Angular Momentum Coupling and Rabi Frequencies for Simple Atomic Transitions

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The Rabi frequency (coupling strength) of an electric-dipole transition is an important experimental parameter in laser-cooling and other atomic physics experiments. Though the relationship between Rabi frequency and atomic wavefunctions and/or atomic lifetimes is discussed in many references, there is a need for a concise, self-contained, accessible introduction to such calculations suitable for use by the typical student of laser cooling (experimental or theoretical). In this paper, I outline calculations of the Rabi frequencies for atoms with sub-structure due to orbital, spin and nuclear angular momentum. I emphasize the physical meaning of the calculations.

I. INTRODUCTION

In designing or implementing many modern atomic physics experiments (e.g. laser cooling, magneto-optical trapping, dipole trapping, optical pumping, etc.) it is important to be able to calculate the coupling strength or Rabi frequency of a laser-driven transition between two atomic states. However, a first attempt to do this can be a frustrating experience.

Many of the older books on atomic spectroscopy were written at a time when coherent excitation was not possible; for this reason these works often focus on multi-line excitation or on spontaneous emission from many, thermally excited levels. In addition to the pedagogical barrier this may present, one may also have to surmount the obstacles of older notations for quantum states or the use of CGS units. Though translating to more modern usage is straightforward in principle, in practice it can be a confusing endeavour. More modern textbooks which treat laser-atom interactions at an introductory level are either aimed at laser dynamics, treat the atoms as two-level systems, or only sketch out the calculations.\[3\]

In fact, there are no two-level atoms, and so practical calculations of Rabi frequencies are more involved. However, the fact that the atomic states have well-defined symmetries - as embodied by the Wigner-Eckart theorem - allows for considerable simplification in the calculations. In this paper, I attempt to provide a pedagogical overview of Rabi-frequency calculations for multi-level atoms. Wherever possible, I try to provide physical pictures corresponding to the math. Since the majority of laser-cooling experiments are performed on hydrogen-like atoms (e.g. Li, Na, K, Rb, Cs, Be\(^+\), Mg\(^+\), Cd\(^+\),...), I treat only single-electron excitation of atoms with such a configuration. Likewise, since the laser-atom interactions are typically electric-dipole transitions, I only calculate Rabi frequencies for such transitions. Though the generalization of the calculations to magnetic dipole, electric quadrupole transitions, etc., is straightforward, the reader is referred to the literature for such calculations.

In Sec. IIA, I review the interaction between a linearly polarized laser field and a two-level atom in the rotating-wave and dipole approximations, as parametrized by the Rabi frequency. Next (Sec. IIB), I outline the repurcussions of degeneracy. After a brief overview of rotational symmetry and the quantum implications in Sec. III, I treat the combination of angular momenta in Sec. IIIA. In Sec. IIIB I explain how the Wigner-Eckart theorem can simplify calculations for transitions between states of well-defined angular momentum, if the transitions may be represented in terms of operators with well-defined rotational symmetry (i.e. as tensor operators).

Using the Wigner-Eckart theorem, I relate the Rabi frequencies of transitions between various angular-momentum sublevels to the excited-state lifetime. I first treat states with well-defined total angular momentum \(\mathbf{J}\) (Sec. IV), before breaking down the explicit dependence upon orbital angular momentum \(\mathbf{L}\) and radial overlap integrals \(R_{nlm'}^{\mu}\) (Sec. IVA). Finally, I discuss the case of atoms with nuclear spin and hyperfine structure in Sec. IVB. The main results of this paper are Eq. (3) (which expresses the Rabi frequency in terms of the laser beam’s electric field, intensity, and the power/beam waist of a Gaussian beam) and Eq. (39), Eq. (49), and Eq. (52), which relate the Rabi frequency to the atom’s lifetime and the electric field of the laser in various angular momentum coupling schemes.

This present work attempts to provide the bare minimum of material necessary for the reader to understand and calculate the Rabi frequency for simple cases. In an attempt to save the reader an exhaustive literature search, I have, wherever possible, drawn mathematical results from a single source - Messiah’s canonical text on quantum mechanics.\[4\] Metcalf and van der Straten’s book places this calculation in the context of laser cooling and trapping of neutral atoms.\[5\] For further background, Cowan and Weissbluth’s books provide excellent reading. Finally, Suhonen’s\[6\] gives a succinct review of angular momentum and irreducible tensor operators, while Silver\[7\] provides further discusson of rotational symmetry and tensors.
II. THE RABI FREQUENCY

A. The Dipole Interaction with two-level atoms

Let us begin by considering the case of a (fictional) atom with only two levels: ground state $|g\rangle$ and excited state $|e\rangle$. Let the energies of these levels be $E_g$ and $E_e$, respectively, and let $\omega_0 = (E_e - E_g)/\hbar$. In general, the state of the atom may be written as $|\Psi\rangle = c_g(t)|g\rangle + c_e(t)|e\rangle$, where $|c_g(t)|^2 + |c_e(t)|^2 = 1$.

Suppose that one applies to this atom a resonant, linearly-polarized laser field of the form $\mathbf{E}(r, t) = \epsilon E_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega_L t)$. Here $E_0$ is the electric-field amplitude, $\mathbf{k}$ is the wavevector, $\omega_L$ is the angular frequency of the laser, which we take to be equal to $\omega_0$, and $\epsilon$ is a unit vector in the direction of polarization ($\epsilon \perp \mathbf{k}$). The basis vectors for the atomic Hilbert space are themselves unit vectors in the direction of polarization ($\epsilon \perp \mathbf{k}$).

Under the assumptions that the laser interaction is weak compared to atomic effects and that the size of the atom is much less than the wavelength of light, we may make the electric-dipole approximation, the interaction Hamiltonian is given by $\hat{V}_I = -\hat{\mu} \cdot \mathbf{E}$. Here $\hat{\mu} = -\epsilon \hat{r}$ is the dipole operator for the atom and $e$ is magnitude of the charge on the electron. The result of the interaction is that $|g\rangle$ and $|e\rangle$ become coupled.

Suppose that the atom is initially in the state $|g\rangle$. If we neglect spontaneous emission from $|e\rangle$, then under the rotating-wave approximation and in the Schrödinger representation, the time dependence of the system is given by

\begin{align}
   c_g(t) &= e^{-iE_g t/\hbar} \cos \left( \frac{\Omega t}{2} \right), \quad \text{(1a)} \\
   c_e(t) &= e^{-iE_e t/\hbar} \sin \left( \frac{\Omega t}{2} \right). \quad \text{(1b)}
\end{align}

(The exponential terms show the time evolution due to the bare atomic Hamiltonian.) Here, I have defined the Rabi frequency of the transition to be

$$\Omega := -\frac{\langle \epsilon | \hat{\mu} \cdot \mathbf{E} | g \rangle}{\hbar}.$$  \hspace{1cm} \text{(2)}

The Rabi frequency measures the strength of the coupling between the atomic states and the applied electromagnetic field. Practically speaking, one doesn’t directly measure the electric field amplitude, but rather the peak intensity $I = \frac{1}{2}c_0E_0^2$ of the laser beam or, more typically, the total power $P$ and beam waist $w_0$ of a Gaussian laser beam ($I = \frac{2P}{\pi w_0^2}$). Thus:

$$\Omega = \frac{cE_0}{\hbar} \langle \epsilon | \hat{\mu} \cdot \mathbf{E} | g \rangle$$ \hspace{1cm} \text{(3a)}$$

\begin{align}
   &= -\frac{\sqrt{\epsilon^2 2I}}{c_0 E_0^2} \langle \epsilon | \hat{\mu} \cdot \mathbf{E} | g \rangle \quad \text{(3b)} \\
   &= -\frac{\sqrt{4\epsilon^2 P}}{4c_0 \pi \hbar^2 c w_0^2} \langle \epsilon | \hat{\mu} \cdot \mathbf{E} | g \rangle \quad \text{(3c)}
\end{align}

Eq. (3) indicates that the state vector of the system oscillates coherently between $|g\rangle$ and $|e\rangle$ with frequency $\Omega/2$ - a behaviour which is called Rabi flopping. On the other hand, the populations oscillate as $|c_g|^2 = \cos^2 \left( \frac{\Omega t}{2} \right) = \frac{1}{2} \left[ 1 + \cos (\Omega t) \right]$ and $|c_e|^2 = \sin^2 \left( \frac{\Omega t}{2} \right) = \frac{1}{2} \left[ 1 - \cos (\Omega t) \right]$. So according to Eq. (1), the Rabi frequency is the frequency at which the populations oscillate. A pulse for which $\Omega t = \pi$ is called a “pi pulse” - it results in complete population transfer to the excited state. Similarly a pulse for which $\Omega t = \pi/2$ is called a “pi-by-two pulse” and results in an equal superposition of ground and excited states. Note that, though a “two-pi pulse” ($\Omega t = 2\pi$) returns the population to the ground state, it takes $\Omega t = 4\pi$ to return the state vector to its initial value. (This is analogous the requirement of a 4\pi rotation to return a spin-$\frac{1}{2}$ particle to its initial state.)

