Chapter 13

Radiative transitions

Previously, we have addressed the quantum theory of atoms coupled to a classical time-independent electromagneic field, cf. our discussion of the Zeeman and Stark effects. However, to develop a complete quantum mechanical description of light-matter interaction, we have to address both the quantum theory of the electromagnetic field and the coupling of light to matter. In the following section, we will address both of these issues in turn. Our motivation for developing such a consistent theory is that it will (a) provide us with a platform to address the problem of radiative transitions in atoms and (b) it forms the basis of the field of **quantum optics**.

13.1 Coupling of matter to the electromagnetic field

Let us then consider the Hamiltonian of a single-electron atom subject to a time-dependent external electromagnetic field,

$$\hat{H}_{\rm atom} = \frac{1}{2m}\left(\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r},t)\right)^2 - e\phi(\mathbf{r},t) + V(\mathbf{r})\,.$$

Here $V(\mathbf{r})$ denotes the binding potential associated with the atomic nucleus. To keep our discussion of a complex problem as simple as possible, we have focussed on the single electron system. However, a generalization of the methodology to multi-electron atoms would not present significant challenges. Expanding the kinetic energy, the atomic Hamiltonian can be recast as $\hat{H}_{\rm atom} = \hat{H}_0 + \hat{H}_{\rm para} + \hat{H}_{\rm dia.}$, where

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r})\,,$$

denotes the usual non-interacting Hamiltonian of the isolated atom,

$$\boxed{\hat{H}_{\rm para}(t) = \frac{e}{m}\mathbf{A}(t)\cdot\hat{\mathbf{p}}\,,}$$

represents the time-dependent paramagnetic term arising from the coupling of the electron to the electromagnetic field, and $\hat{H}_{\rm dia} = (e\mathbf{A})^2/2m$ represents the diamagnetic term. Since we will be interested in the absorption and emission of single photons, we can neglect the influence of diamagnetic term which presents only a tiny perturbation in the atomic system.

Previously, in chapter 11.2, we have see that the quantum Hamiltonian for the electromagnetic field can be expressed as,

$$\boxed{\hat{H}_{\rm rad} = \sum_{\mathbf{k},\lambda=1,2}\hbar\omega_{\mathbf{k}}\left(a^\dagger_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda} + \frac{1}{2}\right)\,,}$$

where the operators $a^\dagger_{\mathbf{k}\lambda}$ and $a_{\mathbf{k}\lambda}$ create and annihilate photons with wavevector $\mathbf{k}$ and polarization λ, and $\omega_{\mathbf{k}} = c|\mathbf{k}|$. These ladder operators obey the (bosonic) commutation relations, $[a_{\mathbf{k}\lambda}, a^\dagger_{\mathbf{k}'\lambda'}] = \delta_{\mathbf{k},\mathbf{k}'}\delta_{\lambda,\lambda'}$, with $[a_{\mathbf{k}\lambda}, a_{\mathbf{k}'\lambda'}] = [a^\dagger_{\mathbf{k}\lambda}, a^\dagger_{\mathbf{k}'\lambda'}] = 0$, and act on photon number states as

$$a_{\mathbf{k}\lambda}|n_{\mathbf{k}\lambda}\rangle = \sqrt{n_{\mathbf{k}\lambda}}|n_{\mathbf{k}\lambda} - 1\rangle$$
$$a^\dagger_{\mathbf{k}\lambda}|n_{\mathbf{k}\lambda}\rangle = \sqrt{n_{\mathbf{k}\lambda} + 1}|N_{\mathbf{k}\lambda} + 1\rangle\,.$$

Here $|n_{\mathbf{k}\lambda}\rangle$ represents a photon number state with $n_{\mathbf{k},\lambda}$ photons in the mode $(\mathbf{k}\lambda)$. Finally, in the Heisenberg representation, we have seen that the vector potential can be expanded in field operators as

$$\boxed{\mathbf{A}(\mathbf{r},t) = \sum_{\mathbf{k},\lambda}\sqrt{\frac{\hbar}{2\epsilon_0\omega_{\mathbf{k}}V}}\left(\hat{\mathbf{e}}_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \hat{\mathbf{e}}^*_{\mathbf{k}\lambda}a^\dagger_{\mathbf{k}\lambda}e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}\right)\,.}$$

Taken together, $\hat{H} = \hat{H}_0 + \hat{H}_{\rm rad} + \hat{H}_{\rm para}(t)$ specify the full quantum mechanical Hamiltonian of the atom light system.

13.1.1 Spontaneous emission

With this background, let us now consider the probability for an atom, initially in a state $|\mathrm{i}\rangle$ to make a transition to a state $|\mathrm{f}\rangle$ leading to the emission of a photon of wavevector $\mathbf{k}$ and polarization λ – a process of spontaneous emission. If we suppose that the radiation field is initially prepared in the vacuum state, $|0\rangle$, then the final state involves one photon, $|\mathbf{k}\lambda\rangle = a^\dagger_{\mathbf{k}\lambda}|0\rangle$. Therefore, making use of Fermi's Golden rule (12.5), with the perturbation $\hat{H}_{\rm para} = \frac{e}{m}\hat{\mathbf{A}}(t)\cdot\hat{\mathbf{p}}$, we have the transition probability

