Lecture 19
Radiative transitions
Previously, we have formulated a quantum theory of atoms (matter) coupling to a classical time-independent electromagnetic field, cf. Zeeman and Stark effects.

To develop a fully quantum theory of light-matter systems, we have to address both the quantum theory of the electromagnetic field and formulate a theory of the coupling of light to matter.

In the following we will address each of these components in turn, starting with light-matter coupling.

Our motivation for developing such a consistent theory is that it:

(a) provides a platform to study radiative transitions in atoms (which will address)

(b) forms the basis of quantum optics (which will not address – but which is well-represented in subsequent courses).
Radiative transitions: outline

- Coupling of matter to electromagnetic field
- Spontaneous emission, absorption and stimulated emission
- Einstein’s A and B coefficients
- Selection rules
- Theory of the laser and coherent states
For a single-electron atom in a time-dependent external EM field, the Hamiltonian takes the form,

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

(with a straightforward generalization to multi-electron atoms).

Previously, we have seen that it is profitable to expand Hamiltonian in $\hat{\mathbf{A}}$, $\hat{H}_{\text{atom}} = \hat{H}_0 + \hat{H}_{\text{para}} + \hat{H}_{\text{dia}}$, where $\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) - e\phi(t)$

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

the paramagnetic term describes coupling of the atom to the EM field, and $\hat{H}_{\text{dia}} = (e\mathbf{A})^2/2m$ represents diamagnetic term.

Since we will be interested in absorption and emission of single photons, influence of diamagnetic term is (as usual) negligible.
Coupling of matter to the electromagnetic field

- When quantized, EM field is described by the photon Hamiltonian,
  \[
  \hat{H}_{\text{rad}} = \sum_{\mathbf{k}, \lambda = 1,2} \hbar \omega_{\mathbf{k}} \left( a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda} + \frac{1}{2} \right), \quad \omega_{\mathbf{k}} = c |\mathbf{k}|,
  \]
  where \( a_{\mathbf{k}\lambda}^\dagger / a_{\mathbf{k}\lambda} \) create/annihilate photons with polarization \( \lambda \).

- These operators obey (bosonic) commutation relations,
  \[
  [a_{\mathbf{k}\lambda}, a_{\mathbf{k}'\lambda'}^\dagger] = \delta_{\mathbf{k},\mathbf{k}'} \delta_{\lambda,\lambda'} \quad \text{and} \quad [a_{\mathbf{k}\lambda}, a_{\mathbf{k}'\lambda'}] = [a_{\mathbf{k}\lambda}^\dagger, a_{\mathbf{k}'\lambda'}^\dagger] = 0
  \]
  and act on photon number states, \( |n_{\mathbf{k}\lambda}\rangle = \frac{1}{\sqrt{n_{\mathbf{k}\lambda}!}} (a_{\mathbf{k}\lambda}^\dagger)^{n_{\mathbf{k}\lambda}} |\Omega\rangle \), as
  \[
  a_{\mathbf{k}\lambda} |n_{\mathbf{k}\lambda}\rangle = \sqrt{n_{\mathbf{k}\lambda}} |n_{\mathbf{k}\lambda} - 1\rangle, \quad a_{\mathbf{k}\lambda}^\dagger |n_{\mathbf{k}\lambda}\rangle = \sqrt{n_{\mathbf{k}\lambda} + 1} |n_{\mathbf{k}\lambda} + 1\rangle
  \]

- With these definitions, the vector potential is given by
  \[
  \hat{A}(\mathbf{r}) = \sum_{\mathbf{k}\lambda = 1,2} \sqrt{\frac{\hbar}{2\epsilon_0 \omega_{\mathbf{k}} V}} \left[ \hat{\mathbf{e}}_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda} e^{i\mathbf{k} \cdot \mathbf{r}} + \hat{\mathbf{e}}_{\mathbf{k}\lambda}^* a_{\mathbf{k}\lambda}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}} \right]
  \]
To determine radiative transition rates, we will exploit Fermi’s Golden rule. To prepare for this, it is convenient to transfer time-dependence to operators (Heisenberg representation).

As with any operator, the field operators obey equations of motion,

\[ \dot{a}_{k\lambda} = \frac{i}{\hbar} \left[ \hat{H}, a_{k\lambda} \right] = i\omega_k [a_{k\lambda}^\dagger a_{k\lambda}, a_{k\lambda}] = -i\omega_k a_{k\lambda} \]

i.e. \( a_{k\lambda}(t) = a_{k\lambda}(0)e^{-i\omega_k t}, a_{k\lambda}^\dagger(t) = a_{k\lambda}^\dagger(0)e^{i\omega_k t} \) and

\[
\hat{A}(r, t) = \sum_{k\lambda} \sqrt{\frac{\hbar}{2\epsilon_0\omega_k V}} \left[ \hat{e}_{k\lambda} a_{k\lambda} e^{i(k \cdot r - \omega_k t)} + \hat{e}_{k\lambda}^* a_{k\lambda}^\dagger e^{-i(k \cdot r - \omega_k t)} \right]
\]
Putting together all of these components, the total Hamiltonian is then given by \( \hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{para}} + \hat{H}_{\text{rad}} \) where (with \( \phi = 0 \))