A perturbation-theory approach to the problem (again, in the rotating-wave approximation) predicts that, for short times, before the population of the ground state has been depleted:

$$|c_e(t)|^2 = g(\omega_0) \langle \Omega_{e\rightarrow g}^2 \rangle^2 t, \quad \text{(4)}$$

so that the rate $W_{e\rightarrow g}$ at which the excited-state population grows due to the applied radiation is:

$$W_{e\rightarrow g} = g(\omega_0) \langle \Omega_{e\rightarrow g}^2 \rangle. \quad \text{(5)}$$

Here $g(\omega_0)$ is the lineshape of the transition (units of inverse angular frequency, with $\frac{1}{\sqrt{\Omega_{e\rightarrow g}}}$ $g(\omega)$ $d\omega = 1$).

Of course, spontaneous emission cannot be ignored. Even in the absence of an applied field, the excited state interacts with the vacuum fluctuations of the electromagnetic field. The situation here is somewhat different than that presented above, since the vacuum modes of the electromagnetic field do not represent a narrow-band, directional source. There are several approaches to the problem. The most straightforward is a rate-equation treatment. Generalizing Eq. (5) to a $|g\rangle \rightarrow |e\rangle$ transition, we must also integrate over all possible modes and sum over the two orthogonal polarizations possible for each wavevector (directions $\epsilon_1$ and $\epsilon_2$). Now, the number of plane-wave modes with wavenumbers in the range $[k, k+dk]$ in a container of volume $V$ is $dn = \frac{V}{(2\pi)^3} d^3k = \frac{V}{(2\pi)^3} \omega^2 \sin \theta d\omega d\theta d\phi$ (in spherical-polar coordinates). As well, the energy density corresponding
to zero-point energy $\frac{1}{2}\hbar \omega$ in each mode is $\rho_E(\omega) = \frac{\hbar \omega}{2\pi}$, and basic electrodynamics tells that the square of the corresponding electric field $E^2 = \frac{\hbar \omega}{2\epsilon_0 V}$. So, if we denote by $A_{g\rightarrow e}$ the rate at which the vacuum fluctuations drive population from $|e\rangle$ to $|g\rangle$, then:

$$A_{g\rightarrow e} = \sum_{i=1,2} g(\omega) \left| \frac{\langle g|\hat{r}|e\rangle}{\hbar} \right|^2 \frac{dn}{\omega} = \frac{e^2}{h^2} \int g(\omega) \langle g|\hat{r}|e\rangle \cdot \epsilon_i |\epsilon_i|^2 E^2 \frac{dn}{\omega} = \frac{e^2}{h^2} \int g(\omega) \langle g|\hat{r}|e\rangle \cdot \epsilon_i |\epsilon_i|^2 \frac{\hbar \omega}{2\epsilon_0 V} \frac{V}{(2\pi)^3} d^3 k$$

$$= \frac{e^2}{2(2\pi)^3\epsilon_0 h} \int g(\omega) \langle g|\hat{r}|e\rangle \cdot \epsilon_i |\epsilon_i|^2 \omega^3 \sin \theta d\omega d\theta d\phi$$

Now, we must consider geometry. $\{\epsilon_1, \epsilon_2, \hat{k}\}$ form an orthogonal triad, oriented with respect to $\langle g|\hat{r}|e\rangle$ as indicated in Fig. 1. Consideration of this diagram indicates that $\epsilon_1 \cdot \langle g|\hat{r}|e\rangle = |\langle g|\hat{r}|e\rangle| \sin \theta \cos \varphi$ and $\epsilon_2 \cdot \langle g|\hat{r}|e\rangle = |\langle g|\hat{r}|e\rangle| \sin \theta \sin \varphi$ so that

$$\sum_i |\langle g|\hat{r}|e\rangle| \cdot \epsilon_i|^2 = |\langle g|\hat{r}|e\rangle|^2 \sin^2 \theta$$

(6)

So finally we have:

$$A_{g\rightarrow e} = \frac{e^2}{2(2\pi)^3\epsilon_0 h} \int g(\omega) |\langle g|\hat{r}|e\rangle|^2 \omega^3 \sin \theta d\omega d\theta d\varphi$$

$$= \frac{e^2}{2(2\pi)^3\epsilon_0 h} \frac{8\pi}{3} \int g(\omega) |\langle g|\hat{r}|e\rangle|^2 \omega^3 d\omega$$

$$= \frac{e^2}{6\pi^2\epsilon_0 h} \int g(\omega) |\langle g|\hat{r}|e\rangle|^2 \omega^3 d\omega.$$

(7)

We make the reasonable assumption that the function $g(\omega)$ is sharply peaked around $\omega_0$ (which is true in practice), so that $\int g(\omega) |\langle g|\hat{r}|e\rangle|^2 \omega^3 d\omega \approx \omega_0^3 |\langle g|\hat{r}|e\rangle|^2 \int g(\omega) d\omega = 2\pi |\langle g|\hat{r}|e\rangle|^2 \omega_0^3$. Finally, we have that

$$A_{g\rightarrow e} = \frac{e^2 \omega_0^3}{3\pi\epsilon_0 h^2} |\langle g|\hat{r}|e\rangle|^2 = \frac{8\pi e^2}{3\epsilon_0 h^3} |\langle g|\hat{r}|e\rangle|^2.$$

(8)

Note that $\langle g|\hat{r}|e\rangle = \langle e|\hat{r}|g\rangle$.

For typical optical dipole-allowed transitions, $A \sim 2\pi \times 10^7 \text{ Hz}$ [3]. We may neglect spontaneous emission (recovering the Rabi-flopping behaviour described by Eqs. (1)) if $\Omega \gg A$. However, this requires very high laser intensities. Although spontaneous emission is driven by only a “half photon” in each vacuum mode, there are an immense number of such modes in three-dimensional space. Thus, it requires a large number of photons in a single (laser) mode to change population at a rate approaching that of spontaneous emission. However, if the field and excited state are separated by energies corresponding to long-wavelength, radio-frequency photons, or if the coupling between them is due to higher-order transitions (electric quadrupole or magnetic dipole), then it may be possible to realize Rabi flopping.

A rate-equation treatment of the above type was first performed by Einstein [3]. For this reason, the rate $A_{g\rightarrow e}$ is called the “Einstein $A$-coefficient.” In the absence of other broadening mechanisms (e.g. Doppler or pressure broadening), it gives the natural lifetime $\tau$ of the excited state and hence the full-width-half maximum $\Gamma = 2\pi \times \Delta \nu$ of the lineshape:

$$A_{g\rightarrow e} = \frac{1}{\tau}$$

(9)

(for a two-level atom). To be explicit, $\Gamma$ in radians per second, whereas $\Delta \nu$ is in Hertz. The lifetime depends only on the dipole moment of the transition between the levels in question (which goes into any Rabi frequency calculation) and the energy-density corresponding to the zero-point fluctuations of the electromagnetic field (fixed for our universe).

In principle, given the wavefunctions corresponding to $|g\rangle$ and $|e\rangle$, we can calculate $\langle g|\hat{r}|e\rangle$. However, in practice one only knows the wavefunctions for the hydrogen atom! Therefore, we have to rely either on approximate and/or numerical calculations, or on measured quantities such as the lifetime, and determine $\langle g|\hat{r}|e\rangle$ using Eq. (8).

The NIST database [3] of atomic lines lists the appropriate Einstein-A coefficients for its various lines. Other databases cite other quantities such as “oscillator strengths (f),” “cross-sections (q),” or “line strengths (S),” I shall not go into the various definitions and relationships here (see [4]).
**B. Degeneracy**

“There are no two-level atoms...” - Bill Phillips

Of course, there are no two-level atoms. However, as long as the two energy levels in question are distinguishable from other levels (through frequency or laser polarization, for example), the transition may be treated as if the atom had only the two, aside from “counting issues” due to degeneracy.

