Chapter 7

Atom-Light Interaction

7.1 Dipole Transitions

Dipole transitions are a workhorse of atomic physics experiments. They are used for laser cooling, state preparation, state measurement, etc. In fact, the transitions are so commonly used that when physicists refer to "forbidden" transitions, what they really mean is that a transition is not allowed under the dipole interaction, and therefore more accurately it is dipole-forbidden.

7.1.1 Interaction Hamiltonian

In Chapter 6 we derived the Hamiltonian for a charged particle in an electromagnetic field (Eq. 6.32) as:

$$H = \frac{[\hat{\boldsymbol{p}} - q\vec{A}(\hat{\boldsymbol{r}}, t)]^2}{2m} + V(\hat{\boldsymbol{r}}) + qU(\hat{\boldsymbol{r}}, t) \tag{7.1}$$

where $\vec{A}$ is the vector potential of the external electromagnetic field, U is the scalar field, and it should be noted that this is a semi-classical treatment where the electromagnetic field is a classical quantity, but the atom is treated quantum mechanically. Since the applied electromagnetic field does not originate from a source charge distribution, we can assume that $\vec{\nabla}U = 0$, and we can expand the squared term to obtain:

$$\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(\hat{\boldsymbol{r}}) - \frac{q}{2m}(\hat{\boldsymbol{p}} \cdot \vec{A} + \vec{A} \cdot \hat{\boldsymbol{p}}) + \frac{q^2}{2m}\vec{A}^2 \tag{7.2}$$

The sum of the first two terms is considered to be $\hat{H}_0$, i.e. the Hamiltonian of the atom without the external electric field. The eigenstates and eigenvalues of $\hat{H}_0$ are assumed to be known. The last term, proportional to $\vec{A}^2$, will be ignored, as we will assume to be operating in the regime where the electromagnetic field is sufficiently weak. This leaves us with the interaction Hamiltonian:

$$\hat{H}_I = -\frac{q}{2m}(\hat{\boldsymbol{p}} \cdot \vec{A} + \vec{A} \cdot \hat{\boldsymbol{p}}) \tag{7.3}$$

Recall that, in coordinate space, $\hat{\boldsymbol{p}} = -i\hbar\vec{\nabla}$, and therefore:

$$\begin{aligned}\hat{\boldsymbol{p}} \cdot \vec{A}\,|\psi\rangle &= -i\hbar\vec{\nabla}(\vec{A}\,|\psi\rangle) \\ &= -i\hbar[(\vec{\nabla}\cdot\vec{A}) + \vec{A}\cdot\vec{\nabla}]\,|\psi\rangle \\ &= [-i\hbar(\vec{\nabla}\cdot\vec{A}) + \vec{A}\cdot\hat{\boldsymbol{p}}]\,|\psi\rangle\end{aligned} \tag{7.4}$$

7.1.2 Gauge Transformations

Recall that the vector potential arises from Maxwell's equations. In particular, from $\vec{\nabla}\cdot\vec{B} = 0$. From vector calculus, remember $\vec{\nabla}\cdot\vec{\nabla}\times\vec{A}) = 0$ for a vector field $\vec{A}(\vec{r},t)$, and so $\vec{A}$ is considered a vector potential for the magnetic field, such that $\vec{B} = \vec{\nabla}\times\vec{A}$.

Plugging this into another of Maxwell's equation, namely $\vec{\nabla}\times\vec{E} = -\partial\vec{B}/\partial t$, we see that

$$\vec{\nabla}\times\left[\vec{E} + \frac{\partial\vec{A}}{\partial t}\right] = 0. \tag{7.5}$$

Again, from vector calculus we know that $\vec{\nabla}\times\vec{\nabla}U = 0$ for a scalar function $U(\vec{r},t)$, and therefore we can designate U as the scalar potential such that

$$\vec{E} + \frac{\partial\vec{A}}{\partial t} = -\vec{\nabla}U. \tag{7.6}$$

The set of the scalar and vector potentials $\{U, \vec{A}\}$ constitute a gauge for describing the electromagnetic field. There exist an infinite number of gauges which generate the same electric and magnetic fields, which are the physically relevant quantities. These gauges therefore equivalently describe the physical system. We can transform from a gauge $\{U, \vec{A}\}$ to a second gauge $\{U', \vec{A}'\}$ by using the following:

$$\vec{A}'(\vec{r},t) = \vec{A}(\vec{r},t) + \vec{\nabla}\chi(\vec{r},t) \tag{7.7}$$

$$U'(\vec{r},t) = U(\vec{r},t) - \frac{\partial}{\partial t}\chi(\vec{r},t) \tag{7.8}$$