\[
\hat{H}_{\text{atom}} = \frac{\hat{p}^2}{2m} + V(r), \quad \hat{H}_{\text{rad}} = \sum_{k\lambda} \hbar \omega_k \left( a_{k\lambda}^\dagger a_{k\lambda} + \frac{1}{2} \right) \quad \text{and}
\]

\[
\hat{H}_{\text{para}}(t) = \frac{e}{m} \hat{A}(r, t) \cdot \hat{p} \quad \text{with}
\]

\[
\hat{A}(r, t) = \sum_{k\lambda} \sqrt{\frac{\hbar}{2\epsilon_0 \omega_k V}} \left[ \hat{e}_{k\lambda} a_{k\lambda} e^{i(k \cdot r - \omega_k t)} + \hat{e}_{k\lambda}^* a_{k\lambda}^\dagger e^{-i(k \cdot r - \omega_k t)} \right]
\]

In the following, we will apply this Hamiltonian to the problem of radiative transitions in single electron atoms.
Spontaneous emission

- Consider probability for an atom, initially in state $|i\rangle$ to make transition to $|f\rangle$ with emission of a photon of wavevector $k$ and polarization $\lambda$ – spontaneous emission.

- If radiation field initially prepared in vacuum state, $|\Omega\rangle$, then final state involves one photon, $a_{k\lambda}^\dagger |\Omega\rangle$.

- Therefore, making use of Fermi’s Golden rule, with the perturbation

$$\hat{H}_{\text{para}}(t) = \frac{e}{m} \hat{A}(r, t) \cdot \hat{p} = \sum_{k\lambda} \sqrt{\frac{\hbar}{2\epsilon_0\omega_k V}} \left[ \hat{e}_{k\lambda} a_{k\lambda} e^{i(k \cdot r - \omega_k t)} + \hat{e}_{k\lambda}^* a_{k\lambda}^\dagger e^{-i(k \cdot r - \omega_k t)} \right] \cdot \frac{e}{m} \hat{p}$$

transition probability given by,

$$\Gamma_{i\rightarrow f}(t) = \frac{2\pi}{\hbar^2} |\langle f | \otimes \langle k\lambda | \hat{H}_{\text{para}} | i \rangle \otimes |\Omega\rangle|^2 \delta(\omega_{if} - \omega)$$
Spontaneous emission

$$\Gamma_{i \rightarrow f, k\lambda} = \frac{2\pi}{\hbar} \left| \langle f | \frac{e}{m} \sqrt{\frac{\hbar}{2\epsilon_0 \omega_k}} V e^{-i \mathbf{k} \cdot \mathbf{r}} \hat{\mathbf{e}}_{k\lambda}^* \cdot \hat{\mathbf{p}} | i \rangle \right|^2 \delta (E_i - E_f - \hbar \omega_k)$$

- To determine transition rate, we must analyse matrix elements of the form $\langle f | e^{-i \mathbf{k} \cdot \mathbf{r}} \hat{\mathbf{e}}_{k\lambda}^* \cdot \hat{\mathbf{p}} | i \rangle$. For typical state, $\langle \hat{\mathbf{e}}_{k\lambda}^* \cdot \hat{\mathbf{p}} \rangle \sim p \sim Zmc\alpha$.

- But what about exponential factor? With $r \sim \hbar/p \simeq \hbar/mZc\alpha$, and $\omega_k = c |\mathbf{k}| \sim \frac{p^2}{2m}$ (for electronic transitions), we have

$$\mathbf{k} \cdot \mathbf{r} \simeq \frac{\omega_k \hbar}{c \rho} \simeq \frac{\hbar p}{mc} \simeq Z\alpha$$

i.e. for $Z\alpha \ll 1$, we can expand exponential as power series in $\mathbf{k} \cdot \mathbf{r}$ with lowest terms dominant.

- Taking zeroth order term, and using $\hat{\mathbf{p}} = \frac{im}{\hbar} [\hat{H}_0, \mathbf{r}]$ (cf. Ehrenfest)

$$\langle f | \hat{\mathbf{e}}_{k\lambda}^* \cdot \hat{\mathbf{p}} | i \rangle = m \hat{\mathbf{e}}_{k\lambda}^* \cdot \langle f | \frac{i}{\hbar} [\hat{H}_0, \mathbf{r}] | i \rangle = im \frac{E_f - E_i}{\hbar} \hat{\mathbf{e}}_{k\lambda}^* \cdot \langle f | \mathbf{r} | i \rangle$$
Spontaneous emission: electric dipole approximation

\[ \langle f | \hat{e}_{k,\lambda}^* \cdot \hat{p} | i \rangle = -im\omega_k \langle f | \hat{e}_{k,\lambda}^* \cdot \hat{r} | i \rangle \]

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

\[ \hat{H}_{\text{para}} = \frac{e}{m} \hat{A}(r, t) \cdot \hat{p} \approx e\hat{E}(r, t) \cdot \hat{r} = -\hat{E}(r, t) \cdot \hat{d} \]

translating to the potential energy of a dipole, with moment \( \hat{d} = -e\hat{r} \), in an oscillating electric field.
Consider now absorption of a photon. If we assume that, in the initial state, there are $n_{k\lambda}$ photons in mode $(k\lambda)$ then, after the transition, there will be $n_{k\lambda} - 1$ photons.