For a simple overview to the changes wrought by degeneracy, let us ignore the details by which the degeneracy arises, and simply assume that the level we had called the ground-state levels implies the possibility of decay into several of these levels. (In practice, further physics such as selection rules may preclude some of the possibilities.) If we denote the total decay rate by \( A_{g\rightarrow e} \), then:

\[
A_{g\rightarrow e} = \sum_{i=1}^{g_{e}} A_{g_{i}\rightarrow e_{i}},
\]

(10)

where \( A_{g_{i}\rightarrow e_{i}} \) is the decay rate from \( e \) to the \( i \)-th sublevel.

Suppose now that the excited state \( e \) is also degenerate, having a \( g_{e} \)-fold degeneracy. Several points may be made. First, from a thermodynamic point of view, we must demand (and the physics will deliver!) that the total decay \( A_{e_{j}} = \sum_{i=1}^{g_{e}} A_{g_{i}\rightarrow e_{i}} \) from each upper sublevel \( e_{j} \) be equal; if this were not the case, then thermal excitation of the excited state would result in unequal steady-state population of the excited state (due to the unequal decay rates). We will see below how this equal total decay rate arises in the case where the degeneracy is due to angular momentum. Second, in a case where the degenerate excited state sublevels are populated with probabilities \( P_{e_{j}} \), then the total decay rate measured is the average of the decay rates of each sublevel (each of which can possibly decay to multiple ground-state sublevels).

\[
A_{g\rightarrow e,\text{distrib.}} = \sum_{j=1}^{g_{e}} P_{e_{j}} \sum_{i=1}^{g_{e}} A_{g_{i}\rightarrow e_{i}},
\]

(11)

For a thermally populated excited state the probabilities \( P_{e_{j}} = 1/g_{e} \) are equal. This is the case for, e.g., the distribution produced by the discharge lamps historically used for atomic spectroscopy. This distribution may or may not be relevant to more modern spectroscopic measurements. (However, perhaps for historical reasons, it is ubiquitous in books on atomic spectroscopy.)

**III. OVERVIEW OF ROTATIONAL SYMMETRY AND ANGULAR MOMENTUM**

In standard atomic systems, degeneracies inevitably arise from angular momentum considerations. Before considering the physics and math behind this degeneracy, it will pay to briefly review rotational symmetry and angular momentum in quantum systems. Symmetry plays a powerful role in classical mechanics, as epitomized by Noether’s theorem. However, in classical mechanics, invariance of the equations of motion does not necessarily imply symmetry of a motional state. In quantum systems, on the other hand, superposition implies that the quantum states themselves may always be expressed so as to reflect the symmetries of the underlying Hamiltonian.

This has far-reaching implications for atomic physics, where the spherically symmetric Coulomb potential dominates the physics. So let us consider rotational symmetry. From a purely geometric point of view, the operators

\[
\mathcal{L}_{x} = i \left( \sin \phi \frac{\partial}{\partial \theta} + \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right)
\]

(12)

\[
\mathcal{L}_{y} = i \left( -\cos \phi \frac{\partial}{\partial \theta} + \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right)
\]

(13)

\[
\mathcal{L}_{z} = -i \frac{\partial}{\partial \phi}
\]

(14)

generate rotations of a function \( f(x, y, z) \) of the spatial coordinates \( x, y, \) and \( z \). That is, if we rotate the function \( f \) an angle \( \theta \) about the axis \( n \), then \( f'(x, y, z) = R f(x, y, z) = e^{-i\theta n \cdot \mathbf{L}} f(x, y, z) \), where \( R \) represents a rotation operator. This is the so-called active view of rotations, where we change the function while holding our coordinate axes fixed.

In quantum mechanics, deBroglie’s fundamental relation \( p = -i\hbar \nabla \) gives the quantities \( \hat{L}_k = i\hbar \mathcal{L}_k \) not just geometrical significance but also dynamical and, by the postulates of quantum mechanics, observable consequences as components of angular momentum (e.g. the quantized outcome of the measurements of angular momentum projections \( \hat{L}_k \)).

Because rotations about different axes do not commute, the operators \( \mathcal{L}_k \) obey the commutation relations \( [\mathcal{L}_i, \mathcal{L}_j] = i\epsilon_{ijk} \mathcal{L}_k \) or, more compactly, \( \mathbf{L} \times \mathbf{L} = i\mathbf{L} \). In the quantum case, the quantum mechanical angular momentum operators \( \hat{L}_k \) obey the related commutation relations \( [\hat{L}_i, \hat{L}_j] = i\epsilon_{ijk} \hat{L}_k \), or \( \hat{L} \times \hat{L} = i\hbar \hat{J} \). These commutation relations identify a general quantum mechanical operator \( \hat{J} \) as being an angular momentum.

Given the fact of that rotations about different axes do not commute, let us focus on only a single axis of rotation - which we will call the \( z \) axis - and ask which directions in space are invariant under rotations about this axis. The eigenvectors of the rotation operator \( R(\phi, e_z) \) are given by

\[
R(\phi, e_z) (e_x + i e_y) = e^{-i\phi} (e_x + i e_y),
\]

\[
R(\phi, e_z) (e_x - i e_y) = e^{i\phi} (e_x - i e_y),
\]

\[
R(\phi, e_z) e_z = e_z
\]

(15)

Of course, the first two eigen“vectors” are not physical vectors at all, since they’re complex. Normally, realizing...
that we are talking about real, three-dimensional space, we would “toss out” these solutions. However, it turns out that these vectors have physical use after all. Indeed, they may seem somewhat similar to the definition of quantum angular momentum raising/lowering operators 

\[ \hat{L}_\pm := \hat{L}_x \pm i \hat{L}_y \]

or the “spherical basis unit vectors”

\[ \mathbf{e}_{\pm 1} := \pm \frac{1}{\sqrt{2}} (\mathbf{e}_x \pm i \mathbf{e}_y), \]

which are proportional to the eigenvectors. This is no coincidence - these entities are useful exactly because of their similarity to the expressions for the eigenvectors of rotation. Due to the vectors’ simple rotational properties, they are particularly useful in describing changes in a physical system induced by rotations. Since quantum-mechanical wave functions are delocalized and complex anyway, the complex-valued unit vectors prove useful in describing quantum systems.

However, the complex nature of \( \mathbf{e}_{\pm 1} \) requires some notation caution, since we must ensure that quantities with a real, physical meaning - such as the dot product \( \mathbf{A} \cdot \mathbf{B} \) of two real vectors - evaluates to a real number. One way to assure this is to expand our vector notation by introducing dual vectors: this is the approach which gives us bras \( \langle \Psi | \) (dual vectors), and kets \( | \Psi \rangle \) (state vectors) in quantum mechanics. A similar approach gives us contravariant vector components \( \mathbf{A}^\mu \) and covariant dual vector components \( \mathbf{A}_\mu \) in relativity. Given a vector \( \mathbf{A} = A_x \mathbf{e}_x + A_y \mathbf{e}_y + A_z \mathbf{e}_z \), we define:

\[
\mathbf{e}^+ := -\frac{1}{\sqrt{2}} \left( \mathbf{e}_x - i \mathbf{e}_y \right) \quad \text{(16a)}
\]

\[
\mathbf{e}^0 := \mathbf{e}_z \quad \text{(16b)}
\]

\[
\mathbf{e}^- := +\frac{1}{\sqrt{2}} \left( \mathbf{e}_x + i \mathbf{e}_y \right) \quad \text{(16c)}
\]

and

\[
A^+ := -\frac{1}{\sqrt{2}} (A_x + i A_y) \quad \text{(17a)}
\]

\[
A^0 := A_z \quad \text{(17b)}
\]

\[
A^- := +\frac{1}{\sqrt{2}} (A_x - i A_y) \quad \text{(17c)}
\]

and let \( \mathbf{e}^q = (\mathbf{e}_q)^* \) and \( \mathbf{e}_q = (\mathbf{e}^q)^* \) (where \( q \in \{-1, 0, +1\} \)). Really, the notation is just a way of keeping track of complex conjugation, but it is consistent with other notations the reader may be familiar with, and also is consistent with various notations in the literature. In terms of these quantities, we may express \( \mathbf{A} \) as:

\[
\mathbf{A} = A_x \mathbf{e}_x + A_y \mathbf{e}_y + A_z \mathbf{e}_z = A^+ \mathbf{e}^+ + A^0 \mathbf{e}^0 + A^- \mathbf{e}^- \quad \text{(18)}
\]

More compactly, \( \mathbf{A} = \sum_q A_q \mathbf{e}^q \).