We see, of course, that these gauge transformations don't change the electric and magnetic fields, since:

$$\vec{B}' = \vec{\nabla}\times\vec{A}' = \vec{\nabla}\times\vec{A} + \vec{\nabla}\times\vec{\nabla}\chi = \vec{\nabla}\times\vec{A} = \vec{B} \tag{7.9}$$

$$\vec{E}' = -\vec{\nabla}U' - \frac{\partial\vec{A}'}{\partial t} = -\vec{\nabla}U + \vec{\nabla}\frac{\partial\chi}{\partial t} - \frac{\partial A}{\partial t} - \frac{\partial\vec{\nabla}\chi}{\partial t} = -\vec{\nabla}U - \frac{\partial A}{\partial t} = \vec{E} \tag{7.10}$$

where in the first equation we have made use of the fact that the curl of a gradient is zero, and in the second equation we use the interchangeability of the temporal and spatial derivatives.

7.1.3 Dipole Interaction

Since the vector potential is not uniquely defined, and we are allowed to choose a gauge to work in. In this case, the Coulomb gauge, defined by $\vec{\nabla} \cdot \vec{A} = 0$, is the obvious choice to simplify Eq. 7.4 and obtain $\hat{\boldsymbol{p}} \cdot \vec{A} = \vec{A} \cdot \hat{\boldsymbol{p}}$. Our interaction Hamiltonian in the Coulomb gauge is therefore:

$$\hat{H}_I = -\frac{q}{m} \vec{A} \cdot \hat{\boldsymbol{p}} \tag{7.11}$$

Another consequence of using the Coulomb gauge is that the solutions to $\hat{\nabla} \cdot \vec{A} = 0$ can be written as plane waves:

$$\vec{A}(\hat{\boldsymbol{r}}, t) = \vec{A}_0 \exp[i(\vec{k} \cdot \hat{\boldsymbol{r}} - \omega t)] \tag{7.12}$$

where $\vec{A}_0$ is a time- and space-independent complex vector. The requirement $\vec{\nabla} \cdot \vec{A} = 0$ is then equivalent to $\vec{k} \cdot \vec{A}_0 = 0$, i.e. the direction of propagation $\vec{k}$ is orthogonal to $\vec{A}_0$.

Recall also that $\vec{E} = -\partial \vec{A}/\partial t - \vec{\nabla} U$, and we can assume $\vec{\nabla} U = 0$ for our gauge. For our plane wave solution, this is equivalent to $\vec{E} = i\omega \vec{A}$. We define the polarization unit vector $\hat{\epsilon}$ such that $\vec{E} = E(\hat{\boldsymbol{r}}, t)\hat{\epsilon}$, and therefore we have $\vec{A}_0 = A_0 \hat{\epsilon}$ and $\vec{E} = i\omega A_0 \hat{\epsilon} \exp[i(\vec{k} \cdot \hat{\boldsymbol{r}} - \omega t)]$, and $\vec{k} \cdot \hat{\epsilon} = 0$. In the Coulomb gauge, the plane wave's polarization is orthogonal to the direction of propagation.

Now consider that vector potential also defines the magnetic field as $\vec{B} = \vec{\nabla} \times \vec{A} = i\vec{k} \times \vec{A}$. This means that we have now defined the set of three orthogonal unit vectors ($\hat{k}$, $\hat{\epsilon}$, $\hat{k} \times \hat{\epsilon}$) for the direction of propagation, electric field polarization, and magnetic field polarization, resp., and we see that:

$$\begin{aligned} \vec{A}(\hat{\boldsymbol{r}}, t) &= A_0 \hat{\epsilon} \exp[i(\vec{k} \cdot \hat{\boldsymbol{r}} - \omega t)] \\ \vec{E}(\hat{\boldsymbol{r}}, t) &= i\omega A_0 \hat{\epsilon} \exp[i(\vec{k} \cdot \hat{\boldsymbol{r}} - \omega t)] \\ \vec{B}(\hat{\boldsymbol{r}}, t) &= ikA_0 (\hat{k} \times \hat{\epsilon}) \exp[i(\vec{k} \cdot \hat{\boldsymbol{r}} - \omega t)] \end{aligned} \tag{7.13}$$

Note that $|\vec{E}|/|\vec{B}| = \omega/k = c$.