Then, if initial state of the atom is $|i\rangle$ and final state is $|f\rangle$,

$$\langle f| \otimes \langle (n_{k,\lambda} - 1)|\hat{H}_{\text{para}}|i\rangle \otimes |n_{k\lambda}\rangle = \langle f| \otimes \langle (n_{k,\lambda} - 1)| e^{\frac{\epsilon_{m}}{m}\sqrt{\frac{\hbar}{2\epsilon_{0}\omega_{k}V}}} \hat{e}_{k\lambda} a_{k\lambda} e^{i\hat{p}\cdot \hat{r}}|i\rangle \otimes |n_{k\lambda}\rangle$$

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

$$\langle f| \otimes \langle (n_{k,\lambda} - 1)|\hat{H}_{\text{para}}|i\rangle \otimes |n_{k\lambda}\rangle = \langle f| \frac{e}{m}\sqrt{\frac{\hbar n_{k\lambda}}{2\epsilon_{0}\omega_{k}V}} e^{i\hat{p}\cdot \hat{r}}\hat{e}_{k\lambda} |i\rangle$$
Consider now absorption of a photon. If we assume that, in the initial state, there are \( n_{k\lambda} \) photons in mode \((k\lambda)\) then, after the transition, there will be \( n_{k\lambda} - 1 \) photons.

As a result, using Fermi’s Golden rule,

\[
\Gamma_{i\rightarrow f}(t) = \frac{2\pi}{\hbar^2} |\langle f | \otimes \langle(n_{k\lambda} - 1)|\hat{H}_{\text{para}}|i\rangle \otimes |n_{k\lambda}\rangle|^2 \delta(\omega_f - \omega)
\]

we obtain the transition amplitude,

\[
\Gamma_{i\rightarrow f, k\lambda} = \frac{2\pi}{\hbar} \left| \langle f | \frac{e}{m} \sqrt{\frac{\hbar n_{k\lambda}}{2\epsilon_0 \omega_k V}} e^{ik \cdot r} \hat{e}_{k\lambda} \cdot \hat{p} |i\rangle \right|^2 \delta(E_f - E_i - \hbar \omega_k)
\]

In particular, we find that the absorption rate \textit{increases} linearly with photon number, \( n_{k\lambda} \).
Similarly, if we consider emission process in which there are already $n_{k\lambda}$ photons in initial state,

using the relation $a_{k\lambda}^\dagger |n_{k\lambda}\rangle = \sqrt{n_{k\lambda} + 1}|(n_{k\lambda} + 1)\rangle$, we have revised transition rate,

$$\Gamma_{i\rightarrow f, k\lambda} = \frac{2\pi}{\hbar} \left| \left\langle f | \frac{e}{m} \sqrt{\frac{\hbar (n_{k\lambda} + 1)}{2\epsilon_0 \omega_k V}} e^{-ik \cdot \hat{r}} \hat{e}_{k\lambda} \cdot \hat{p} | i \right\rangle \right|^2 \delta(E_f - E_i - \hbar \omega_k)$$

Enhancement of transition rate by photon occupancy known as stimulated emission.
Altogether, in dipole approximation \( \langle f | \hat{e}_{k\lambda} \cdot \hat{p} | i \rangle \approx -im\omega_k \langle f | \hat{e}_{k\lambda} \cdot r | i \rangle \)

\[
\Gamma_{i\rightarrow f, k\lambda} \approx \frac{\pi \omega_k}{\epsilon_0 V} |\langle f | \hat{e}_{k\lambda} \cdot \hat{d} | i \rangle|^2 \left\{ \begin{array}{ll}
 n_{k\lambda} \delta(E_f - E_i - \hbar\omega_k) & \text{absorption} \\
 (n_{k\lambda} + 1) \delta(E_i - E_f - \hbar\omega_k) & \text{emission}
\end{array} \right. 
\]

where \( \hat{d} = -e r \) is electric dipole operator.

If there are no photons present initially, \( \Gamma_{i\rightarrow f, k\lambda} \) reduces to result for spontaneous emission.