As an example, we may express a general position vector \( \mathbf{r} \) as

\[
\mathbf{r} = \sqrt{\frac{4\pi}{3}} r \left[ Y^1_1 \mathbf{e}^{-1} + Y^0_0 \mathbf{e}^0 + Y^{+1}_1 \mathbf{e}^{+1} \right]
\]

\[
= r \left[ C^1_1 \mathbf{e}^{-1} + C^0_0 \mathbf{e}^0 + C^{+1}_1 \mathbf{e}^{+1} \right], \quad \text{(19)}
\]

where \( C^l_m := \sqrt{\frac{4\pi}{2l+1}} Y^l_m \) are the “normalized spherical harmonics” introduced by Racah, which save us writing innumerable factors of \( \sqrt{\frac{4\pi}{2l+1}} \). Note that, if the expansion coefficients are in fact to be equal to the usual spherical harmonics, then we must write the expansion in the above form, using the unit vectors \( \mathbf{e}^m \). This implies that the spherical harmonics transform as “covariant” quantities in this notation.

In terms of these definitions, the dot product of two vectors \( \mathbf{A} \) and \( \mathbf{B} \) is given by \( \mathbf{A} \cdot \mathbf{B} = \sum_q A^q B_q = \sum_q A_q^* B_q = \sum_q (-1)^q A_{-q} B_q \). Note that \( \mathbf{e}^q \cdot \mathbf{e}_r = \delta_{q,r} \). The multiplicity of equivalent expressions may seem daunting, but the reader will find all of them in the literature, so I have included them here. I will stick to notation such as \( \mathbf{A} \cdot \mathbf{B} = \sum_q A^q B_q \).

A. Coupled angular momenta: Clebsch-Gordon and \( n \cdot j \) Symbols

If we combine two states with definite rotational symmetry (i.e. angular momentum eigenstates), then the resulting state will reflect these symmetries. Consider, for example, a single outer electron in an atom. The electron has both orbital angular momentum \( \hat{L} \) and spin \( \hat{S} \), with quantum numbers \( l, m_l \) and \( s, m_s \), respectively. The components of these angular momenta satisfy the usual commutation relations. However, the combined system has angular momentum \( \hat{J} = \hat{L} + \hat{S} \) with quantum numbers \( j \) and \( m \). The combined system can be expressed either in terms of the state vectors \( |lm_isms\rangle \) or in terms of the state vectors \( |lsjm\rangle \). The two choices are consistent - we can write the states \( |lsjm\rangle \) in terms of the states \( |lm_isms\rangle \):

\[
|lsjm\rangle = \sum_{m_l,m_s} C_{lj,m_l,m_s}^{ljs} |lm_isms\rangle. \quad \text{(20)}
\]

Here, the expansion coefficients \( C_{lj,m_l,m_s}^{ljs} \) are the Clebsch-Gordon coefficients:

\[
C_{lj,m_l,m_s}^{ljs} = \langle lm_isms | lsjm \rangle. \quad \text{(21)}
\]

The reader has no doubt encountered the Clebsch-Gordon coefficients before. They simply represent overlap between the state \( |lm_isms\rangle \) and the state \( |lsjm\rangle \) - that is to say, the “amount” of \( |lm_isms\rangle \) “in” the state \( |lsjm\rangle \).

However, in performing angular-momentum calculations, it is usually more convenient to introduce the Wigner \( 3 \cdot j \) symbols:
\[
\begin{aligned}
&\left( \frac{l}{m_l} \frac{s}{m_s} \frac{j}{m} \right) = (-1)^{l-s-m} \frac{\sqrt{2j+1}}{\sqrt{2l+1}} |lm_l(sm_s|lsj-m) .
\end{aligned}
\]

By convention, the Clebsch-Gordon coefficients are taken to be real. Thus, the 3-j symbols are also real (positive or negative) numbers. The 3-j symbols exhibit a number of simple relationships with other 3-j symbols where the arguments are permuted. An even permutation of symbols leaves the 3-j symbol unchanged:

\[
\left( \frac{l}{m_l} \frac{s}{m_s} \frac{j}{m} \right) = \left( \frac{j}{m} \frac{l}{m_l} \frac{s}{m_s} \right) = \left( \frac{s}{m_s} \frac{j}{m} \frac{l}{m_l} \right)
\]

whereas an odd permutation introduces only a phase factor:

\[
(-1)^{l+s+j} \left( \frac{l}{m_l} \frac{s}{m_s} \frac{j}{m} \right) = \left( \frac{s}{m_s} \frac{l}{m_l} \frac{j}{m} \right), \text{ etc.}
\]

Finally, we have the relationship

\[
\left( \frac{l}{m_l} \frac{s}{m_s} \frac{j}{m} \right) = (-1)^{l+s+j} \left( \frac{l}{-m_l} \frac{s}{-m_s} \frac{j}{-m} \right)
\]

There are similar relationships between Clebsch-Gordon coefficients, but these relationships are encumbered by various factors of \(\sqrt{2j+1}\), etc., and are less wieldy to work with.

Roughly speaking, the 3-j symbol gives the probability (amplitude) that angular momentum \(l\) with projection \(m_l\) will add up with an angular momentum \(s\) with projection \(m_s\) to produce an angular momentum \(j\) with projection \(-m\) - but normalized to the total number \(2j+1\) of possible distinct orientations of \(j\). This choice of normalization is responsible for the \(\sqrt{2j+1}\) in the denominator on the right side of Eq. (22), and is necessary for the convenient permutational symmetries of the 3-j symbols to hold. There is another way to interpret the 3-j symbols, as corresponding to the probability (amplitude) that if one adds an angular momentum \(\hat{L}\) (with projection \(m_l\)) and an angular momentum \(\hat{S}\) (with projection \(m_s\)) and then subtracts an angular momentum \(\hat{J}\) (with projection \(m\)) so that \(-\hat{J}\) has projection \(-m\), one obtains an angular momentum 0 - that is, a scalar (rotationally invariant) quantity. Physically, this simply reflects the fact that in a system that conserves angular momentum, angular momentum is conserved! The probability is again normalized to the total number \(2j+1\) of angular momentum states \(j\).

The 3-j symbols arise in combining two angular momenta to make a third (or, alternatively, coupling 3 angular momenta to form a \(j = 0\) scalar state). Similar considerations arise in combining 3 angular momenta. Consider angular momenta \(j_1, m_1, j_2, m_2, j_3, m_3\) which we combine to form an overall angular momentum \(j, m\). We can do this by first coupling \(j_1\) and \(j_2\) to form an angular momentum eigenstate \(j_{12}\) (with projection \(m_{12}\)), and then couple \(j_{12}\) with \(j_3\) to obtain the state \(|j_1(j_2j_3)j_{12}j_{23}jm\rangle\). However, we can also first couple \(j_2\) and \(j_3\) to form an angular momentum \(j_{23}\) (with projection \(m_{23}\)), and then combine \(j_1\) with \(j_{23}\) to form \(|j_1(j_2j_3)j_{23}jm\rangle\). Either scheme is appropriate - however, the two kets \(|j_1(j_2j_3)j_{12}j_{23}jm\rangle\) and \(|j_1(j_2j_3)j_{23}jm\rangle\) are not, in general, the same. Nonetheless, we can expand the state \(|j_1(j_2j_3)j_{12}j_{23}jm\rangle\) in terms of the various states \(|j_1(j_2j_3)j_{23}jm\rangle\):

\[
|j_1(j_2j_3)j_{12}j_{23}jm\rangle = \sum_{j_{23}} |j_1(j_2j_3)j_{23}jm\rangle |j_1(j_2j_3)j_{23}jm\rangle.
\]

The Wigner 6-j symbol is defined as:

\[
\{ \frac{j_1}{j_2} \frac{j_2}{j_3} \frac{j_3}{j} \frac{j}{j_{23}} \} = \frac{(-1)^{j_1+j_2+j_3+j}}{\sqrt{(2j_{12}+1)(2j_{23}+1)}} |j_1(j_2j_3)j_{23}jm\rangle |j_1(j_2j_3)j_{23}jm\rangle.
\]

6-j symbols are a notationally convenient way of keeping track of the coupling between 3 angular momenta. Similarly to case of the 3-j symbols, one may interpret the 6-j symbols in terms of adding 3 angular momenta, and subtracting a fourth to obtain a \(j = 0\) scalar. The 6-j symbol has the nice symmetry that its value is unchanged by the interchange of any two of the three columns, or by switching the upper and lower members of any two columns.