$$\Gamma_{\mathrm{i}\to\mathrm{f}}(t) = \frac{2\pi}{\hbar^2}|\langle\mathrm{f}|\otimes\langle\,\mathbf{k}\lambda|\hat{H}_{\rm para}|\mathrm{i}\rangle\otimes|\Omega\rangle|^2\delta(\omega_{\rm if} - \omega_{\mathbf{k}})$$

where $\omega_{\rm if} = (E_{\rm i} - E_{\rm f})/\hbar$. Then substituting the field operator expansion of $\hat{\mathbf{A}}$, we have

$$\Gamma_{\mathrm{i}\to\mathrm{f},\mathbf{k}\lambda} = \frac{2\pi}{\hbar}\left|\langle\mathrm{f}|\otimes\langle\,\Omega|a_{\mathbf{k}\lambda}\frac{e}{m}\sqrt{\frac{\hbar}{2\epsilon_0\omega_{\mathbf{k}}V}}\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}a^\dagger_{\mathbf{k}\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle\otimes|\Omega\rangle\right|^2\delta(\omega_{\rm if} - \omega_{\mathbf{k}})$$

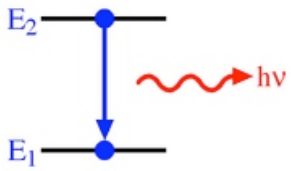
As a result, we finally obtain

$$\boxed{\Gamma_{\mathrm{i}\to\mathrm{f},\mathbf{k}\lambda} = \frac{2\pi}{\hbar}\left|\langle\mathrm{f}|\frac{e}{m}\sqrt{\frac{\hbar}{2\epsilon_0\omega_{\mathbf{k}}V}}\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle\right|^2\delta(E_{\rm i} - E_{\rm f} - \hbar\omega_{\mathbf{k}})}$$

To determine the transition rate, we have to analyse matrix elements of the form $\langle\mathrm{f}|e^{i\mathbf{k}\cdot\mathbf{r}}\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle$. Let us begin by estimating its magnitude. For a typical atomic state, $\langle\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\hat{\mathbf{p}}\rangle \simeq p \simeq Zmc\alpha$, where we have included a general nuclear charge, Z. But what about the exponential factor? With $r \sim \hbar/p \simeq \hbar/mZc\alpha$, and $\omega_{\mathbf{k}} = c|\mathbf{k}| \simeq \frac{p^2}{2m}$ (for electronic transitions), we have

$$\mathbf{k}\cdot\mathbf{r} \simeq \frac{\omega_{\mathbf{k}}}{c}\frac{\hbar}{p} \simeq \frac{\hbar p}{mc} \simeq Z\alpha\,.$$

This means that, for $Z\alpha \ll 1$, we can expand the exponential as a power series in $\mathbf{k}\cdot\mathbf{r}$ with the lowest terms being dominant. Taking the zeroth order term, and making use of the operator identity, $\hat{\mathbf{p}} = \frac{i}{\hbar}[\hat{H}_0, \mathbf{r}]$ which follows from



Schematic showing spontaneous emission from an initial state at energy $E_{\rm i} = E_2$ to a final state at energy $E_{\rm f} = E_1$.

the Heisenberg equations of motion for operators, the matrix element may be written as

$$\langle \mathrm{f}|\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle = m\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\langle \mathrm{f}|\frac{i}{\hbar}[\hat{H}_0,\mathbf{r}]|\mathrm{i}\rangle = im\frac{E_\mathrm{f}-E_\mathrm{i}}{\hbar}\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\langle \mathrm{f}|\mathbf{r}|\mathrm{i}\rangle = -im\omega_{\mathbf{k}}\langle \mathrm{f}|\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\mathbf{r}|\mathrm{i}\rangle\,.$$

This result, which emerges from the leading approximation in $Z\alpha$, is known as the **electric dipole approximation**. Effectively, we have set (exercise)

$$\boxed{\frac{e}{m}\hat{\mathbf{A}}(\mathbf{r},t)\cdot\hat{\mathbf{p}}\simeq e\hat{\mathbf{E}}(\mathbf{r},t)\cdot\mathbf{r}\,,}$$

translating to the potential energy of a dipole, with moment $\mathbf{d}=-e\mathbf{r}$, in an oscillating electric field.

13.1.2 Absorption and stimulated emission

Let us now consider the absorption of a photon with wave number, $\mathbf{k}$, and polarization, λ. If we assume that, in the initial state, there are $n_{\mathbf{k}\lambda}$ photons in state $(\mathbf{k}\lambda)$ then, after the transition, there will be $n_{\mathbf{k}\lambda}-1$. Then, if the initial state of the atom is $|\mathrm{i}\rangle$ and the final state is $|\mathrm{f}\rangle$, the transition amplitude involves the matrix element,

$$\begin{aligned}&\langle \mathrm{f}|\otimes\langle\,(n_{\mathbf{k},\lambda}-1)|\hat{H}_\mathrm{para}|\mathrm{i}\rangle\otimes|n_{\mathbf{k}\lambda}\rangle\\ &\quad=\langle \mathrm{f}|\otimes\langle\,(n_{\mathbf{k},\lambda}-1)|\frac{e}{m}\sqrt{\frac{\hbar}{2\epsilon_0\omega_{\mathbf{k}}V}}\hat{\mathbf{e}}_{\mathbf{k}\lambda}a_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle\otimes|n_{\mathbf{k}\lambda}\rangle\end{aligned}$$