The coincidence of \( n_{k\lambda} \)-independent coefficients for absorption and emission coincide is known as **detailed balance**.
Absorption and stimulated emission

$$\Gamma_{i\rightarrow f, k\lambda} \approx \frac{\pi \omega_k}{\epsilon_0 V} |\langle f|\hat{e}_{k\lambda} \cdot \hat{d}|i\rangle|^2 \left\{ \begin{array}{l} \frac{n_{k\lambda}}{\lambda} \delta(E_f - E_i - \hbar\omega_k) \quad \text{absorption} \\ (n_{k\lambda} + 1) \delta(E_i - E_f - \hbar\omega_k) \quad \text{emission} \end{array} \right\}$$

- Integrated transition rate associated with a small solid angle $d\Omega$ in the direction $k$ given by

$$dR_{i\rightarrow f, \lambda} = \sum_{k \in d\Omega} \Gamma_{i\rightarrow f, k\lambda} = d\Omega \ V \int \frac{k^2 dk}{(2\pi)^3} \Gamma_{i\rightarrow f, k\lambda}$$

- If we assume that the photon number, $n_{k\lambda}$ is isotropic, independent of angle $\Omega$, using the dispersion relation $\omega_k = ck$, we obtain

$$\frac{dR_{i\rightarrow f, \lambda}}{d\Omega} = \frac{V}{c^3} \int \frac{\omega^2 d\omega}{(2\pi)^3} \frac{\pi \omega}{\epsilon_0 V} |\langle f|\hat{e}_{k\lambda} \cdot \hat{d}|i\rangle|^2 \left\{ \begin{array}{l} n_{\lambda}(\omega) \delta(E_f - E_i - \hbar\omega) \\ (n_{\lambda}(\omega) + 1) \delta(E_i - E_f - \hbar\omega) \end{array} \right\}$$

$$\frac{dR_{i\rightarrow f, \lambda}}{d\Omega} = \frac{\omega^3}{8\pi^2 \epsilon_0 \hbar c^3} |\langle f|\hat{e}_{k\lambda} \cdot \hat{d}|i\rangle|^2 \left\{ \begin{array}{l} n_{\lambda}(\omega) \\ n_{\lambda}(\omega) + 1 \end{array} \right\}$$

where $\hbar\omega = |E_f - E_i|$.

- From this expression, we can obtain the power loss as $P_{\lambda} = \hbar\omega R_{\lambda}$. 
Einstein’s A and B coefficients

In fact, frequency dependence of spontaneous emission rate can be inferred using ingenious argument due to Einstein who showed that stimulated and spontaneous transitions must be related.

- Consider ensemble of atoms exposed to black-body radiation at temperature $T$. Let us consider transitions between states $|\psi_j\rangle$ and $|\psi_k\rangle$, with $E_k - E_j = \hbar \omega$.

- If number of atoms in two states given by $n_j$ and $n_k$, transition rates per atom given by:

  absorption $j \rightarrow k$ \hspace{1cm} $B_{j \rightarrow k} u(\omega)$
  stimulated emission $k \rightarrow j$ \hspace{1cm} $B_{k \rightarrow j} u(\omega)$
  spontaneous emission $k \rightarrow j$ \hspace{1cm} $A_{k \rightarrow j}(\omega)$

  where $u(\omega)$ denotes energy density of radiation.

- $A$ and $B$ are known as **Einstein’s A and B coefficients**, and, as we have seen, are properties of atomic states.
Einstein’s A and B coefficients

- absorption \( j \rightarrow k \) \( B_{j \rightarrow k} u(\omega) \)
- stimulated emission \( k \rightarrow j \) \( B_{k \rightarrow j} u(\omega) \)
- spontaneous emission \( k \rightarrow j \) \( A_{k \rightarrow j}(\omega) \)

In thermodynamic equilibrium the rates must balance, so that

\[
n_k [A_{k \rightarrow j}(\omega) + B_{k \rightarrow j} u(\omega)] = n_j B_{j \rightarrow k} u(\omega)
\]

At the same time, relative populations of two states given by Boltzmann factor,

\[
\frac{n_j}{n_k} = \frac{e^{-E_j / k_B T}}{e^{-E_k / k_B T}} = e^{\hbar \omega / k_B T}
\]

Thus we have:

\[
A_{k \rightarrow j}(\omega) = \left[ B_{j \rightarrow k} e^{\hbar \omega / k_B T} - B_{k \rightarrow j} \right] u(\omega)
\]
Einstein’s A and B coefficients

\[ A_{k \rightarrow j}(\omega) = \left[ B_{j \rightarrow k} e^{\frac{\hbar \omega}{k_B T}} - B_{k \rightarrow j} \right] u(\omega) \]

- For black-body, energy density \( u(\omega) \) set by Planck formula,

\[ u(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \bar{n}(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \]

\[ A_{k \rightarrow j}(\omega) = \left[ B_{j \rightarrow k} e^{\frac{\hbar \omega}{k_B T}} - B_{k \rightarrow j} \right] \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \]

- Since \( A_{k \rightarrow j} \) is intrinsic (independent of temperature), \( T \) must cancel on right hand side, i.e.

\[ B_{k \rightarrow j} = B_{j \rightarrow k} \quad \text{and} \quad A_{k \rightarrow j}(\omega) = B_{k \rightarrow j} \frac{\hbar \omega^3}{\pi^2 c^3} \]

- So, \( A \) and \( B \) coefficients are related, and if we can calculate \( B \) coefficient for stimulated emission from Fermi’s Golden rule, we can infer \( A \), and vice versa.
Selection rules: parity

\[
\Gamma_{i \rightarrow f, k \lambda} \sim \frac{\pi \omega_k}{\epsilon_0 V} |\langle f|\hat{e}_{k \lambda} \cdot \hat{d}|i\rangle|^2 \begin{cases} 
 n_{k \lambda} \delta(E_f - E_i - \hbar \omega_k) & \text{absorption} \\
 (n_{k \lambda} + 1) \delta(E_i - E_f - \hbar \omega_k) & \text{emission}
\end{cases}
\]

- Formulae for rates $\Gamma_{i \rightarrow f, k \lambda}$ show that radiative transitions will not occur between states $|i\rangle$ and $|f\rangle$ unless at least one component of the dipole matrix element $\langle f|\hat{d}|i\rangle$ is non-zero.