To obtain some insight as to the meaning of a 6-j symbol, consider the quantity \(\{ s \frac{l}{l'} \frac{l'}{l''} \} \). In terms of the definition
\[ \{s \, \ell \, j \, \ell' \, j' \} = \frac{(-1)^{s+\ell+1+j'}}{\sqrt{(2j+1)(2\ell'+1)}} (s\ell j' j'm) (s\ell j' j'm), \]

we see that the 6-j symbol is proportional to the overlap between two states. The first is one in which the initial orbital angular momentum \( \ell \) is first coupled to the unit angular momentum of the laser field to form the new angular momentum \( \ell' \), which is then in turn coupled to the original spin \( s \) (which is unaffected by the laser!) to form the final total angular momentum \( j' \). The second state is one in which spin \( s \) is first coupled to orbital angular momentum \( \ell \) to form total atomic angular momentum \( j \), and then \( j \) is coupled to the unit angular momentum of the laser field to form total angular momentum \( j' \) - the angular momentum of the final state. So essentially the 6-j symbol is related to the two different ways of thinking about the atom-laser coupling: either as affecting the total angular momentum of the atom, or as affecting only its orbital angular momentum. The factor of \( 1/\sqrt{(2j+1)(2\ell'+1)} \) normalizes to the product of the total numbers of intermediate states, and is necessary for the 6-j symbols’ permutation symmetries.

One may also introduce 9-j symbols, etc., but I promise the reader that I will not do so here!

B. Introduction to the Wigner-Eckart Theorem

The entire reason for introducing the whole apparatus of the previous pages is that the notation makes explicit the symmetry of states, vectors, operators, etc. under rotations. Thus, the language is well-suited to describing systems that exhibit rotational symmetry. This symmetry can save us an immense amount of work if we make use of it, and the notation allows this.

The greatest implication of rotational symmetry is embodied in the Wigner-Eckart theorem\(^\text{11}\). Suppose that we have two states of well-defined rotational symmetry, and some physical interaction that also exhibits a well-defined rotational symmetry couples the two states. To rephrase, suppose that two angular-momentum eigenstates \( |\alpha jm\rangle \) and \( |\alpha' j'm'\rangle \) are coupled by an irreducible tensor operator \( T^{(k)} \) with components \( T^k_q \) (see Refs. 51, 52, 26, 27). Here, the labels \( \alpha, \alpha' \) represent any additional labels in addition to angular momentum needed to uniquely specify the quantum states. For example, in describing the orbital of a hydrogen atom, one would need to specify the principal quantum number \( n \). The matrix element for the transition is \( \langle \alpha' j'm' | T^k_q | \alpha jm \rangle \). However, since each term in the matrix element has well-defined rotational symmetry, so too must the overall matrix element. To put it in more active terms (in view of the quantum relationship between generators of rotations and angular momentum), angular momentum is conserved in the transition.

The Wigner-Eckart theorem essentially splits the calculation of the matrix element into a term that embodies the peculiar specifics of the particular interaction and a term that embodies the purely geometric considerations demanded by the rotational symmetry - that is, by conservation of angular momentum. To be quantitative, the Wigner-Eckart theorem states that\(^\text{15}\)

\[
\langle \alpha' j'm' | T^k_q | \alpha jm \rangle = (-1)^{j'-m'} \langle \alpha' j' | T^{(k)} | \alpha j \rangle \left( \begin{array}{ccc} j' & k & j \\ -m' & q & m \end{array} \right),
\]

Note that the reduced matrix element (or double-bar matrix element) is a constant independent of the quantum numbers \( m_j, \, m'_j, \) and \( q \). That is to say, \( \langle \alpha' j' | T^{(k)} | \alpha j \rangle \) is the same regardless of the relative orientations of the angular momenta \( j, \, j', \) and \( k \) (the angular momentum associated with the operator). \( \langle \alpha' j' | T^{(k)} | \alpha j \rangle \) expresses the physics of the particular interaction at hand - and, as such, it does contain information about the angular momenta of the initial and final states and the effective angular momentum of the interaction driving transitions between these states. However, the dependence of the transition strength on the relative orientation of the rotationally symmetric quantities is a question of pure geometry given the well-characterized rotational symmetries of the quantities involved. It is entirely independent of the details of the interaction and the same for any transition between angular momentum eigenstates driven by an interaction with the rotational symmetry characteristic of angular momentum \( k \). This universal geometric part of the transition matrix element is given by the factor of \( (-1)^{j'-m'} \left( \begin{array}{ccc} j' & k & j \\ -m' & q & m \end{array} \right) \).

The practical upshot of the Wigner-Eckart theorem is that the transition matrix elements for a particular coupling between angular momentum eigenstates \( j, \, j' \) is the same for all the states - up to a multiplicative geometric factor which factors in relative orientations. This geometric factor \( (-1)^{j'-m'} \left( \begin{array}{ccc} j' & k & j \\ -m' & q & m \end{array} \right) \) (which may be zero!) can be looked up in standard tables or computed with standard software packages. The reduced matrix element, on the other hand, describes the actual specific physics at hand, and must be calculated explicitly for each physical setup.
IV. RABI FREQUENCIES FOR AN ATOM WITH SPIN AND ORBITAL ANGULAR MOMENTUM

After the long digression on angular momentum, let us return to the question of the Rabi frequency. Our digression has equipped us with the tools to calculate the transition strength with a minimum of tedium.

For an atom with a single outer electron (ground state), consider laser-driven electric-dipole transitions between states \( |njm\rangle \) and \( |n'j'm'\rangle \). Here, \( j \) (\( j' \)) is the vector sum of the electron’s orbital angular momentum (the angular variation of the electron’s wave function) and the electron spin. However, in the electric dipole approximation, the electric field of the laser does not couple to the electron spin. So, if you will, the electric field couples only to the “\( l \) (\( l' \)) part” of \( j \) (\( j' \)). (Note that in the rest of the paper, I will neglect fine-structure, hyperfine-structure and Zeeman splittings, in order to focus on the essential commonality of the various transitions.)

One way to calculate the Rabi frequency, then, would be to decompose \( j \) into \( l \) and \( s \), and evaluate the transition matrix element between different eigenstates of \( \hat{L}^2 \), \( \hat{L}_z \), with the electronic spin being “carried along for the ride.” This is the approach suggested in Ref.[2].

However, the Wigner-Eckart theorem offers us a simpler approach - particularly if we wish to calculate the Rabi frequency in terms of the excited-state lifetime. The point is that it doesn’t matter how the angular momentum \( j \) arises. It only matters that the initial and final states are states of well-defined rotational symmetry (angular momentum) and that the interaction potential may be expressed in a similar manner.

In particular, we have that \( \hat{V}_l = -\hat{\mu} \cdot \hat{E} \). In order to evaluate the dot product, we have to pick a coordinate system. We know from the quantum theory of angular momentum that only one component of \( \hat{J} \) can have a well-defined value, and by convention, we call that direction the \( z \) direction. Now, an isolated atom has spherical symmetry, and by that token, it does not matter which direction we choose to call the \( z \)-direction. However, in practice, the perfect spherical symmetry is broken by some outside perturbation. In typical atom-trapping experiments, this is provided by a uniform applied magnetic field - referred to as the “quantization field.” The magnetic field “picks out” a “preferred direction” in space and breaks the degeneracy of the different atomic states through the well-known Zeeman effect. In this case, it is wise to pick as the \( z \)-axis the axis of this background field. We need not worry about the particular directions of \( x \) and \( y \) for which we shall calculate in the spherical basis \( \hat{e}_{z+1}, \hat{e}_0, \hat{e}_{-1} \).

Once we have picked a \( z \), or quantization, axis we can then express the laser electric field components in that basis. By convention, a laser field (component) parallel to the \( z \) axis is said to have “\( \pi \) polarization.” A laser field which, in the rotating-wave approximation, drives a lower level \( |njm\rangle \) to an upper level \( |n'j'(m+1)\rangle \) is said to have “\( \sigma^+ \) polarization” and a laser field which drives a lower level \( |njm\rangle \) to an upper level \( |n'j'(m-1)\rangle \) is said to have “\( \sigma^- \) polarization.” In considering such a transition, a \( \sigma^+ \) (\( \sigma^- \)) field would, in the rotating-wave approximation, have an electric field with only a \( \hat{e}_{z+1} \) (\( \hat{e}_{z-1} \)) component.

The atom’s dipole moment is given by \( \hat{\mu} = -e\hat{r} \). Using Eq. (19), \( \hat{f} = \hat{r} \sum_q C_q^l \hat{e}^q \). In terms of the above expressions:

\[
\hat{V}_l = -\hat{\mu} \cdot \hat{E} = e \sum_q C_q^l \hat{e}^q. \tag{30}
\]

This finally expresses the interaction Hamiltonian in a way which brings to the forefront the rotational symmetry of the situation and which, more significantly, allows us to calculate the Rabi frequency using the Wigner-Eckart theorem.

