff} due to incomplete shielding. This enhances the electromagnetic interaction between the electron's spin and its orbital motion around the nucleus.

- **Relativistic Effects**: Electrons in heavy atoms move at speeds comparable to the speed of light (especially in inner shells), making relativistic corrections to the electron's mass and magnetic moment significant. Spin-orbit coupling is a relativistic effect and becomes stronger with increasing electron velocity.

- **Proportionality to Z^4**: The interaction energy grows rapidly with Z, surpassing the electron-electron repulsion energy (which scales as $\sim Z$ for outer electrons in multi-electron atoms).

2.3 Competition Between Interactions

- **For Light Atoms (Z small)**: Electron-electron repulsion (Coulomb interaction) is the strongest force. It causes orbitals to couple first into $\mathbf{L}$ and spins into $\mathbf{S}$ (LS coupling), as the energy splitting due to Coulomb repulsion is much larger than spin-orbit splitting.

- **For Heavy Atoms (Z large)**: Spin-orbit coupling overtakes Coulomb repulsion as the dominant interaction. Each electron's $\mathbf{l}_i$ and $\mathbf{s}_i$ couple into $\mathbf{j}_i$ first, and the weaker Coulomb interaction then couples the $\mathbf{j}_i$ into $\mathbf{J}$ (JJ coupling).

2.4 Mathematical Perspective: Hamiltonian Terms

The total Hamiltonian for a multi-electron atom includes:

1. **Coulomb Interaction ($H_{\textbf{Coulomb}}$)**: Drives LS coupling, pro-

portional to $\sim \frac{1}{r_{ij}}$ (electron-electron repulsion).
2. **Spin-Orbit Interaction ($H_{\mathbf{SO}}$)**: Drives JJ coupling, proportional to $\sim \mathbf{l}_i \cdot \mathbf{s}_i$, which increases with Z.

In heavy atoms, $|H_{\mathrm{SO}}| > |H_{\mathrm{Coulomb}}|$ for outer electrons, so the eigenstates are better described by jj coupling. In light atoms, $|H_{\mathrm{Coulomb}}| \gg |H_{\mathrm{SO}}|$, so LS coupling is valid.

2.5 Example: Transition from LS to JJ Coupling

- **Light Atoms (e.g., Carbon, $Z = 6$)**: Terms like ${}^3P_0, {}^3P_1, {}^3P_2$ (LS-coupled triplet states) are good approximations.

- **Heavy Atoms (e.g., Lead, $Z = 82$)**: Outer electrons (e.g., $6p^2$ configuration) form states like ${}^3P_{1/2,3/2}$, where each electron's $\mathbf{j}_i$ (e.g., $p_{1/2}$ and $p_{3/2}$) couple to form total J.

3 Residual Electrostatic Energy in Quantum Physics

In quantum physics, residual electrostatic energy refers to the remaining electron-electron interaction energy that persists after accounting for the average Coulomb repulsion in multi-electron atoms. For atoms with two valence electrons (e.g., helium or alkaline earth metals), this residual energy plays a critical role in explaining the splitting of spectral lines, particularly in the context of LS coupling (Russell-Saunders coupling). Here's a detailed breakdown:

3.1 Context of Two Valence Electrons

Atoms with two valence electrons (e.g., $\mathrm{He}, \mathrm{Be}, \mathrm{Mg}$) exhibit spectral lines that split into closely spaced components due to electron-electron interactions. This splitting arises from two primary effects:
- Residual electrostatic energy (electron-electron repulsion beyond the central field approximation).
- Spin-orbit coupling (relativistic interaction between electron spin and orbital motion).

The residual electrostatic energy is distinct from spin-orbit coupling and dominates the fine structure of spectral lines in lighter atoms.

3.2 Definition of Residual Electrostatic Energy

Residual electrostatic energy is the non-averaged component of the electron-electron Coulomb interaction that cannot be captured by the central field approximation. In the central field model, each electron experiences an averaged potential from the nucleus and other electrons, which simplifies the Hamiltonian. However, this approximation neglects the tensor component of the electron-electron repulsion, which depends on the relative orientation of the electrons' spins and orbits.

Mathematically, the residual electrostatic energy can be expressed as:

$$H_{\text{residual}} = \frac{e^2}{4\pi\epsilon_0} \sum_{i<j} \frac{1}{r_{ij}} - \text{average Coulomb term}$$

where r_{ij} is the distance between electrons i and j. This term splits energy levels with the same total orbital angular momentum L and total spin S into different fine structure components (e.g., $^3P_0, ^3P_1, ^3P_2$ for $L = 1, S = 1$).