We can plug this solution into Eq. 7.11 to obtain:

$$\hat{H}_I = -\frac{q}{m} A_0 e^{-i\omega t} \exp(i\vec{k} \cdot \hat{\boldsymbol{r}}) \hat{\epsilon} \cdot \hat{\boldsymbol{p}} \tag{7.14}$$

Let's now consider the term with $\vec{k} \cdot \hat{\boldsymbol{r}}$ in the exponential. We expect that the expectation value of $\hat{\boldsymbol{r}}$ will be of magnitude similar to the Bohr radius a_0. Therefore we can safely assume that $\vec{k} \cdot r \approx k a_0 \approx a_0/\lambda \ll 1$. We can therefore expand the exponential as

$$\hat{H}_I = -\frac{q}{m} A_0 e^{-i\omega t} (1 + i\vec{k} \cdot \hat{\boldsymbol{r}} + \dots) \hat{\epsilon} \cdot \hat{\boldsymbol{p}} \tag{7.15}$$

Clearly the interaction Hamiltonian can be expanded in powers of $\vec{k} \cdot \hat{\boldsymbol{r}}$. For now we will only consider the leading (zero-order) term. This is known as the dipole approximation, and in essence it means that the atom does not see the spatial variation of the field due to the small spatial extent of the atomic wave function compared to the wavelength of the applied

field. This approximation gives rise to the so-called electric dipole interaction Hamiltonian, and is typically denoted by E1:

$$\hat{H}_I^{(\mathrm{E1})} = -\frac{q}{m}\frac{E_0}{i\omega}e^{-i\omega t}\hat{\epsilon}\cdot\hat{\boldsymbol{p}} \tag{7.16}$$

where we have used $E_0 = i\omega A_0$ as the electric field amplitude. This is one form of the dipole interaction Hamiltonian. It is possible to write it another way by realizing that:

$$[\hat{\boldsymbol{r}}, \hat{H}_0] = \frac{i\hbar}{m}\hat{\boldsymbol{p}} \tag{7.17}$$

and therefore we can write our interaction Hamiltonian as:

$$\hat{H}_I^{(\mathrm{E1})} = \frac{q}{\hbar\omega}E_0 e^{-i\omega t}\hat{\epsilon}\cdot(\hat{\boldsymbol{r}}\hat{H}_0 - \hat{H}_0\hat{\boldsymbol{r}}) \tag{7.18}$$

If we now try to calculate the matrix element of this interaction Hamiltonian between two eigenstates of $\hat{H}_0$, we see that:

$$\langle f|\hat{H}_I^{(\mathrm{E1})}|i\rangle = \frac{q}{\hbar\omega}E_0 e^{-i\omega t}\langle f|\hat{\epsilon}\cdot(\hat{\boldsymbol{r}}\hat{H}_0 - \hat{H}_0\hat{\boldsymbol{r}})|i\rangle \tag{7.19}$$

We can also use the fact that $\hat{H}_0|k\rangle = E_k|k\rangle = \hbar\omega_k|k\rangle$ (as well as the Hermitian conjugate of this expression) to obtain:

$$\langle f|\hat{H}_I|i\rangle = -q\frac{\omega_{fi}}{\omega}E_0 e^{-i\omega t}\langle f|\hat{\epsilon}\cdot\hat{\boldsymbol{r}}|i\rangle \tag{7.20}$$

where $\omega_{fi} = \omega_f - \omega_i$ is the angular frequency splitting corresponding to the energy difference between the initial and final states. Since we are usually interested in driving near-resonant transitions, we can safely assume that $\omega_{fi} \approx \omega$, and we obtain what is commonly known as the dipole interaction Hamiltonian:

$$\langle f|\hat{H}_I|i\rangle = -qE_0 e^{-i\omega t}\hat{\epsilon}\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle = -q\vec{E}(0,t)\cdot\langle f|\hat{\boldsymbol{r}}|i\rangle \tag{7.21}$$

which is also often written without the inner product as:

$$\hat{H}_I = -q\vec{E}(0,t)\cdot\hat{\boldsymbol{r}} \tag{7.22}$$

where the assumption is that the electric field is treated classically, and the atom quantum-mechanically. This is often referred to as the semi-classical treatment of atom-field interaction. The form of this expression also matches the classically expected energy of a dipole in an external electric field.