The Rabi frequency is given by:

\[
\Omega_{g \to e} = \frac{1}{\hbar} \langle n'j'm'|eE_0 \sum_q C_q^{j'}|njm\rangle = \frac{eE_0}{\hbar} \sum_q \xi(q|n'j'm'|\hat{r}C_q^l|njm). \tag{31}
\]

Now \( \hat{r} \) is an isotropic (scalar) operator, which has no effect in the space \( |jm\rangle \). Thus, the transformation properties of the constituents in the sum above will be set by the angular momentum eigenstates and the operators \( C_q^l \propto Y_q^l \). But here the Wigner-Eckart theorem simplifies life, for it assures us that, regardless of the values of \( j, m, j', m', q \):

\[
\langle n'j'm'|\hat{r}C_q^l|njm\rangle = (-1)^{j'-j-1} \langle n'j'||\hat{r}C_q^l||nj\rangle \begin{pmatrix} j' & 0 & j \\ m' & q & m \end{pmatrix}. \tag{32}
\]

The \( 3-j \) symbols may be looked up in tables or calculated, and the so-called reduced matrix element \( \langle n'j'm'||\hat{r}C_q^l||njm\rangle \) is independent of the various projection quantum numbers. (The symbol \( C_q^l \) represents the first-order tensor of which the \( C_q^l \) are components.) So finally:

\[
\Omega_{g \to e} = \frac{eE_0}{\hbar} \sum_q (-1)^{j'-j-1} \langle n'j'|\hat{r}C_q^l||nj\rangle \sum_q \xi(q|n'j'm'|j,m). \tag{33}
\]

Various selection rules follow from Eq. (33), since the \( 3-j \) symbol vanishes unless \( j' - j = 0, \pm 1 \), and \( m' - m = 0 \), \( \pm 1 \).

One interpretation of Eq. (33) is as follows. The factor \( \xi(q|n'j'm'|j,m) \) and the reduced matrix element express the size of the dipole moment induced in the atom by the applied electric field of the laser. The sum over \( 3-j \) symbols then expresses the relative orientation between the electric field and the dipole moment of the atom when it is in a superposition of states \( |n'j'\rangle \) and \( |nj\rangle \).
For laser-cooling experimentalists, our work is now all but over. For we can use the lifetime of the excited state to determine the reduced matrix element in Eq. (33), in the case of an excited state \( |n'j'm'\rangle \) which can only decay to the manifold \( |njm\rangle \) (typical of \( S \to P \) transitions). First, recall that Eqs. (8) and (10) tell us how to calculate the total decay rate from the particular excited state \( |n'j'm'\rangle \). Next, note that \( \langle njm|\hat{r}C_q^{1*}|n'j'm'\rangle = \langle n'j'm'\hat{r}C_q^{1*}|njm\rangle = \langle n'j'm'\hat{r}(-1)^qC_q^{1*}|njm\rangle \). (Basically, this statement reflects the fact that if an absorbed photon increases (decreases) the angular momentum of the atomic state, then an emitted photon must do the converse). Putting this all together, we have:

\[
\Gamma = A_{|nj\rangle-|n'j'm'\rangle} = \sum_{q,m} A_{|nmj\rangle-|n'j'm'\rangle} \\
= \frac{8\pi^2 e^2}{3\epsilon_0\hbar\lambda_0^3} \sum_{q,m} |\langle njm|\hat{r}C_q^{1}|n'j'm'\rangle|^2 \\
= \frac{8\pi^2 e^2}{3\epsilon_0\hbar\lambda_0^3} \sum_{q,m} |\langle n'j'm'|\hat{r}C_{-q}^{1}|njm\rangle|^2 \\
= \frac{8\pi^2 e^2}{3\epsilon_0\hbar\lambda_0^3} |\langle n'j'||\hat{r}C^{(1)}||nj\rangle|^2 \sum_{q,m} \left( \begin{array}{ccc} j & 1 & j' \\ -m & -q & m' \end{array} \right) \left( \begin{array}{ccc} j & 1 & j' \\ -m & -q & m' \end{array} \right) \\
= \frac{1}{2j' + 1} \delta_{j_3,j'_3}\delta_{m_3,m'_3}. \tag{34}
\]

Now we can simplify the sum over squares of 3-j symbols by their tabulated properties. In particular Eq. (C.15a) of Messiah\[2\] tells us that

\[
\sum_{q,m} \left( \begin{array}{ccc} j & 1 & j' \\ -m & -q & m' \end{array} \right) \left( \begin{array}{ccc} j & 1 & j' \\ -m & -q & m' \end{array} \right) = \frac{1}{2j' + 1}. \tag{36}
\]

(The fact that the sum evaluates to \(1/(2j' + 1)\) is a result of the normalization of the 3-j symbols.)

Thus,

\[
\Gamma = \frac{1}{2j' + 1} \frac{8\pi^2 e^2}{3\epsilon_0\hbar\lambda_0^3} |\langle n'j'||\hat{r}C^{(1)}||nj\rangle|^2. \tag{37}
\]

By a systematic and careful comparison with the results of the next section (see Appendix B), the phase of the reduced matrix element can be fixed as \((-1)^{j+j'}\) (where \(j'\) is the larger of \(j'\) and \(j\)), so that

\[
\langle n'j'||\hat{r}C^{(1)}||nj\rangle = (-1)^{j+j'} \sqrt{2j' + 1} \frac{3\epsilon_0\hbar\lambda_0^3}{8\pi^2 e^2}. \tag{38}
\]

So finally, for a transition whose lifetime is known to be \(1/\Gamma\), the Rabi frequency may be calculated as:

\[
\Omega_{e-g} = \frac{E_0}{\hbar} \sqrt{\frac{3\epsilon_0\hbar\lambda_0^3}{8\pi^2}} (-1)^{j+j'} \frac{1}{2j' + 1} \sum_{q} e^q \left( \begin{array}{ccc} j' & 1 & j \\ -m' & q & m \end{array} \right). \tag{39}
\]

Expressions in terms of intensity or laser power/waist may be worked out with the aid of Eq. (3).

The case in which the excited state can decay to multiple \(n\) or \(j\) levels is more complicated, and the reader is referred to Ref\[13\] or Ref \[12\] for more information. However, we will deal with the case of multiple ground-state hyperfine levels in Sec. IVB.
A. Breaking down to orbital angular momentum states

For theorists, there is still work to be done in relating Eq. (33) to theoretical calculations of atomic wave functions. Eq. (33) expresses the Rabi frequency in terms of the reduced matrix element $\langle n'l's'j'|\hat{p}\hat{C}^{(1)}|nlsj\rangle$. However, the \( \hat{r}\hat{C}^{(1)} \) only affects the spatial part of the electron state and leaves the spin alone. Thus, in calculating Rabi frequencies from scratch, we would like to break down the angular momentum into its constituent parts: \( \hat{J} = \hat{L} + \hat{S} \).

We can re-express \( \hat{r}\hat{C}^{(1)} \) more accurately as the tensor product of \( \hat{r}\hat{C}^{(1)} \) and the identity operator \( \hat{I}_s \) acting on the spin state. So we are interested in calculating

$$\langle n'l's'j'|\hat{r}\hat{C}^{(1)} \otimes \hat{I}_s|nlsj\rangle.$$  \hspace{1cm} (40)

We can simplify this calculation by using Eq. (C.89) of Messiah\textsuperscript{[11]} in the present notation:

$$\langle n'l's'j'|\hat{r}\hat{C}^{(1)} \otimes \hat{I}_s|nlsj\rangle = \delta_{s,s'}(n'l'|\hat{r}\hat{C}^{(1)}|nl)$$

$$\times (-1)^{j+l'+s'+1}\sqrt{(2j'+1)(2j+1)} \left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\}. \hspace{1cm} (41)$$

Now, \( \hat{r} \) acts only on the radial part of the wave function, and \( \hat{C}^{(1)} \) acts only on the angular part. So \( \langle n'l'|\hat{r}\hat{C}^{(1)}|nl\rangle = \langle n'l'|\hat{r}|\hat{C}^{(1)}|nl\rangle = R_{n'l'}^n(l)|C(l)|l\rangle \). Here \( R_{n'l'}^n(l) \) is the radial integral $\int R_{n'l'}^{nl}(r)R_{nl}^{n'} r^2 dr$, where the radial wave function \( R_{nl}(r) \) is the output of the theoretical calculation of the electronic wave function.