Then, using the relation $a_{\mathbf{k}\lambda}|n_{\mathbf{k}\lambda}\rangle=\sqrt{n_{\mathbf{k}\lambda}}|(n_{\mathbf{k}\lambda}-1)\rangle$,

$$\langle \mathrm{f}|\otimes\langle\,(n_{\mathbf{k},\lambda}-1)|\hat{H}_\mathrm{para}|\mathrm{i}\rangle\otimes|n_{\mathbf{k}\lambda}\rangle=\langle \mathrm{f}|\frac{e}{m}\sqrt{\frac{\hbar n_{\mathbf{k}\lambda}}{2\epsilon_0\omega_{\mathbf{k}}V}}e^{i\mathbf{k}\cdot\mathbf{r}}\hat{\mathbf{e}}_{\mathbf{k}\lambda}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle$$

As a result, using Fermi's Golden rule, we obtain the transition amplitude,

$$\Gamma_{\mathrm{i}\to\mathrm{f},\mathbf{k}\lambda}=\frac{2\pi}{\hbar}\left|\langle \mathrm{f}|\frac{e}{m}\sqrt{\frac{\hbar n_{\mathbf{k}\lambda}}{2\epsilon_0\omega_{\mathbf{k}}V}}e^{i\mathbf{k}\cdot\mathbf{r}}\hat{\mathbf{e}}_{\mathbf{k}\lambda}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle\right|^2\delta(E_\mathrm{f}-E_\mathrm{i}-\hbar\omega_{\mathbf{k}})$$

In particular, we find that the absorption rate *increases* linearly with photon number, $n_{\mathbf{k}\lambda}$.

Similarly, if we now consider the emission process in which there is are already $n_{\mathbf{k},\lambda}$ photons in the initial state, we have the revised transition rate,

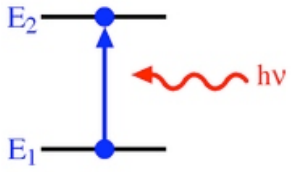
$$\Gamma_{\mathrm{i}\to\mathrm{f},\mathbf{k}\lambda}=\frac{2\pi}{\hbar}\left|\langle \mathrm{f}|\frac{e}{m}\sqrt{\frac{\hbar(n_{\mathbf{k},\lambda}+1)}{2\epsilon_0\omega_{\mathbf{k}}V}}e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{\mathbf{e}}^*_{\mathbf{k}\lambda}\cdot\hat{\mathbf{p}}|\mathrm{i}\rangle\right|^2\delta(E_\mathrm{f}-E_\mathrm{i}-\hbar\omega_{\mathbf{k}})\,.$$

This enhancement of the transition rate by the photon occupancy is known as **stimulated emission**.

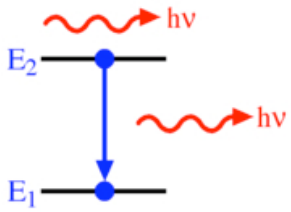
Altogether, in the dipole approximation, we have the transition rates,

$$\boxed{\Gamma_{\mathrm{i}\to\mathrm{f},\mathbf{k}\lambda}=\frac{\pi\omega_{\mathbf{k}}}{\epsilon_0 V}|\langle \mathrm{f}|\hat{\mathbf{e}}_{\mathbf{k}\lambda}\cdot\mathbf{d}|\mathrm{i}\rangle|^2\begin{cases}n_{\mathbf{k}\lambda}\;\delta(E_\mathrm{f}-E_\mathrm{i}-\hbar\omega_{\mathbf{k}}) & \text{absorption}\\ (n_{\mathbf{k}\lambda}+1)\;\delta(E_\mathrm{i}-E_\mathrm{f}-\hbar\omega_{\mathbf{k}}) & \text{emission}\end{cases}}$$

If there are no photons present initially, this expression reduces to that obtained from spontaneous emission. The $n_{\mathbf{k}\lambda}$-independent component of the



Schematic showing absorption from an initial state at energy $E_\mathrm{i}=E_1$ to a final state at energy $E_\mathrm{f}=E_2$.



Schematic showing the stimulated emission from an initial state at energy $E_\mathrm{i}=E_2$ to a final state at energy $E_\mathrm{f}=E_1$.

expression for absorption and emission coincide, an equality known as **detailed balance**.

If we are interested in the total rate, $d\Gamma_\lambda$ at which photons of polarization λ are scattered into the solid angle $d\Omega$, we must compute $dR_\lambda = \sum_{\mathbf{k}\in d\Omega} \Gamma_{\mathrm{i}\to\mathrm{f},\mathbf{k}\lambda}$. Since, in the elemental volume $d^3k = k^2 dk\, d\Omega$, there are $d^3kV/(2\pi)^3$ states, we may set $\sum_{\mathbf{k}} = \frac{V}{(2\pi)^3}\int k^2 dk\, d\Omega$. Finally, if we assume that the photon occupation of state $(\mathbf{k}\lambda)$ is isotropic, dependent only on $|\mathbf{k}|$, we find that the integrated transition rate per unit solid angle is given by $\frac{dR_\lambda}{d\Omega} = V\int \frac{k^2 dk}{(2\pi)^3}\Gamma_{\mathrm{i}\to\mathrm{f},\mathbf{k}\lambda}$ from which we obtain

$$\boxed{\frac{dR_\lambda}{d\Omega} = \frac{1}{4\pi\epsilon_0}\frac{\omega^3}{2\pi\hbar c^3}|\langle \mathrm{f}|\hat{\mathbf{e}}_{\mathbf{k}\lambda}\cdot\mathbf{d}|\mathrm{i}\rangle|^2 \begin{cases} n_\lambda(\omega) & \text{absorption} \\ n_\lambda(\omega)+1 & \text{emission} \end{cases}}$$