Let's review the approximation we have made in this semi-classical treatment:

(i) $q^2\hat{\boldsymbol{A}}^2/m \approx 0$ (Weak field approximation)

(ii) $\omega_{fi} \approx \omega$ (Near resonance approximation)

(iii) $\vec{k}\cdot\hat{\boldsymbol{r}} \ll 1$ (Dipole approximation)

While these may seem necessary, a fully quantized treatment of the field reveals that the $\hat{\boldsymbol{A}}^2$ term disappears from the Hamiltonian, and additionally it is not necessary to make approximation (ii) to achieve at Eq. 7.22. In fact, merely introducing the gauge transformation using the scalar function $\chi(t) = -(\hat{\epsilon}\cdot\hat{\boldsymbol{r}})A_0 e^{-i\omega t}$, and using Eq. 7.7

$$\vec{A}'(\hat{\boldsymbol{r}},t) = \vec{A}(\hat{\boldsymbol{r}},t) + \vec{\nabla}\chi(t) = A_0\hat{\epsilon}\exp[i(\vec{k}\cdot\hat{\boldsymbol{r}} - \omega t)] - A_0\hat{\epsilon}e^{-i\omega t} \tag{7.23}$$

The dipole approximation then amounts to setting $\vec{k}\cdot\hat{\boldsymbol{r}} = 0$, and therefore $\vec{A}' = 0$. The scalar potential in the new gauge is given by

$$U'(\hat{\boldsymbol{r}},t) = U(\hat{\boldsymbol{r}},t) - \frac{\partial}{\partial t}\chi(\hat{\boldsymbol{r}},t) = -i\omega(\hat{\epsilon}\cdot\hat{\boldsymbol{r}})A_0 e^{-i\omega t} = -E_0 e^{-i\omega t}(\hat{\epsilon}\cdot\hat{\boldsymbol{r}}) \tag{7.24}$$

Inserting this new gauge $\{\vec{A}', U'\}$ into Eq. 7.1, we see that the interaction Hamiltonian in this alternative gauge is just given by Eq. 7.22.

It should then be clear that the dipole approximation, $\vec{k}\cdot\hat{\boldsymbol{r}} \ll 1$, i.e. approximation (iii), is the only one required to obtain the resulting interaction Hamiltonian.

7.1.4 Dipole Transition Rules

The dipole interaction is characterized by the matrix elements of the position vector operator $\hat{\boldsymbol{r}} = \hat{x}\hat{e}_x + \hat{y}\hat{e}_y + \hat{z}\hat{e}_z$, where we have written it explicitly as vector sum of the one-dimensional position operators and the unit vectors $\hat{e}_i$. By writing the one-dimensional position operators in spherical coordinates, we obtain:

$$\begin{aligned}\hat{\boldsymbol{r}} &= \hat{r}\sin(\theta)\cos(\phi)\hat{e_x} + \hat{r}\sin(\theta)\sin(\phi)\hat{e_y} + \hat{r}\cos(\theta)\hat{e_z} \\ &= \hat{r}\left[\sqrt{\frac{2\pi}{3}}(Y_1^{-1} - Y_1^1)\hat{e}_x + \sqrt{\frac{2\pi}{3}}i(Y_1^{-1} + Y_1^1)\hat{e}_y + \sqrt{\frac{4\pi}{3}}Y_1^0\hat{e}_z\right]\end{aligned} \tag{7.25}$$

where we have written the angular dependence as functions of the spherical harmonics Y_1^m for $m \in \{-1, 0, 1\}$. Grouping the terms by Y_l^m function yields:

$$\begin{aligned}\hat{\boldsymbol{r}} &= \hat{r}\sqrt{\frac{4\pi}{3}}\left[Y_1^{-1}\left(\frac{\hat{e}_x + i\hat{e}_y}{\sqrt{2}}\right) + Y_1^0\hat{e}_z + Y_1^1\left(\frac{-\hat{e}_x + i\hat{e}_y}{\sqrt{2}}\right)\right] \\ &= \hat{r}\sqrt{\frac{4\pi}{3}}[Y_1^{-1}\hat{\sigma}_+ + Y_1^0\hat{\pi} + Y_1^1\hat{\sigma}_-]\end{aligned} \tag{7.26}$$