It remains to evaluate \( \langle l'||\hat{C}^{(1)}|l\rangle \). To do this, note that, by the Wigner-Eckart theorem,

$$\langle l',0|C_0^0|l,0\rangle = (-1)^{j'}\langle l'|\hat{C}^{(1)}|l\rangle \left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\}. \hspace{1cm} (42)$$

On the other hand, using Eq. (C.16) of Messiah\textsuperscript{[11]}

$$\langle l',0|C_0^0|l,0\rangle = \langle l',0|\sqrt{\frac{4\pi}{3}}Y_0^0|l,0\rangle$$

$$= (-1)^l\sqrt{\frac{4\pi}{3}} \int Y_{l'}^{*l'}Y_l^0 Y_l^0 d\Omega$$

$$= \sqrt{(2l'+1)(2l+1)} \left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\} \left\{ l \begin{array}{ccc} 1 & 1 & l \end{array} \right\}. \hspace{1cm} (43)$$

Comparing these expressions, we see that:

$$\langle l'||\hat{C}^{(1)}|l\rangle = (-1)^{-j'}\sqrt{(2l'+1)(2l+1)} \left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\}. \hspace{1cm} (44)$$

At this point, it may be worth working out the explicit value of the 3-j symbol. From Table 2 of Edmonds\textsuperscript{[23,59]}, with the projection numbers set to 0

$$\left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\} = (-1)^{l'-1}\sqrt{\frac{(l+1)}{(2l+3)(2l+1)}}. \hspace{1cm} (45)$$

Now, \( l \to l \pm 1 \) in our transition, which means that, if we use the symbol \( l_> \) to denote the larger of \( l' \) and \( l \),

$$\left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\} = (-1)^{l_>}\sqrt{\frac{l_>}{(2l'+1)(2l+1)}}. \hspace{1cm} (46)$$

This, in turn, implies that

$$\langle l'||\hat{C}^{(1)}|l\rangle = (-1)^{-j'}\sqrt{l_>}. \hspace{1cm} (47)$$

Finally, (dropping the \( \delta_{s,s'} \) with the understanding that it is implicit)

$$\langle n'l's'j'|\hat{r}\hat{C}^{(1)} \otimes \hat{I}_s|nlsj\rangle = (-1)^{j+l_>+s'+1}R_{n'l'}^{nl}$$

$$\times \sqrt{(l_>)(2l'+1)(2l+1)} \left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\}. \hspace{1cm} (48)$$

The interpretation of the 6-j symbol was discussed when these symbols were first introduced in Sec. [111A]. The 3-j symbol is present simply because we must express the reduced-matrix element via the Wigner-Eckart theorem in terms of some (non-reduced) matrix element, and we chose above to represent it in terms of \( \langle l',0|C_0^0|l,0\rangle \). The various square roots arise from the normalization of the 3-j and 6-j symbols.

Finally, we can put the above together with Eq. (33) for the complete but somewhat lengthy expression:

$$\Omega_{e-g} = (-1)^{j'+j+l_>+s'+1-m'} R_{n'l'}^{nl} \frac{eE_0}{\hbar}$$

$$\times \sqrt{(l_>)(2l'+1)(2l+1)} \left\{ l' \begin{array}{ccc} 1 & 1 & l \end{array} \right\}$$

$$\times \sum_q e^q \left\{ j' \begin{array}{ccc} 1 & 0 & j \end{array} \right\}. \hspace{1cm} (49)$$

The quantity \( E_0 \) is given to us by the experimentalist, as is the relative orientation of the laser polarization and the quantization axis (typically due to the applied “quantization” magnetic field). The quantity \( R_{n'l'}^{nl} \) is given to us by the theorist. The rest of the quantities are specified purely by the geometry and are independent of the details of the system.

B. Rabi frequencies in the case of hyperfine structure

The case of an atom with hyperfine structure (due to nuclear angular momentum \( \hat{I} \)) is somewhat more complicated than the above cases. However, the idea is the same. The Wigner-Eckart theorem still holds, and so Eq. (33) still applies, but with \( j \) replaced with the total angular momentum quantum number \( F \) (where \( \hat{F} = \hat{I} + \hat{J} \)). Thus:
\[ \Omega_{\epsilon \rightarrow g} = \frac{eE_0}{\hbar} (-1)^{F' - m_F} \langle n' F' || \hat{R}\tilde{C}^{(1)} || nF \rangle \times \sum_q \epsilon^q \left( \begin{array}{ccc} F' & 1 & F \\ -m_F & q & m_F \end{array} \right). \] (50)

As before, the laser (in the electric dipole approximation) interacts only with the orbital-angular-momentum part \( \hat{L} \) of the electronic angular momentum \( \hat{J} = \hat{L} + \hat{S} \). Writing the quantum number \( I \) first in labelling the states, we use Eq. (C.90) of Messiah\textsuperscript{[3]} to write:

\[ \langle n' F' || \hat{R}\tilde{C}^{(1)} || nF \rangle \equiv \langle n' I' j' F' || \hat{R}\tilde{C}^{(1)} || n I j F \rangle \\
= \delta_{I', I} \delta_{j', j} (-1)^{F' + I' + j + 1} \sqrt{(2F' + 1)(2F + 1)} \times \left\{ \begin{array}{ccc} j' & 1 & j \\ F & I' & F' \end{array} \right\} \langle n' j || \hat{R}\tilde{C}^{(1)} || n j \rangle. \] (51)

\[ \Omega_{\epsilon \rightarrow g} = \frac{eE_0}{\hbar} (-1)^{2F' + I' + j + 1 - m_F} \sqrt{(2F' + 1)(2F + 1)} \left\{ \begin{array}{ccc} j' & 1 & j \\ F & I' & F' \end{array} \right\} \langle n' j || \hat{R}\tilde{C}^{(1)} || n j \rangle \sum_q \epsilon^q \left( \begin{array}{ccc} F' & 1 & F \\ -m_F & q & m_F \end{array} \right). \] (52)

(The delta functions have been suppressed for the sake of brevity, and I’ve used the fact that \((-1)^2 = 1\).

V. CONCLUSION

In the end, then, the interaction of an atom with an applied laser field induces a dipole moment of magnitude \( eR_{nl}^{m_l} \) in the atom. The interaction between the dipole moment and the field then drives transitions between different atomic levels. Since the interaction has well-defined rotational symmetry, angular momentum must be conserved overall. The transition probability is thus “modulated” by the probability amplitude for angular momentum to be conserved in a particular transition, depending on the relative orientation of the atom and the applied field. This “modulation” is embodied by the Wigner-Eckart theorem which, if you will, “splits up” the transition probability amongst the different states whose coupling conserves angular momentum. The total transition rate out of an excited state (driven by vacuum fluctuations) is the same for all states in a given degenerate angular momentum manifold, as it must be. This latter rate is given by the Einstein \( A \) coefficient, and allows connection with experimentally determined quantities.

The 6-j symbol, roughly speaking, accounts for the probability (amplitude) that one can change the overall angular momentum from \( F \) to \( F' \) by the 1 unit of photon angular momentum by changing the electron’s angular momentum from \( j \) to \( j' \) (since the laser field only couples to the electron).

Using Eq. (48) to express the value of \( \langle nj || \hat{R}\tilde{C}^{(1)} || n' j' \rangle \), it follows that the Rabi frequency in the case of hyperfine structure is:

\[ \Omega_{\epsilon \rightarrow g} = \frac{eE_0}{\hbar} \sqrt{(2F' + 1)(2F + 1)} \left\{ \begin{array}{ccc} j' & 1 & j \\ F & I' & F' \end{array} \right\} \sum_q \epsilon^q \left( \begin{array}{ccc} F' & 1 & F \\ -m_F & q & m_F \end{array} \right). \] (52)

APPENDIX A: COMPARISON WITH OTHER WORK

Some or all of the results in this paper may be found scattered throughout the literature. However, it can be challenging to compare results found in different works. This is due in part to different systems of units, different choices of active vs. passive rotations, different definitions of reduced matrix elements in the Wigner-Eckart theorem, or different arrangements of the elements of 3-j and 6-j symbols, but most of all to differences in sign/phase conventions. As long as the reader picks one convention and sticks with it, results will be self-consistent - barring algebra errors along the way! When algebra errors occur, it is inevitably in determining the sign of the matrix elements.