- If matrix elements are zero for certain pairs, they are disallowed (at least in the electric dipole approximation) leading to selection rules.

- Since dipole operator $\hat{d} = -e \mathbf{r}$ changes sign under parity ($\mathbf{r} \rightarrow -\mathbf{r}$), matrix element $\langle f|\hat{d}|i\rangle$ will vanish if $|f\rangle$ and $|i\rangle$ have same parity.

1. The parity of the wavefunction must change in an electric dipole transition.
Selection rules: spin

\[ \Gamma_{i \rightarrow f, k\lambda} \simeq \frac{\pi \omega_k}{\epsilon_0 V} |\langle f| \hat{e}_{k\lambda} \cdot \hat{d} |i\rangle|^2 \left\{ \begin{array}{ll} n_{k\lambda} \delta(E_f - E_i - \hbar \omega_k) & \text{absorption} \\ (n_{k\lambda} + 1) \delta(E_i - E_f - \hbar \omega_k) & \text{emission} \end{array} \right. \]

- Separating wavefunction into spatial and spin components, \( |f\rangle = |\phi_f\rangle \otimes |\chi_f\rangle \), since dipole operator acts only on spatial part,

\[ \langle f| \hat{d} |i\rangle = -\langle \chi_f| \chi_i \rangle \int d^3r \phi_f^*(r) e r \phi_i(r) \]

i.e. spin term, \( \langle \chi_f| \chi_i \rangle \), vanishes unless \( |\chi_i\rangle \) and \( |\chi_f\rangle \) are identical,

\[ \Delta s = 0, \quad \Delta m_s = 0 \]

2. The spin state is not altered in an electric dipole transition.
Selection rules: orbital angular momentum

\[ \Gamma_{i\rightarrow f,k\lambda} \approx \frac{\pi \omega_k}{\epsilon_0 V} |\langle f| \hat{e}_{k\lambda} \cdot \hat{d}|i\rangle|^2 \left\{ n_{k\lambda} \frac{\delta(E_f - E_i - \hbar \omega_k)}{(n_{k\lambda} + 1) \delta(E_i - E_f - \hbar \omega_k)} \right\} \]

- From the operator identity, \([\hat{L}_i, r_j] = i\hbar \epsilon_{ijk} r_k\), it follows that
  \[ [\hat{L}_z, z] = 0, \quad [\hat{L}_z, x \pm iy] = \pm(x \pm iy)\hbar \]

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

- Similarly, since \[ \langle \ell', m'|[\hat{L}_z, x \pm iy]|\ell, m\rangle = \pm\hbar \langle \ell', m'|x \pm iy|\ell, m\rangle, \]
  \[ (m' - m \neq 1)\langle \ell', m'|x \pm iy|\ell, m\rangle = 0 \]

Therefore, to get non-zero component of dipole matrix element, require \( \Delta m_\ell = 0, \pm 1 \).
Selection rules: orbital angular momentum

- Using operator identity \([\hat{L}^2, [\hat{L}^2, r]] = 2\hbar^2(r\hat{L}^2 + \hat{L}^2 r)\), we have

\[
\langle \ell', m' | [\hat{L}^2, [\hat{L}^2, r]] | \ell, m \rangle = [\ell' (\ell' + 1) - \ell (\ell + 1)]^2 \langle \ell', m' | r | \ell, m \rangle
= 2[\ell' (\ell' + 1) + \ell (\ell + 1)] \langle \ell', m' | r | \ell, m \rangle
\]

i.e. \((\ell + \ell')(\ell + \ell' + 2)[(\ell' - \ell)^2 - 1] \langle \ell', m' | r | \ell, m \rangle = 0\). Since \(\ell, \ell' \geq 0\), dipole matrix element non-vanishing only if \(\ell' = \ell \pm 1\).

4 To effect an electric dipole transition, we must have \(\Delta \ell = \pm 1\).

- One may summarize the selection rules for \(\ell\) and \(m_\ell\) is by saying that the photon carries off (or brings in, in an absorption transition) one unit of angular momentum.

- N.B. it is possible, though much less likely in the case of an atom, for EM field to interact with magnetic dipole or electric quadrupole moment with different selection rules.
Selection rules: polarization

\[ \Gamma_{i \rightarrow f, k, \lambda} = \frac{\pi \omega_k}{\epsilon_0 V} \left| \langle f | \hat{e}_{k \lambda} \cdot \hat{d} | i \rangle \right|^2 \left\{ \begin{array}{ll}
 n_{k, \lambda} \delta(E_f - E_i - \hbar \omega_k) & \text{absorption} \\
 (n_{k, \lambda} + 1) \delta(E_i - E_f - \hbar \omega_k) & \text{emission}
\end{array} \right. \]

- For transitions with \( \Delta m_\ell = 0 \), the dipole matrix element \( \langle f | \hat{d} | i \rangle \sim \hat{e}_z \) – 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 \( \langle f | \hat{d} | i \rangle \sim (1, \mp i, 0) \).