Here we have denoted the polarization basis with the unit vectors $\hat{\sigma}_\pm = 2^{-1/2}(\pm\hat{e}_x + i\hat{e}_y)$, and $\hat{\pi} = \hat{e}_z$. It should be noted that our choice of coordinate system so far has been arbitrary. There is nothing in this treatment which would set a preferential axis. In a typical system, however, a constant magnetic field is applied along a particular axis, and in this case it makes sense to align the z-axis with the magnetic field, since this is the axis along which we are interested in the stationary states of the Hamiltonian (i.e. the states with a well-defined J_z eigenvalue. This is typically denoted the *quantization axis*, and it is denoted by the $\hat{\pi}$ polarization eigenvector which is equivalent to the spatial $\hat{e}_z$ axis in our description.

It is often colloquially stated that the $\hat{\sigma}_\pm$ polarization components are due to left- or right-hand circularly polarized light, but this statement is only true for circularly polarized light propagating along the quantization axis ($\hat{k} = \hat{e}_z$). It is in fact also possible to obtain $\hat{\sigma}_\pm$ polarization components from linearly polarized light incident on the atom from a direction not parallel to the quantization axis. Consider, as an example, light propagating in the $\hat{k} = \hat{e}_x$ direction, and linearly polarized such that $\hat{\epsilon} = \hat{e}_y$. The polarization vector, written in the polarization basis, is then $\hat{\epsilon} = 2^{-1/2}(-i)(\hat{\sigma}_+ + \hat{\sigma}_-)$.

Now consider the matrix element in question, $\langle f|\hat{\epsilon}\cdot\hat{\boldsymbol{r}}|i\rangle$. The angular part of this matrix element for the three polarization components can be written as:

$$\langle f|\hat{\epsilon}\cdot\hat{\boldsymbol{r}}|i\rangle = \langle n_f, l_f, m_f|\hat{\epsilon}\cdot\hat{\boldsymbol{r}}|n_i, l_i, m_i\rangle \propto \int_0^{2\pi}\int_0^{\pi} \left(Y_{l_f}^{m_f}\right)^* Y_1^{m_\epsilon} Y_{l_i}^{m_i} \sin(\theta) d\theta d\phi \tag{7.27}$$

where $m_\epsilon = -1, 0, +1$ for $\hat{\epsilon} = \hat{\sigma}_-, \hat{\pi}, \hat{\sigma}_+$-polarized light, resp. It can be shown that this integral vanishes unless the following conditions are met:

$$\begin{aligned} m_f - m_i &= m_\epsilon \\ l_f - l_i &= \pm 1 \end{aligned} \tag{7.28}$$

These conditions are the selection rules for dipole allowed transitions. Since the dipole interaction Hamiltonian has odd parity, it couples states with opposite parity ($l_f - l_i = \pm 1$). We also see that $\hat{\sigma}_\pm$-polarized light adds (+) or subtracts (-) a quantum of angular momentum from the z-axis of angular momentum.

7.2 Higher Order Transitions

There are several reasons why one may want to consider transitions between two states with a vanishing dipole interaction Hamiltonian. For example, atomic clocks prefer to use narrow transitions with a very narrow linewidth or, equivalently, a small interaction Hamiltonian matrix element. As we saw from Eq. 7.15, we can expand the exponential term in the electromagnetic field in powers of $\vec{k}\cdot\hat{\boldsymbol{r}}$, which is much less than unity assuming $a_0/\lambda \ll 1$. Clearly, these higher order terms will yield matrix elements much smaller than those of the dipole interaction Hamiltonian, and so would be more suited to narrow linewidth applications.