Two other works which succinctly express Rabi frequencies in the case of fine and/or hyperfine structure are Metcalf and van der Straten\textsuperscript{[20]} and Farell and MacGillivray\textsuperscript{[21]}. Metcalf and van der Straten’s Eq. (4.32) is consistent with Eqs. (33) and (41) of this work. However, there are sign issues with Eqs. (4.26) and (4.27) of Metcalf and van der Straten. In the first equation, their \( \sqrt{\frac{4\pi}{3}} \int \sin \theta d\theta d\phi Y_{lm}^\dagger(\theta, \phi) Y_{1q}(\theta, \phi) Y_{1m}(\theta, \phi) \) should be...
\[ \sqrt{\frac{\alpha}{3}} \sin \theta \text{d} \theta \text{d} \phi Y^*_{nm}(\theta, \phi) Y_{l'k}(\theta, \phi) Y_{lm}(\theta, \phi) \] (note the complex conjugation). Furthermore, their Eq. (4.27) does not always agree in sign with the properly expressed integral of the three spherical harmonics. In addition, their expression (4.33) is not consistent in sign with Eq. (52) of this work.

Farrell and MacGillivray write their states as \(|nslj\rangle\) rather than \(|nlsj\rangle\) as is done in the present work. This produces a different overall sign. However, if the reader consistently applied their convention, self-consistent results would ensue - except that Farrell and MacGillivray use Eq. (4.136) of Sobelman, which is incorrect as pointed out in Sec. 10.4. Thus, though their results will be self-consistent for transitions between fixed \(l, l'\) they could be inconsistent if used to treat simultaneous coherently driven excitations to multiple \(l'\) levels.

Eq. (41) for the \(|n'l's'j'\rangle \langle 6|C|nlsj\rangle\) agrees in magnitude and sign with Eq. (23.1.24) of Weissbluth and with Eq. (14.54) of Cowan (who uses \(|nslj\rangle\) rather than \(|nlsj\rangle\)). Eq. (44) for the reduced matrix element \(|\langle l'|C|l\rangle|\) agrees with Eq. (14.55) of Cowan but, as discussed previously, disagrees with Eq. (4.126) of Sobelman.

Issues of different or even inconsistent minus signs become irrelevant when one calculates incoherent rates. Thus, for example, Eq. (37) for the Einstein A coefficient agrees with Eq. (14.32) of Cowan and Eq. (9.47) of Sobelman (though Cowan expresses his result in terms of wavenumbers, and Sobelman uses CGS units).

**APPENDIX B: SIGN OF EQ. (38)**

From Eq. (48), the phase of \(|n'l's'j'\rangle \langle 6|C|nlsj\rangle\) is determined by the sign of \((-1)^{j'+s'}(\{l' s' j'\} \{l s j\})\). It is possible to evaluate this phase by employing cautious reasoning and the fact that in an electric-dipole transition, \(l \rightarrow l \pm 1\) and that \(j \rightarrow j \pm 1, 0\). Note, however, that transitions in which \(j \rightarrow j \pm 1\) but \(l \rightarrow l \pm 1\) do not occur - such transitions do not satisfy the triangle relations necessary for the 6-j symbol to be non-zero.

We can determine the sign of the 6-j symbol on a case-by-case basis using the symmetry properties of the 6-j symbols and Table 5 of Edmonds (which is also available in other forms in other references). First, note that, permuting the columns of the six-j symbol, and then flipping the rows of the resulting first and second columns, \(\{l' s' j'\} \{l s j\}\) is not consistent with \(\{l' s' j'\} \{l s j\}\). This form is suitable for comparison with Edmonds.

For the case \(j' = j + 1\), \(l' = l + 1\) we have that \(j' > j\), \(l' > l\) and

\[ \{ s' j' l'\} = \{ s' j l\} \propto (-1)^{j'+l'+s'} = (-1)^{j+l+s'} \]

(B1)

For the case \(j' = j\), \(l' = l + 1\) we have that \(l' > l\) and

\[ \{ s' j' l'\} = \{ s' j l\} \propto (-1)^{j+l+s'} = (-1)^{j+l+s'} \]

(B2)

For the case \(j' = j\), \(l' = l - 1\) we have that \(l > l'\) and

\[ \{ s' j' l'\} = \{ s' l - 1 j\} \propto (-1)^{j+l+s'} = (-1)^{j+l+s'} \]

(B3)

And finally, for the case \(j' = j - 1\), \(l' = l - 1\), we have that \(j > j'\), \(l' > l\) and

\[ \{ s' j' l'\} = \{ s' l j\} \propto (-1)^{j+l+s'} = (-1)^{j+l+s'} \]

(B4)

So in all cases, \(\{ s' j' l'\} = \propto (-1)^{j+l+s'}\).

As for the 3-j symbol, Table 2 of Edmonds indicates that \(\{ 0 1 0 \} \propto (-1)^{(l'+l+1)/2}\). Now, given that \(l' = l \pm 1\), \((l'+l+1)/2 = [(l \pm 1) + l + 1]/2\) which is either \((2l + 2)/2\) (if \(l' = l + 1\)) or \(2l/2\) (if \(l' = l - 1\)). So in either case, \(\{ 0 1 0 \} \propto (-1)^{l'}\).

Putting these results together, we have that \(|njl\rangle \langle 6|C|n'j'\rangle\) is \((-1)^{2s+j+l+2l>}. Since \(s' = 1/2\) and \(l>\) is an integer, \((-1)^{2s+j+l+2l>} = 1\). So finally, we have that \(|njl\rangle \langle 6|C|n'j'\rangle\) is \((-1)^{2s+j+l+2l>}, as assumed in Eq. (48).

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45 Metcalf’s book on Laser Cooling does an excellent job outlining the physics of laser coupling in multi-level atoms, but - no doubt for brevity - skips the details.
46 This approximation is responsible for the factors of $\frac{1}{2}$ appearing below in the state vectors’ time evolution.
47 There isn’t universal agreement as to the definition of the Rabi frequency. While many sources[^3][^4] use the definition of Eq. (3), others[^5] define the Rabi frequency to be one-half of $\Omega$. However, the definition in question can always be determined by comparing the Rabi-flopping equations with Eq. (4).
48 Even in the absence of other broadening mechanisms, the finite period of time $\tau$ for which the perturbative treatment is valid implies a finite Fourier width to the transition (e.g. $\text{sin}(\omega_\perp \tau)$, in the case of a square-wave envelope).
49 In units natural to the problem, we can express the $A$-coefficient as $A_{g\rightarrow e} = \alpha^2 (R_\infty) (\frac{1}{R_\infty})^3 |\langle g | \hat{R} | e \rangle|^2 \approx (2\pi \times 1.278 \text{ GHz} z) \frac{|\ell_1 \ell_2 \ell_3 |}{\lambda^2} |\langle g | \hat{R} | e \rangle|^2$. Here $\alpha$ is the fine-structure constant giving the fundamental coupling between charged matter and electromagnetic fields, $R_\infty$ is the Rydberg constant, and $\hat{R} = \hat{\rho}_0$ is the position operator in units of Bohr radii $a_0$.
50 If $R_\gamma(\theta)$, $R_\rho(\theta)$, and $R_\perp(\theta)$ represent the rotation operator for a rotation about the original $x$, $y$, and $z$ axes by angle $\theta$ respectively, then we take the Euler angles $\alpha$, $\beta$, $\gamma$ to be such that $e^{-i\hat{R}_\gamma(\theta)} f(x, y, z) = R_\gamma(\alpha) R_\beta(\theta) R_\perp(\gamma) f(x, y, z)$. This is the convention followed by Messiah.
51 The distinction and commonality of the geometrical generators of rotations and the dynamical, quantum angular momentum components is discussed by Dirac[^8] Wigner[^7] and Thompson[^9] amongst others.
52 As Silver points out conventions for expressing the Wigner-Eckart theorem group various minus signs and factors of $\sqrt{2j+1}$ with the reduced matrix element.
53 In the absence of a background magnetic field, an unambiguous choice for the $z$-axis is the direction $\mathbf{k}$ of the beam’s propagation.
54 In this scheme the only way for the laser to be $\pi$-polarized is if the electric field is linearly polarized and parallel to the $z$ axis. That is, the $\mathbf{k}$ vector of the laser must be perpendicular to the quantization axis. If the laser’s electric field is not parallel to the quantization axis, then the laser will have $\sigma^+$ and $\sigma^-$ components even if the field is linearly polarized.
55 In fact, the product $\frac{\hbar}{\mathbf{e}} \langle \ell'j' | i_j^{(1)} | nj \rangle$ is $\sqrt{2j+1}$ times the dipole moment, due to the normalization of the $3j$ symbols. That is, the multiplicity of possible excited-state levels “dilutes” the transition strength to a given level.
Note that this expression disagrees in sign with Eq. (4.136) of Sobelman. However, Sobelman’s equation may be a misprint, as it disagrees Eq. (4.55) of his own book, which equation is consistent with Edmond’s Table 2. The inconsistency leads to an incorrect sign in Sobelman’s Eq. (4.138), where the phase should be $(-1)^l$. 