  (a) If the wavevector of photon lies along \( z \), the emitted light is circularly polarized with a polarization which depends on helicity.

  (b) If the wavevector lies in \( xy \) place, the emitted light is linearly polarized, while in general it is elliptically polarized.
Selection rules: LS coupling

- In the presence of spin-orbit coupling, stationary states labelled by quantum numbers $J, m_J, \ell, s$ where $\hat{J} = \hat{L} + \hat{S}$.

- The selection rules in this case can be inferred by looking for the conditions for non-zero matrix elements $\langle J', m_{J'}, \ell', s' | r | J, m_J, \ell, s \rangle$.

- By expanding states $| J, m_J, \ell, s \rangle$ in basis states $| \ell, m_{\ell} \rangle \otimes | s, m_s \rangle$, one may uncover the following set of selection rules:

  1. For dipole transitions to take place, we require that

     $\Delta m_J = 0, \pm 1$  
     $\Delta j = 0, \pm 1$ not $0 \to 0$

- N.B. These conclusions are consistent with photon carrying on unit of angular momentum.
When coupled to a quantized electromagnetic field, the total Hamiltonian for atomic system given by

$$\hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{para}} + \hat{H}_{\text{rad}}$$

where

$$\hat{H}_{\text{atom}} = \frac{\hat{p}^2}{2m} + V(r), \quad \hat{H}_{\text{rad}} = \sum_{k\lambda} \hbar \omega_k \left( a_{k\lambda}^\dagger a_{k\lambda} + \frac{1}{2} \right)$$

denotes the Hamiltonian of the isolated atomic and radiation field, and

$$\hat{H}_{\text{para}}(t) = \frac{e}{m} \hat{A}(r, t) \cdot \hat{p}$$

denotes the coupling with

$$\hat{A}(r, t) = \sum_{k\lambda} \sqrt{\frac{\hbar}{2\epsilon_0 \omega_k V}} \left[ \hat{e}_{k\lambda} a_{k\lambda} e^{i(k \cdot r - \omega_k t)} + \hat{e}_{k\lambda}^* a_{k\lambda}^\dagger e^{-i(k \cdot r - \omega_k t)} \right]$$
Radiative transitions: recap

- The transition rate between an initial and final state of the atom and electromagnetic field can be estimated using Fermi’s Golden rule

\[
\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar^2} |\langle f | \hat{H}_{\text{para}} | i \rangle|^2 \delta(\omega_{if} - \omega)
\]

where \( \hbar \omega_{if} = E_i - E_f \).

- Crucially, since the photon creation/annihilation operators obey the relations, \( a_{k\lambda}^\dagger |n_{k\lambda}\rangle = \sqrt{n_{k\lambda} + 1} |(n_{k\lambda} + 1)\rangle \) and \( a_{k\lambda} |n_{k\lambda}\rangle = \sqrt{n_{k\lambda}} |(n_{k\lambda} - 1)\rangle \) the transition rate depends on the photon number, \( n_{k\lambda} \).

- When \( Z_\alpha \ll 1 \), the effective range of the interaction of the atom with the field is small (i.e. \( kr \sim Z_\alpha \)) and we can effect the dipole approximation,

\[
\langle f | e^{-i k \cdot r} \hat{e}_{k\lambda} \cdot \hat{p} | i \rangle \approx \frac{im \omega_k}{e} \langle f | \hat{e}_{k\lambda} \cdot d | i \rangle, \quad d = -e r
\]
In the electric dipole approximation, the transition rate is given by

\[
\Gamma_{i \rightarrow f, k\lambda} \simeq \frac{\pi \omega_k}{\epsilon_0 V} |\langle f | \hat{\mathbf{e}}_{k\lambda} \cdot \hat{\mathbf{d}} | i \rangle|^2 \begin{cases} n_{k\lambda} \delta(E_f - E_i - \hbar \omega_k) & \text{absorption} \\ (n_{k\lambda} + 1) \delta(E_i - E_f - \hbar \omega_k) & \text{emission} \end{cases}
\]

where \( \hat{\mathbf{d}} = -e\mathbf{r} \) is electric dipole operator.

- The coincidence of \( n_{k\lambda} \)-independent coefficients for absorption and emission coincide is known as \textit{detailed balance}.
- From these results, we turn now to consider the principle of the operation of an atomic laser.
Theory of laser

- Principle of stimulated emission provides basis of laser operation: light amplification by stimulated emission of radiation.

- However, laser not only amplifies light, but provides source of **monochromatic** (single mode), **coherent** (spatial/temporal), **directional** and **intense** radiation.