7.2.1 First-order Hamiltonian

When a transition is not allowed using the dipole approximation, we have to consider higher order terms in the expansion of the field shown in Eq. 7.15. The next (first) order in the expansion is given by:

$$H_I^{(1)} = -i\frac{q}{m}kA_0 e^{-i\omega t}(\hat{k}\cdot\hat{\boldsymbol{r}})(\hat{\epsilon}\cdot\hat{\boldsymbol{p}}) \tag{7.29}$$

We can now use the vector identity $(\vec{A}\cdot\vec{B})(\vec{C}\cdot\vec{D}) = (\vec{A}\times\vec{C})\cdot(\vec{B}\times\vec{D}) + (\vec{B}\cdot\vec{C})(\vec{A}\cdot\vec{D})$ to rewrite this Hamiltonian as

$$H_I^{(1)} = -i\frac{q}{m}kA_0 e^{-i\omega t}\left[(\hat{k}\times\hat{\epsilon})(\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}) + (\hat{\epsilon}\cdot\hat{\boldsymbol{r}})(\hat{k}\cdot\hat{\boldsymbol{p}})\right] \tag{7.30}$$

We will treat the two terms in square brackets separately.

We can rewrite the first term using Eq. 1.1 and Eq. 7.13

$$H_I^{\mathrm{M1}} = -\frac{q}{m}\vec{B}(0,t)\cdot\hat{\boldsymbol{L}} \tag{7.31}$$

where we have labeled this Hamiltonian with the M1 label to denote that this the interaction of the magnetic dipole with the magnetic field. This term is commonly referred to as the magnetic dipole interaction. Our semi-classical treatment cannot account for the electron spin, as this is a purely quantum-mechanical property. However, we can use our prior experience with the total magnetic moment Eq. 3.27 to add in the electron spin term:

$$H_I^{(\mathrm{M1})} = -\frac{q}{m}\vec{B}(0,t)\cdot(\hat{\boldsymbol{L}} + g_s\hat{\boldsymbol{S}}) \tag{7.32}$$

where $g_s \approx 2$ is the electron spin g-factor.

Similar to the treatment in Section 7.1.3, the second term in Eq. 7.30 can be written as

$$H_I^{(\mathrm{E2})} = i\frac{qk}{\hbar\omega}\left(\vec{E}(0,t)\cdot\hat{\boldsymbol{r}}\right)\left[\hat{k}\cdot(\hat{\boldsymbol{r}}\hat{H}_0 - \hat{H}_0\hat{\boldsymbol{r}})\right] \tag{7.33}$$

Where we have denoted this Hamiltonian with the E2 label, denoting that this is known as the electric quadrupole transition Hamiltonian. The transition matrix elements are

$$\langle f|H_I^{(\mathrm{E2})}|i\rangle = -iq\frac{\omega_{fi}}{\omega}\left[\vec{E}(0,t)\cdot\hat{\boldsymbol{r}}\right](\vec{k}\cdot\hat{\boldsymbol{r}}) \tag{7.34}$$

Similarly to Eq. 7.22, this can be rewritten using a gauge transformation to obtain:

$$H_I^{(\mathrm{E2})} = -iq(\vec{E}(0,t)\cdot\hat{\boldsymbol{r}})(\vec{k}\cdot\hat{\boldsymbol{r}}) \tag{7.35}$$

This interaction looks very similar to the dipole interaction term, scaled by a factor of $i(\vec{k}\cdot\hat{\boldsymbol{r}})$, however it is slightly more complicated. The two factors of $\hat{\boldsymbol{r}}$ give rise to multiplied position terms of the form $\hat{x}_i\hat{x}_j$, and so there are six potential combinations. For example, the quadratic term $\hat{z}^2$ gives:

$$\hat{z}^2 = \hat{r}^2\cos^2(\theta) \tag{7.36}$$

$$= \frac{4}{3}\sqrt{\frac{\pi}{5}}Y_2^0 + \frac{2\sqrt{\pi}}{3}Y_0^0 \tag{7.37}$$

Here, the term proportional to Y_0^0 can be ignored since it is a constant, and the orthogonality between different spherical harmonics ensures that these terms will never contribute to transitions between different states. The quadratic terms can then be written as:

$$\begin{aligned}\hat{x}^2 &= \hat{r}^2 \sin^2(\theta)\cos^2(\phi) \\ &= \sqrt{\frac{2\pi}{15}}\left(Y_2^{-2} - \sqrt{\frac{2}{3}}Y_2^0 + Y_2^2\right) \qquad (7.38)\\ \hat{y}^2 &= \hat{r}^2 \sin^2(\theta)\sin^2(\phi) \\ &= \sqrt{\frac{2\pi}{15}}\left(-Y_2^{-2} - \sqrt{\frac{2}{3}}Y_2^0 - Y_2^2\right) \qquad (7.39)\\ \hat{z}^2 &= \frac{4}{3}\sqrt{\frac{\pi}{5}}Y_2^0 \qquad (7.40)\end{aligned}$$

where all terms proportional to Y_0^0 have been dropped.