Here, in carrying out the integral, we have used the relation $\omega_{\mathbf{k}} = c|\mathbf{k}|$ and $\hbar\omega = |E_\mathrm{f} - E_\mathrm{i}|$. For a thermal distribution of photons, with the energy density specified by the Planck formula,

$$u(\omega) = \frac{\hbar\omega^3}{\pi c^3}\bar{n}_\lambda(\omega), \qquad \bar{n}_\lambda(\omega) = \frac{1}{e^{\hbar\omega_{\mathbf{k}}/k_\mathrm{B}T}-1},$$

this equates a stimulated absorption/emission rate,

$$\boxed{\frac{dR_\lambda}{d\Omega} = \frac{1}{4\pi\epsilon_0}\frac{1}{2\hbar^2}|\langle \mathrm{f}|\hat{\mathbf{e}}_{\mathbf{k}\lambda}\cdot\mathbf{d}|\mathrm{i}\rangle|^2 u(\omega)}$$

From these expressions, we can obtain the power loss as $P_\lambda = \hbar\omega R_\lambda$. Before discussing the selection rules implied by the form of the dipolar coupling, it is first helpful to digress and discuss connections of this result to a famous result due to Einstein.

▷ INFO. **Einstein's A and B coefficients:** In fact, the frequency dependence of the spontaneous emission rate can be inferred without invoking quantum field theoretic methods by means of an ingenious argument due to Einstein which showed that the stimulated and spontaneous transitions must be related. Consider an ensemble of atoms exposed to a black-body radiation field at temperature T. Let us consider transitions between two states $|\psi_j\rangle$ and $|\psi_k\rangle$, with $E_k - E_j = \hbar\omega$. Suppose the numbers of atoms in the two states are n_j and n_k. The possible transitions and their rates per atom are given by:

absorption	$j \to k$	$B_{j\to k}u(\omega)$
stimulated emission	$k \to j$	$B_{k\to j}u(\omega)$
spontaneous emission	$k \to j$	$A_{k\to j}(\omega)$

where $u(\omega)$, the energy density of radiation per unit ω. A and B are known as Einstein's A and B coefficients, and, as we have seen, are properties of the atomic states concerned.

Now, in thermodynamic equilibrium, the rates must balance, so that

$$n_k\left[A_{k\to j}(\omega) + B_{k\to j}u(\omega)\right] = n_j B_{j\to k}u(\omega)\,.$$

At the same time, the relative populations of the two states (assumed non-degenerate for simplicity), are given by a Boltzmann factor

$$\frac{n_j}{n_k} = \frac{e^{-E_j/k_\mathrm{B}T}}{e^{-E_k/k_\mathrm{B}T}} = e^{\hbar\omega/k_\mathrm{B}T}\,.$$

Thus we have:

$$A_{k\to j}(\omega) = \left[B_{j\to k}e^{\hbar\omega/k_\mathrm{B}T} - B_{k\to j}\right]u(\omega)\,. \tag{13.1}$$

For a black-body, the energy density $u(\omega)$ is just given by Planck's formula, $u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3}\frac{1}{e^{\hbar\omega/k_{\rm B}T}-1}$. The $A_{k\to j}$ coefficient in Eq. (13.1) certainly cannot depend on temperature, so T must cancel on the right hand side. Hence,

$$B_{k\to j} = B_{j\to k} \qquad \text{and} \qquad A_{k\to j}(\omega) = B_{k\to j}\frac{\hbar\omega^3}{\pi^2 c^3}\,.$$

So, the A and B coefficients are related, and if we can calculate the B coefficient for stimulated emission from Fermi's golden rule, we can infer A, and *vice versa*.

13.2 Selection Rules

It is clear from the formulae for the transition rates that no transition, either spontaneous or stimulated, will occur between the states $|\mathrm{i}\rangle$ and $|\mathrm{f}\rangle$ unless at least one component of the dipole transition matrix element $\langle\mathrm{f}|\hat{\mathbf{d}}|\mathrm{i}\rangle$ is non-zero. It is often possible to show that the matrix elements are zero for certain pairs of states. If so, the transition is not allowed (at least in the electric dipole approximation), and the results can often be summarised in terms of simple **selection rules** governing the allowed changes in quantum numbers in transitions.

Since the dipole operator $\hat{\mathbf{d}} = q\mathbf{r}$ changes sign under parity ($\mathbf{r}\to-\mathbf{r}$), the matrix element $\langle\mathrm{f}|\hat{\mathbf{d}}|\mathrm{i}\rangle$ will trivially vanish if the states $|\mathrm{f}\rangle$ and $|\mathrm{i}\rangle$ have the same parity. Therefore, **the parity of the wavefunction must change in an electric dipole transition**.