- In atomic laser, the gain medium provided by a gas of atoms confined to a cavity and bound by highly reflective mirrors.
Theory of laser: rate equations

Consider gas of atoms in a cavity subject to an EM field of intensity $I \propto n(\omega)$ and angular frequency $\omega$ tuned to energy difference between two discrete energy levels of the atoms, i.e. $\hbar \omega = E_2 - E_1$.

Taking into account stimulated absorption, atoms are transferred from level 1 to level 2 at a rate

$$\Gamma_{12} = WN_1 n(\omega)$$

where $N_1$ atoms in level 1 and $W$ includes matrix elements.

From spontaneous and stimulated emission processes, the rate of transfer of atoms from level 2 to level 1 is given by

$$\Gamma_{21} = WN_2 (n(\omega) + 1)$$
Since transfer of particles from level 2 to 1 leads to creation of photons in cavity while from 1 to 2 they involve absorption, the rate of change of photon number is given by \( \dot{n} = W(N_2(n + 1) - N_1n) \).

However, to make use of cavity as a photon source, we have to allow photons to leak from the cavity through imperfect mirrors. Taking into account this and other loss processes, we have

\[
\dot{n} = DWn + N_2W - \frac{n}{\tau_{ph}}
\]

where \( D = N_2 - N_1 \) denotes population imbalance and \( 1/\tau_{ph} \) is the total loss rate.
\[ \Gamma_{k\lambda} \sim |\langle f | \hat{e}_{k\lambda} \cdot \hat{d} | i \rangle|^2 \begin{cases} n_{k\lambda} & \text{abs.} \\ (n_{k\lambda} + 1) & \text{emiss.} \end{cases} \]

- Without further external processes, photons would escape from cavity and the system would relax into ground state – To create a steady-state photon population, energy must be pumped into the system in the form of excitations.

- Achieved by transferring atoms between 1 and 2 via level 3 by non-resonant optical pump. If lifetime of 3 is short, occupancy is effectively zero, rate of transfer of particles from 2 to 1,

\[ \dot{N}_2 \simeq -w_{21} N_2 + w_{12} N_1 - (N_2 - N_1) Wn \simeq -\dot{N}_1 \]

where we have dropped small contribution from spontaneous emission, and \( w_{12}, w_{21} \) denote net non-resonant transition rates.
Theory of laser: stationary equations

\[ \dot{N}_2 \approx -w_{21} N_2 + w_{12} N_1 - (N_2 - N_1) Wn \approx -\dot{N}_1 \]

- Without cavity photons \((n = 0)\), since \(N_1 + N_2 \approx N\), in steady state,

\[
D^{(0)} = N_2^{(0)} - N_1^{(0)} = N \frac{w_{12} - w_{21}}{w_{12} + w_{21}}
\]

denotes unsaturated inversion.

- Restoring the cavity photons, we have

\[
\dot{D} = \dot{N}_2 - \dot{N}_1 = \frac{D^{(0)} - D}{T} - 2DWn
\]

where \(1/T = w_{12} + w_{21}\) represents typical relaxation rate.
Theory of laser: stationary equations

\[ \dot{n} = DWn - \frac{n}{\tau_{ph}}, \quad \dot{D} = \frac{D^{(0)} - D}{T} - 2DWn \]

- In steady-state operation, \( \dot{n} = \dot{D} = 0 \), population imbalance

\[ D \equiv N_2 - N_1 = \frac{D^{(0)}}{1 + 2TWn} \]

- From this result, we find the steady state photon number

\[ n = \frac{D^{(0)}W - 1/\tau_{ph}}{2TW/\tau_{ph}} \]

- This result shows that the system will only start lasing when the unsaturated inversion exceeds a threshold, \( D^{(0)} > 1/\tau_{ph}W \).
Although the analysis above addressed the threshold conditions for the laser, 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 on a considerable detour – see Part III quantum optics.

However, we can gain some insight into the properties and physical manifestations of coherent states by looking at a toy example; but first we must define what we mean by a coherent state.
A coherent state is defined as an eigenstate of the annihilation operator,

\[ a|\beta\rangle = \beta|\beta\rangle \]

Since \( a \) is not Hermitian, \( \beta \) can take complex eigenvalues.

The eigenstates are constructed from the harmonic oscillator ground state by the action of the unitary operator,

\[ |\beta\rangle = \hat{U}(\beta)|0\rangle, \quad \hat{U}(\beta) = e^{\beta a^\dagger - \beta^* a}, \quad \hat{U}^\dagger(\beta)\hat{U}(\beta) = I \]

The proof follows from the identity (problem set I),

\[ a\hat{U}(\beta) = \hat{U}(\beta)(a + \beta), \quad \text{i.e.} \quad a\hat{U}(\beta)|0\rangle = \beta\hat{U}(\beta)|0\rangle \]

i.e. \( \hat{U} \) is a translation operator, \( \hat{U}^\dagger(\beta)a\hat{U}(\beta) = a + \beta \).
Coherent states

\[ |\beta\rangle = \hat{U}(\beta)|0\rangle, \quad \hat{U}(\beta) = e^{\beta a^\dagger - \beta^* a} \]