Similarly, the cross terms give:

$$\begin{aligned}\hat{x}\hat{y} &= \hat{r}^2 \sin^2(\theta)\sin(\phi)\cos(\phi) \\ &= \hat{r}^2 i\sqrt{\frac{2\pi}{15}}(Y_2^{-2} - Y_2^2) \qquad (7.41)\\ \hat{x}\hat{z} &= \hat{r}^2 \sin(\theta)\cos(\theta)\cos(\phi) \\ &= \hat{r}^2\sqrt{\frac{2\pi}{15}}(Y_2^{-1} - Y_2^1) \qquad (7.42)\\ \hat{y}\hat{z} &= \hat{r}^2 \sin(\theta)\cos(\theta)\sin(\phi) \\ &= \hat{r}^2 i\sqrt{\frac{2\pi}{15}}(Y_2^{-1} + Y_2^1) \qquad (7.43)\end{aligned}$$

Due to the direction of propagation being of relevance to the transition, the behavior is more complex than for the dipole transitions. However, do note that for circularly polarized light propagating in the z-direction we obtain behavior quite similar to the same configuration for the dipole interaction, namely that a circularly polarized field changes the z-component of the atom's angular momentum by a single quantum.

Clearly, by increasing the order of $\vec{k}\cdot\hat{\boldsymbol{r}}$ we can describe increasingly weak transitions. The second-order term gives rise to magnetic quadrupole and electric octopole transitions, and so on. The interaction interplay between the propagation direction, polarization, and quantization axis also becomes increasingly complex.

7.2.2 Selection rules for first-order transitions

First of all, note that both the magnetic dipole and electric quadrupole interaction Hamiltonians have even parity. Therefore the initial and final states must have the same parity in order for the matrix elements to be non-zero. This also means that these first-order transitions can not happen between states which have a dipole-allowed transition.

The magnetic dipole Hamiltonian will have terms proportional to $\hat{L}_i + 2\hat{S}_i$, where $i \in \{x, y, z\}$. For the z components, recall that the eigenstates of H_0 are by design also eigenstates of L_z and

S_z. Therefore the orthogonality of the eigenstates guarantees that $\Delta l = \Delta m_l = \Delta m_s = 0$. For the x and y components, we need to remember that we can write these in terms of the angular momentum ladder operators $L_\pm = L_x \pm iL_y$, and likewise for $\vec{S}$. The ladder operators change the z-component of their corresponding angular momentum by 1, and therefore we know that $\Delta l = 0$, $\Delta m_l = \pm 1$, and $\Delta m_s = \pm 1$.

The magnetic dipole interaction is often used in atomic physics experiments to drive transitions between different states in the same level of the atom, such as different hyperfine states or Zeeman sublevels, using microwave fields, typically on the order of several GHz in frequency.

The angular components of the electric quadrupole transition matrix elements can be written similarly to Eq. 7.27:

$$\langle f|\hat{H}_I^{(\mathrm{E2})}|i\rangle = \langle n_f, l_f, m_f|\hat{H}_I^{(\mathrm{E2})}|n_i, l_i, m_i\rangle \propto \int_0^{2\pi}\int_0^{\pi} \left(Y_{l_f}^{m_f}\right)^* Y_2^{m_\epsilon} Y_{l_i}^{m_i} \sin(\theta) d\theta d\phi \tag{7.44}$$

for $m_\epsilon \in \{-2, -1, 0, 1, 2\}$. This overlap integral can be shown to vanish unless:

$$\begin{aligned} m_f - m_i &= m_\epsilon \\ l_f - l_i &= 0, \pm 2 \end{aligned} \tag{7.45}$$

Electric dipole transitions can therefore couple states which differ in orbital angular momentum by ± 2. They can therefore drive, for example, S-to-D transitions, which are therefore typically referred to as quadrupole transitions.