Moreover, in the absence of spin-orbit interaction, since the wavefunction can be separated into spatial and spin components, $|\mathrm{f}\rangle = |\phi_{\mathrm{f}}\rangle\otimes|\chi_{\mathrm{f}}\rangle$, with χ_{f} being the spin wavefunction, and the dipole operator only acts on the spatial part of the wavefunction, so the matrix element becomes

$$\langle\mathrm{f}|\hat{\mathbf{d}}|\mathrm{i}\rangle = \langle\chi_{\mathrm{f}}|\chi_{\mathrm{i}}\rangle\int d^3r\,\phi^*_{\mathrm{f}}(\mathbf{r})\,q\mathbf{r}\phi_{\mathrm{i}}(\mathbf{r})\,.$$

The spin term $\langle\chi_{\mathrm{f}}|\chi_{\mathrm{i}}\rangle$ (and therefore the matrix element) vanishes unless $|\chi_{\mathrm{i}}\rangle$ and $|\chi_{\mathrm{f}}\rangle$ are identical. This can be expressed by the selection rule

$$\boxed{\Delta s = 0, \qquad \Delta m_s = 0\,.}$$

The spin state is not altered in an electric dipole transition.

Let us now consider the selection rules for the orbital angular momenta. From the operator identity, $[\hat{L}_i, r_j] = i\hbar\epsilon_{ijk}r_k$ (exercise), it follows that

$$[\hat{L}_z, z] = 0, \qquad [\hat{L}_z, x\pm iy] = \pm(x\pm iy)\hbar\,,$$

We therefore obtain the relation,

$$\langle\ell', m'|[\hat{L}_z, z]|\ell, m\rangle = (m'-m)\hbar\langle\ell', m'|z|\ell, m\rangle = 0\,.$$

Similarly, since $\langle\ell', m'|[\hat{L}_z, x\pm iy]|\ell, m\rangle = \pm\langle\ell', m'|x\pm iy|\ell, m\rangle$, it follows that

$$(m'-m\mp1)\langle\ell', m'|x\pm iy|\ell, m\rangle = 0\,.$$

Therefore, to get non-zero component of the dipole matrix element, we require.

$$\boxed{\Delta m_\ell = 0, \pm1\,.}$$

Similarly, using operator identity $[\hat{\mathbf{L}}^2,[\hat{\mathbf{L}}^2,\mathbf{r}]] = 2\hbar^2(\mathbf{r}\hat{\mathbf{L}}^2 + \hat{\mathbf{L}}^2\mathbf{r})$ (exercise), we have

$$\begin{aligned}\langle \ell', m'|[\hat{\mathbf{L}}^2,[\hat{\mathbf{L}}^2,\mathbf{r}]]|\ell, m\rangle &= [\ell'(\ell'+1) - \ell(\ell+1)]^2\langle \ell', m'|\mathbf{r}|\ell, m\rangle \\ &= 2[\ell'(\ell'+1) + \ell(\ell+1)]\langle \ell', m'|\mathbf{r}|\ell, m\rangle\end{aligned}$$

i.e. $(\ell+\ell')(\ell+\ell'+2)[(\ell'-\ell)^2-1]\langle \ell', m'|\mathbf{r}|\ell, m\rangle = 0$. Since $\ell, \ell' \geq 0$, we can conclude that, to effect an electric dipole transition, we must have

$$\boxed{\Delta\ell = \pm 1\,.}$$

One may summarize the selection rules for ℓ and m_ℓ is by saying that the photon carries off (or brings in, in an absorption transition) one unit of angular momentum. It should be noted, however, that these rules were derived for the specific case of an electric dipole transition of the system. It is possible, though much less likely in the case of an atom, for the electromagnetic field to interact with some other observable such as the magnetic dipole moment or the electric quadrupole moment. In such transitions the selection rules are different. For example, the magnetic dipole operator is $\hat{\boldsymbol{\mu}} = -\mu_B\hat{\mathbf{L}}/\hbar$ (or $-2\mu_B\hat{\mathbf{S}}/\hbar$ for the spin) and since the angular momentum does not change sign under the parity transformation, there is no change of parity in a magnetic dipole transition. To avoid confusion, we shall continue to confine the discussion to electric dipole transitions, which are responsible for the prominent lines in atomic spectra.

For transitions with $\Delta m_\ell = 0$, the dipole matrix element $\langle \mathrm{f}|\mathbf{d}|\mathrm{i}\rangle \sim \hat{\mathbf{e}}_z$ and there is no component of polarization along z-direction. Similarly, for electric dipole transitions with $m' = m \pm 1$, $\langle \ell', m'|x \mp iy|\ell, m\rangle = 0 = \langle \ell', m'|z|\ell, m\rangle$, and $\langle \mathrm{f}|\mathbf{d}|\mathrm{i}\rangle \sim (1, \mp i, 0)$. In this case, if the wavevector of photon lies along z, the emitted light is circularly polarized with a polarization which depends on helicity. Conversely, if the wavevector lies in xy place, the emitted light is linearly polarized, while in general the polarization is elliptical.