- Since \( \hat{U}(\beta) = e^{\beta a^\dagger - \beta^* a} = e^{-|\beta|^2/2} e^{\beta a^\dagger} e^{-\beta^* a} \) and \( e^{-\beta^* a}|0\rangle = |0\rangle \), we can write

\[ |\beta\rangle = e^{-|\beta|^2/2} e^{\beta a^\dagger} |0\rangle \]

- With \( |n\rangle = \frac{1}{\sqrt{n!}} (a^\dagger)^n |0\rangle \), we can write

\[ |\beta\rangle = \sum_n e^{-|\beta|^2/2} \frac{\beta^n}{\sqrt{n!}} |n\rangle \]

showing that the probability of observing \( n \) excitations

\[ P_n = |\langle n|\beta\rangle|^2 = e^{-|\beta|^2} \frac{|\beta|^{2n}}{n!} \]

is a Poisson distribution with average occupation, \( \langle \beta|a^\dagger a|\beta\rangle = |\beta|^2 \).
Driven quantum harmonic oscillator

But how can we prepare a system in a coherent state?

Consider a single two-level atom resonantly coupled to a single cavity mode – the quantum Hamiltonian of the coupled system,

\[ \hat{H} = \frac{1}{2} \hbar \omega \sigma_z + \hbar \omega \left( a\dagger a + \frac{1}{2} \right) + \hbar g (\sigma_- a + \sigma_+ a\dagger) \]

When excitations of two level system are driven by an external pump, it can behave as a classical dipole source for the cavity mode leading to the driven harmonic oscillator Hamiltonian,

\[ \hat{H} \simeq \hat{H}_{\text{rad}} + V(t) = \hbar \omega \left( a\dagger a + \frac{1}{2} \right) + i\hbar (f(t)a\dagger - f^*(t)a) \]

where \( f(t) = f_0 e^{-i\omega t} \)
Driven quantum harmonic oscillator

\[ \hat{H} = \hbar \omega \left( a^\dagger a + \frac{1}{2} \right) + i\hbar \left( f(t)a^\dagger - f^*(t)a \right) \]

\[ f(t) = f_0 e^{-i\omega t} \]

- If photon system is prepared in ground state, \( |0\rangle \), the perturbation drives the system into a coherent state.

- To understand how, let us turn to the interaction representation,

\[ i\hbar \partial_t |\psi(t)\rangle_I = V_I |\psi(t)\rangle_I \] where \( |\psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar} |\psi(t)\rangle_S \). With \( e^{i\omega t a^\dagger a} e^{-i\omega t a^\dagger a} = e^{-i\omega t a} \),

\[ V_I(t) = e^{i\hat{H}_0 t/\hbar} i\hbar \left( f(t) a^\dagger - f^*(t) a \right) e^{-i\hat{H}_0 t/\hbar} = i\hbar \left( f_0 a^\dagger - f_0^* a \right) \]

- Since \( V_I(t) \) is time-independent, the time-evolution operator, defined by the equation \( i\hbar \partial_t U_I(t) = V_I U_I(t) \), is given simply by

\[ U_I(t) = \exp \left[ (f_0 a^\dagger - f_0^* a) t \right] \]
Driven quantum harmonic oscillator

\[ U_1(t) = \exp \left [ \left ( f_0 a^\dagger - f_0^* a \right ) t \right ] \]

Therefore, if the system was prepared in the ground state \( |0\rangle \) at \( t = 0 \), at later times,

\[ |\psi(t)\rangle_I = \exp \left [ \left ( f_0 a^\dagger - f_0^* a \right ) t \right ] |0\rangle = e^{-|f_0|^2 t^2 / 2} e^{f_0 a^\dagger t} |0\rangle \]

Reexpressed in the Schrödinger representation,

\[ |\psi(t)\rangle_S = e^{-i\hat{H}_0 t / \hbar} |\psi(t)\rangle_I = e^{-|f_0|^2 t^2 / 2} e^{f_0 e^{-i\omega t} a^\dagger t} |0\rangle \]

A classical oscillatory force drives a system prepared in the vacuum state into a coherent state with an excitation number which climbs as \( |f_0|^2 t^2 \).
12 Field theory: from phonons to photons:
From particles to fields: classical field theory of harmonic atomic chain; quantization of atomic chain; phonons. Classical theory of the EM field; waveguide; quantization of the EM field and photons.

13 Time-dependent perturbation theory:
Rabi oscillations in two level systems; perturbation series; sudden approximation; harmonic perturbations and Fermi’s Golden rule.

14 Radiative transitions:
Light-matter interaction; spontaneous emission; absorption and stimulated emission; Einstein’s A and B coefficients; dipole approximation; selection rules; †lasers.
15 Scattering theory
Elastic scattering; cross section; method of particle waves; Born approximation; scattering of identical particles.

16 Relativistic quantum mechanics:
Klein-Gordon equation; Dirac equation; relativistic covariance and spin; free relativistic particles and the Klein paradox; antiparticles; coupling to EM field: minimal coupling and the connection to non-relativistic quantum mechanics; †field quantization.