3.3 Role in Spectral Line Splitting

For two valence electrons, the residual electrostatic energy causes term splitting within a given electron configuration (e.g., $1s^2, 2s^2, 2p^2$). Key points include:

- **LS Coupling**: The residual energy couples the electrons' orbital angular momenta (L_1, L_2) and spins (S_1, S_2) into total angular momentum L and S. The energy splitting depends on the relative orientation of L and S (e.g., singlet vs. triplet states).

Example: In helium's $2p^2$ configuration, the residual energy splits the ^3P term into three levels ($^3P_0, {}^3P_1, {}^3P_2$) and the ^1D term into one level ($^1D_2$). These splits manifest as closely spaced spectral lines in emission or absorption spectra.

- **Comparison to Spin-Orbit Coupling**: While spin-orbit coupling also causes fine structure splitting, it is a relativistic effect that becomes significant in heavier atoms. Residual electrostatic energy dominates in lighter atoms (e.g., helium).

3.4 Mathematical Formulation

In LS coupling, the residual electrostatic energy is often treated using perturbation theory. The interaction Hamiltonian includes terms like:

$$H_{\text{residual}} \propto \sum_{i<j} \frac{1}{r_{ij}} \left[\frac{3(\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} - \mathbf{s}_i \cdot \mathbf{s}_j \right]$$

where $\mathbf{s}_i$ and $\mathbf{s}_j$ are electron spins, and $\mathbf{r}_{ij}$ is the vector between electrons. This term depends on the relative orientation of spins and orbital motion, leading to energy shifts proportional to $L \cdot S$.

3.5 Experimental Evidence

The splitting of spectral lines due to residual electrostatic energy is observed in experiments like:
- **Optical spectroscopy**: Fine structure in helium's $2p \rightarrow 1s$ transition (e.g., the D-line in sodium).
- **Electron paramagnetic resonance (EPR)**: Splitting of hyperfine lines in free radicals, where residual interactions modify energy levels.

4 Selection rules for electric-dipole induced transitions

Overview of Selection Rules for Electric Dipole Transitions

In atomic physics, the selection rules for electric dipole-induced transitions in atoms arise from the requirement that the electric dipole transition matrix element $\langle \psi_f | \hat{\mathbf{d}} | \psi_i \rangle$ (where $\hat{\mathbf{d}} = -e\hat{\mathbf{r}}$ is the dipole operator) must be non-zero. These rules govern the allowed changes in quantum numbers between initial (i) and final (f) states of the electron.

- Mathematically, the transition matrix element for a dipole transition is:

$$\langle \psi_{\text{final}} | H_{\text{dipole}} | \psi_{\text{initial}} \rangle = \langle \chi_{\text{final}}^{\text{spin}} | \chi_{\text{initial}}^{\text{spin}} \rangle \cdot \langle \phi_{\text{final}}^{\text{orbital}} | H_{\text{dipole}} | \phi_{\text{initial}}^{\text{orbital}} \rangle$$

where χ and ϕ are spin and orbital wavefunctions, respectively. For the matrix element to be non-zero, the spin overlap integral $\langle \chi_{\text{final}} | \chi_{\text{initial}} \rangle$ must be non-zero, which implies a set of selection rules, as described below.

1. Principal Quantum Number (n)

There is no strict selection rule for n, but transitions are more probable for small $|\Delta n|$.

$$\Delta n = n_f - n_i = \text{any integer (though probabilities decrease for large } |\Delta n|)$$

2. Orbital Angular Momentum Quantum Number (l)

$$\Delta l = l_f - l_i = \pm 1$$

- The **Parity** of the state (even/odd, determined by $(-1)^l$) must change. Hence, The orbital angular momentum must change by ±1.
Example: Transitions between s-orbitals ($l = 0$) and p-orbitals ($l = 1$) are allowed ($\Delta l = \pm 1$), but transitions between s-orbitals ($\Delta l = 0$) or $p \to d$ ($\Delta l = +2$) are forbidden for electric dipole transitions.

3. Magnetic Quantum Number (m_l)

$$\Delta m_l = m_{l,f} - m_{l,i} = 0, \pm 1$$

- The magnetic quantum number can change by 0, $+1$, or -1.
- The specific value depends on the polarization of the incident light:

- Linearly polarized light along the z-axis: $\Delta m_l = 0$.
- Circularly polarized light (right/left-handed): $\Delta m_l = +1/-1$ (related to angular momentum conservation with the photon).