Finally, in the presence of spin-orbit coupling, stationary states are labelled by quantum numbers J, m_J, ℓ, s where $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. In this case, the selection rules can be inferred by looking for the conditions for non-zero matrix elements $\langle J', m_{J'}, \ell', s'|\mathbf{r}|J, m_J, \ell, s\rangle$. By expanding states $|J, m_J, \ell, s\rangle$ in the basis states $|\ell, m_\ell\rangle\otimes|s, m_s\rangle$, one may uncover the following set of selection rules: For dipole transitions to take place, we require that

$$\boxed{\Delta m_j = 0, \pm 1 \qquad \Delta j = 0, \pm 1 \quad \text{not} \quad 0 \to 0}$$

▷ INFO. As another example of selection rules, consider a charged particle moving in a one-dimensional harmonic potential. The wavefunctions are characterised by the quantum number n, so the state $|n\rangle$ corresponds to energy $(n+1/2)\hbar\omega$. An oscillating electric field in the x-direction can induce transitions between states $|n\rangle$ and $|n'\rangle$, governed by matrix elements of the form $\langle n'|\,x\,|n\rangle$. These can be evaluated by use of the ladder operators $\hat{a}$ and $\hat{a}^\dagger$. Since $x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)$, the matrix element becomes

$$\langle n'|\,x\,|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}\langle n'|n+1\rangle + \sqrt{n}\langle n'|n-1\rangle\right)\,,$$

and therefore vanishes unless $n = n' \pm 1$. Hence the selection rule, in the electric dipole approximation, is $\Delta n = \pm 1$.

13.3 Lasers

Finally, to close this section, we will consider a principle application of light matter interaction – the laser. The laser provides a light source which enables modern spectroscopy. The term "laser" is an acronym for "light amplification by stimulated emission of radiation". However, a laser not only amplifies light, but it acts as a special kind of light source which is characterised by a number of properties:

Monochromaticity: The emission of the laser generally corresponds to just one of the atomic transitions of the gain medium (in contrast to discharge lamps, which emit on all transitions). The spectral line width can be much smaller than that of the atomic transition. This is because the emission is affected by the optical cavity. In certain cases, the laser can be made to operate on just one of the modes of the cavity. Since the Q of the cavity[1] is generally rather large, the mode is usually much narrower than the atomic transition, and the spectral line width is orders of magnitude smaller than the atomic transition.

Coherence: In discussing the coherence of an optical beam, we must distinguish between spatial and temporal coherence – laser beams have a high degree of both. **Spatial coherence** refers to whether there are irregularities in the optical phase in a cross-sectional slice of the beam. **Temporal coherence** refers to the time duration over which the phase of the beam is well defined. In general, the temporal coherence time, $t_{\rm coh}$ is given as the reciprocal of the spectral line width, $\Delta\nu$. Thus the coherence length $\ell_{\rm coh}$ is given by,

$$\ell_{\rm coh} = ct_{\rm coh} = \frac{c}{\Delta\nu}\,.$$

Typical values of the coherence length for a number of light sources are given in the table below:

Source	$\Delta\nu$ (Hz)	$t_{\rm coh}$ (s)	$\ell_{\rm coh}$ (m)
Na discharge lamp (D-lines at 589nm)	5×10^{11}	2×10^{-12}	6×10^{-4}
Multi-mode HeNe laser (632.8nm line)	1.5×10^{9}	6×10^{-10}	0.2
Single-mode HeNe laser (632.8nm line)	1×10^{6}	1×10^{-6}	300

These figures explain why it is much easier to conduct interference experiments with a laser than with a discharge lamp. If the path difference exceeds $\ell_{\rm coh}$ you will not get interference fringes, because the light is incoherent.

Brightness: The brightness of lasers arises from two factors. First of all, the fact that the light is emitted in a well-defined beam means that the power per unit area is very high, even though the total amount of power can be rather low. Then we must consider that all the energy is concentrated within the narrow spectrum of the active atomic transition. This means that the spectral brightness (i.e. the intensity in the beam divided by the width of the emission line) is even higher in comparison with a white light source like a light bulb. For example, the spectral brightness of a 1 mW laser beam could easily be millions of time greater than that of a 100 W light bulb.

Ultra-short pulse generation: In some cases, lasers can be made to operate in pulses. The time duration of the pulses t_p is linked to the spectral

Arthur Leonard Schawlow 1921-1999

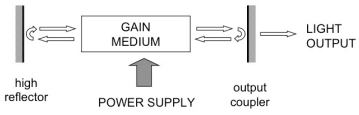
American physicist and corecipient, with Nicolaas Bloembergen of the US and Kai Manne Borje Siegbahn of Sweden, of the 1981 Nobel Prize for Physics for his work in developing the laser and in laser spectroscopy. In 1949 he went to Columbia University, where he began collaborating with Charles Townes on the development of masers, lasers, and laser spectroscopy. Schawlow worked on the project that led to the construction of the first working maser in 1953 (for which Townes received a share of the 1964 Nobel Prize for Physics). Schawlow was a research physicist at Bell Telephone Laboratories from 1951 to 1961. In 1958 he and Townes published a paper in which they outlined the working principles of the laser, though the first such working device was built by another American physicist, Theodore Maiman, in 1960. In 1961 Schawlow became a professor at Stanford University. He became a world authority on laser spectroscopy, and he and Bloembergen earned their share of the 1981 Nobel Prize by using lasers to study the interactions of electromagnetic radiation with matter.

[1] Recall that the Q-factor is approximately the number of oscillations required for a freely oscillating system's energy to fall by a factor of $1/e^{2\pi}$ of its original energy.

band width of the laser light $\Delta\nu$ by the "uncertainty" product $\Delta t \Delta\nu \sim 1$. This follows from taking the Fourier transform of a pulse of duration t_p. As an example, the bandwidth of the 632.8nm line in the HeNe laser is 1.5 GHz (see above), so that the shortest pulses that a HeNe laser can produce would be 0.67 ns long. This is not particularly short by modern standards. Dye lasers typically have gain bandwidths greater than 10^{13}Hz, and can be used to generate pulses shorter than 100fs. This is achieved by a technique called "mode-locking". These short pulsed lasers are very useful for studying fast processes in physics, chemistry and biology.

13.3.1 Operating principles of a laser

Light amplification is achieved by stimulated emission. Ordinary optical materials do not amplify light. Instead, they tend to absorb or scatter the light, so that the light intensity out of the medium is less than the intensity that went in. To get amplification you have to drive the material into a non-equilibrium state by pumping energy into it. Positive optical feedback is achieved by inserting the amplifying medium inside a resonant cavity. Light in the cavity passes through the gain medium and is amplified. It then bounces off the end mirrors and passes through the gain medium again, getting amplified further. This process repeats itself until a stable equilibrium condition is achieved when the total round trip gain balances all the losses in the cavity.



The losses in the cavity fall into two categories: useful, and useless. The useful loss comes from the output coupling. One of the mirrors (called the "output coupler") has reflectivity less than unity, and allows some of the light oscillating around the cavity to be transmitted as the output of the laser. The value of the transmission is chosen to maximise the output power. If the transmission is too low, very little of the light inside the cavity can escape, and thus we get very little output power. On the other hand, if the transmission is too high, there may not be enough gain to sustain oscillation, and there would be no output power. The optimum value is somewhere between these two extremes. Useless losses arise from absorption in the optical components (including the laser medium), scattering, and the imperfect reflectivity of the other mirror (the "high reflector").

In general we expect the gain to increase as we pump more energy into the laser medium. At low pump powers, the gain will be small, and there will be insufficient gain to reach the oscillation condition. The laser will not start to oscillate until there is enough gain to overcome all the losses. This implies that the laser will have a threshold in terms of the pump power.

13.3.2 Gain mechanism

Laser operation relies upon the phenomenon of stimulated emission. In a gas of atoms in thermal equilibrium, the population of lower levels will always be greater than the population of upper levels. Therefore, if a light beam is incident on the medium, there will always be more upward transitions due to absorption than downward transitions due to stimulated emission. Hence there will be net absorption, and the intensity of the beam will diminish on progressing through the medium.

To amplify the beam, we require that the rate of stimulated emission exceeds the rate of absorption. If the light beam is sufficiently intense that we can ignore spontaneous emission, and the levels are non-degenerate, this implies that the number of atoms in some upper level, N_2, must exceed that of the lower level N_1. This is a highly non-equilibrium situation, and is called **popu-**

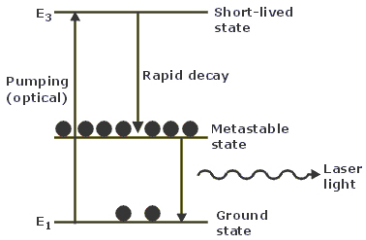
lation inversion. Once we have population inversion, we have a mechanism for generating gain in the laser medium. The art of making a laser operate is to work out how to get population inversion for the relevant transition.

To develop a theory of the laser threshold, we can consider separately the rate equations for the photon and atomic excitation. Starting with photons, let us consider excitations created by the transitions between just two levels of the atom – a lower level 1, and an excited state 2. If the dipole matrix elements, W, between the two levels are independent of position and frequency, the net downwards transition rate is given by

$$W\left(N_2(n+1) - N_1 n\right)$$

where n denotes the total number of photons in the cavity, and $N_{1,2}$ is the number of atoms in states $1, 2$. The first term represents the contribution from stimulated and spontaneous emission, while the latter is associated with absorption. Taking into account photon loss from the leaky cavity, the rate of change of photon number is therefore given by

$$\boxed{\dot{n} = DWn + N_2 W - \frac{n}{\tau_{\rm ph}}\,,} \tag{13.2}$$



where $D = N_2 - N_1$ represents the population imbalance and $1/\tau_{\rm ph}$ is the photon loss rate. This equation shows that the gain in a laser medium is directly proportional to the degree of population inversion. Laser operation will occur when there is enough gain to overcome the losses in the cavity. This implies that a minimum amount of population inversion must be obtained before the laser will oscillate.

To achieve population inversion atoms must be "pumped" into the upper level 2. This can be achieved by a variety of techniques: Lasers are classified as being either three-level of four-level systems. In the following, we will consider the case of a three-level laser, although four-level lasers are more common. Examples of four-level lasers include Helium Neon or Nd:YAG. In a four-level laser, the levels comprise the ground state (0), the two lasing levels (1 and 2), and a fourth level (3) which is used as part of the pumping mechanism. In the three-level system, such as the first laser, ruby, level 1 is the ground state, and pumping is achieved by exiting atoms to level 3 with a bright flash lamp or by an electrical discharge, and then allowing them to decay rapidly to level 2. In this case, the corresponding rate equations for the populations of levels 1 and 2 can be written as

$$\dot{N}_2 \simeq -w_{21} N_2 + w_{12} N_1 - (N_2 - N_1) W n \simeq -\dot{N}_1\,,$$

where w_{12}, w_{21} denote the "effective" transition rates between states 1 and 2 due to the pumping via the third state, and we have dropped the small contribution from spontaneous emission. From this equation, we can deduce that $N_1 + N_2 = N$, a constant, i.e. the decay from state 3 is so rapid that its population is always negligible. In this case, we obtain

$$\boxed{\dot{D} = \frac{D_0 - D}{T} - 2DWn\,.} \tag{13.3}$$

where $D_0 = N(w_{12} - w_{21})/(w_{12} + w_{21})$ denotes the **unsaturated inversion** (i.e. the degree of population inversion that would exist if there were no photons in the cavity, $n = 0$) and $1/T = w_{12} + w_{21}$.