4. Spin Quantum Number (s) and Total Spin (S)

For single-electron atoms (or in the LS coupling scheme for multi-electron atoms):

$$\Delta s = 0 \quad \text{and} \quad \Delta S = 0$$

- The spin quantum number of the electron (or total spin of the atom) does not change.
- Electric dipole transitions are spin-allowed only if the total spin S is conserved.

These selection rules are fundamental for interpreting atomic spectra (e.g., allowed/forbidden lines in emission/absorption) and are derived from the theory of angular momentum coupling and the symmetry of the electromagnetic interaction.

5 Selection Rules for Spin Transitions

In atomic physics, the allowedness of transitions involving changes in total spin quantum number (ΔS) is governed by selection rules for electromagnetic dipole (E1) transitions, which are the dominant mechanism for most atomic spectral lines. Here's a breakdown of why $\Delta S = 0$ transitions are allowed while $\Delta S = 1$ transitions are forbidden:

5.1 Fundamental Symmetry of Electromagnetic Interactions

The electromagnetic field (responsible for dipole transitions) interacts with the orbital motion of electrons (via the electric dipole moment $\propto \mathbf{r}$) but does not directly couple to the electron spin (the spin interacts weakly via magnetic dipole or higher-order interactions, which are much less probable). The dipole interaction Hamiltonian is:

$$H_{\text{dipole}} \propto \mathbf{E} \cdot \sum_i e_i \mathbf{r}_i$$

where $\mathbf{E}$ is the electric field and $\mathbf{r}_i$ is the position of electron i. This operator does not involve spin operators ($\mathbf{s}_i$), meaning it cannot change the total spin state of the atom.

5.2 Selection Rule for Total Spin (S): $\Delta S = 0$

In the LS coupling scheme (valid for light atoms, where spin-orbit coupling is weak), the total spin S is a "good quantum number," meaning it is conserved during dipole transitions. Since the dipole Hamiltonian does not act on spin, the initial and final states must have the same total spin:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = 0$$

- **Allowed transition example**: A singlet state ($S = 0$) can transition to another singlet state ($S = 0$), e.g., ${}^1S_0 \rightarrow {}^1P_1$.
- **Forbidden transition example**: A singlet state ($S = 0$) cannot transition to a triplet state ($S = 1$), as this would require $\Delta S = 1$, violating the selection rule.

5.3 Why $\Delta S = 1$ Transitions Are Forbidden

A transition with $\Delta S = 1$ would require the dipole operator to change the total spin, but: - The dipole operator does not act on spin states (it only acts on spatial/orbital wavefunctions).
- The spin wavefunction is therefore "blind" to the dipole interaction, meaning the spin part of the wavefunction must remain unchanged during the transition.
- Mathematically, the transition matrix element for a dipole transi-

tion is:

$$\langle\psi_{\text{final}}|H_{\text{dipole}}|\psi_{\text{initial}}\rangle = \langle\chi_{\text{final}}^{\text{spin}}|\chi_{\text{initial}}^{\text{spin}}\rangle \cdot \langle\phi_{\text{final}}^{\text{orbital}}|H_{\text{dipole}}|\phi_{\text{initial}}^{\text{orbital}}\rangle$$

where χ and ϕ are spin and orbital wavefunctions, respectively. For the matrix element to be non-zero, the spin overlap integral $\langle\chi_{\text{final}}|\chi_{\text{initial}}\rangle$ must be non-zero, which requires $S_{\text{final}} = S_{\text{initial}}$ (i.e., $\Delta S = 0$).

5.4 Exceptions and Higher-Order Interactions

While $\Delta S = 1$ transitions are forbidden for electric dipole (E1) transitions, they can occur via magnetic dipole (M1) or electric quadrupole (E2) transitions, which:
- Are weaker (typically $\sim 10^3 - -10^6$ times less probable than E1 transitions).
- Involve spin-dependent interactions (e.g., M1 transitions couple to the magnetic moment, which includes spin).

However, in most atomic spectroscopy (e.g., visible light transitions), E1 transitions dominate, and $\Delta S = 1$ transitions are effectively forbidden.

5.5 Example: Helium Atom

In helium, the singlet-triplet gap (e.g., ${}^1S_0 \leftrightarrow {}^3S_1$) is a classic example:

- Transitions between singlet ($S = 0$) and triplet ($S = 1$) states ($\Delta S = 1$) are electric dipole forbidden and are rarely observed in optical spectra.
- Transitions within the same spin multiplicity ($\Delta S = 0$), like ${}^1P_1 \rightarrow {}^1S_0$, are allowed and dominate the spectrum.