In steady-state, $\dot{n} = \dot{D} = 0$, and Eq. (13.3) translates to a population imbalance,

$$D \equiv N_2 - N_1 = \frac{D_0}{1 + 2TWn} .$$

From this result, we find the steady state photon number is given by

$$\boxed{n = \frac{D_0 W - 1/\tau_{\rm ph}}{2TW/\tau_{\rm ph}} .}$$

When $D_0 > 1/W\tau_{\rm ph}$, the **laser threshold condition**, there is a rapid increase in the number of photons in the cavity and the system starts lasing.

Although this analysis addresses the threshold conditions, it does not provide any insight into the coherence properties of the radiation field. In fact, one may show that the radiation field generated by the laser cavity forms a **coherent or Glauber state**. The proof of this statement and the coherence properties that follow would take us too far into the realm of laser physics. However, we can gain some insight into this statement by studying a toy example.

13.4 Driven harmonic oscillator

Consider a quantum harmonic oscillator Hamiltonian driven by some external classical field,

$$\hat{H} = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) + \hbar \left(f^*(t) a + f(t) a^\dagger \right) .$$

Here $f(t)$, which represents an (as yet) arbitrary function of time, t, characterises the coupling between the harmonic oscillator and the classical pump. For example, if $f(t)$ is real, the function couples directly to the displacement, $a + a^\dagger \sim x$. If the system is prepared in the ground state of the harmonic oscillator, the perturbation drives the system into a coherent state.

To understand how, let us consider the time-evolution in the interaction representation, $i\hbar\partial_t |\psi(t)\rangle_{\rm I} = V_{\rm I} |\psi(t)\rangle_{\rm I}$ where $|\psi(t)\rangle_{\rm I} = e^{i\hat{H}_0 t/\hbar} |\psi(t)\rangle_{\rm S}$ and, defining $\tilde{f} = f e^{i\omega t}$,[2]

$$V_{\rm I}(t) = e^{i\hat{H}_0 t/\hbar} \hbar \left(f^*(t) a + f(t) a^\dagger \right) e^{-i\hat{H}_0 t/\hbar} = \hbar \left(\tilde{f}^*(t) a + \tilde{f}(t) a^\dagger \right) .$$

To solve for the time-evolution operator, $i\hbar\partial_t U_{\rm I}(t) = V_{\rm I} U_{\rm I}(t)$, let us consider the coherent state, $|\alpha\rangle = \hat{U}(\alpha)|0\rangle$ where $\hat{U}(\alpha) = \exp[\alpha a^\dagger - \alpha^* a]$, where $\alpha = \alpha(t)$. Equivalently, making use of the BCH identity, the unitary operator may be written as

$$\hat{U}(\alpha) = e^{-\alpha^*\alpha/2} e^{\alpha a^\dagger} e^{-\alpha^* a} .$$

Then, taking the time derivative, and making use of the identity, $[e^{\alpha a^\dagger}, a] e^{-\alpha a^\dagger} = -\alpha$, one obtains

$$\partial_t \hat{U}(\alpha) = \left[\dot{\alpha} a^\dagger - \dot{\alpha}^* a + \frac{i}{2} {\rm Im}(\dot{\alpha}^* \alpha) \right] \hat{U}(\alpha) .$$

Therefore, setting $\alpha(t) = -i \int_0^t dt' \tilde{f}(t')$, we obtain the solution

$$U_{\rm I}(t) = \exp \left[\alpha(t) a^\dagger - \alpha^*(t) a + i\varphi(t) \right] ,$$

[2]Here we have made use of the identity (exercise), $e^{i\omega t a^\dagger a} a e^{-i\omega t a^\dagger a} = e^{-i\omega t} a$.

where $\varphi(t) = \int_0^t dt' \frac{1}{2}\mathrm{Im}(\dot{\alpha}^*\alpha)$.

If the driving force $f(t) = f_0 e^{-i\omega t}$ (with f_0 real), we have $\alpha(t) = -i\int_0^t dt' f_0 = -if_0 t$ and $\varphi(t) = 0$ leading to the solution, $U_{\rm I}(t) = \exp[-if_0(a^\dagger + a)t]$. Therefore, if the system was prepared in the harmonic oscillator ground state $|0\rangle$ at time $t = 0$, the solution at time t is given by $|\psi(t)\rangle_{\rm I} = \exp[-if_0(a^\dagger + a)t]|0\rangle = e^{-(f_0 t)^2/2} e^{-if_0 a^\dagger t}|0\rangle$. Then, reexpressed in the Schrödinger representation,

$$|\psi(t)\rangle_{\rm S} = e^{-i\hat{H}_0 t/\hbar}|\psi(t)\rangle_{\rm I} = e^{-(f_0 t)^2/2} e^{-if_0 e^{-i\omega t} a^\dagger t}|0\rangle\,.$$

As a result, we can conclude that a classical oscillatory force drives a system prepared in the vacuum into a coherent state. Applied to an optical cavity, an oscillating classical dipole generates a coherent state of light – the principle that underlies the operation of a laser.