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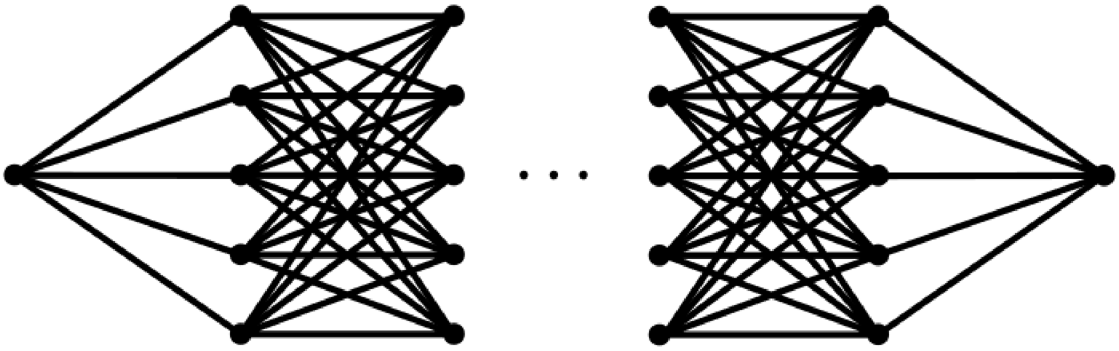
MODERN LIGHT-MATTER INTERACTIONS



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1.1 TIME-EVOLUTION OF QUANTUM SYSTEMS

In order to describe the quantum interactions of light and matter, we will begin by reviewing the fundamental mathematics which govern the evolution of general quantum systems. Then, we will develop a framework of perturbation theory which is most useful for our purposes.

A highly general quantum mechanical system with Hamiltonian $H(t)$ can be described as the unitary time-evolution of a state vector $|\psi(t)\rangle$ via the Schrödinger equation

$$i\hbar\partial_t |\psi(t)\rangle = H(t) |\psi(t)\rangle . \tag{1.1.1}$$

We can then define the unitary time-evolution operator $U(t, t')$ to express the time-dependent state $|\psi(t)\rangle$ in terms of the state at a previous initial time t_{init} as

$$|\psi(t)\rangle = U(t, t_{init}) |\psi(t_{init})\rangle . \tag{1.1.2}$$

As a brief reminder, the unitary time evolution operator satisfies a few simple but important properties:

1. $U(t_1, t_1) = 1$, where 1 is the identity operator – letting no time pass will not evolve the state

2. $U(t_3, t_2)U(t_2, t_1) = U(t_3, t_1)$ – sequential time evolution

3. $U(t_1, t_2) = U^\dagger(t_1, t_2)$ – unitarity.

The time-dependent Schrodinger equation can then be equivalently formulated as an equation for the unitary time-evolution operator,

$$i\hbar\partial_t U(t, t_{init}) = H(t)U(t, t_{init}). \tag{1.1.3}$$

This has the benefit that it removes reference to the time dependent state $|\psi(t)\rangle$, allowing us to work with operators.

We will now "solve" this equation in a self-consistent manner. We begin by formally integrating both sides of the operator equation:

$$i\hbar \int_{t_{init}}^{t} dt'\ \partial_t U(t', t_{init}) = i\hbar (U(t, t_{init}) - U(t_{init}, t_{init}))$$
$$= \int_{t_{init}}^{t} dt'\ H(t')U(t', t_{init}). \tag{1.1.4}$$

Using property 1 from above, we may then write

$$U(t, t_{init}) = 1 + \left(\frac{1}{i\hbar}\right) \int_{t_{init}}^{t} dt'\ H(t')U(t', t_{init}). \tag{1.1.5}$$

We have converted a differential equation into an integral equation, since U is expressed in terms of itself through an integral. Although this will not provide us with an analytical solution, it will provide a form useful for further theoretical analysis. To derive this form, we plug the left-hand side of the equation into the right-hand side, which gives

$$U(t, t_{init}) = 1 + \left(\frac{1}{i\hbar}\right) \int_{t_{init}}^{t} dt'\ H(t')$$
$$+ \left(\frac{1}{i\hbar}\right)^2 \int_{t_{init}}^{t} dt' \int_{t_{init}}^{t'} dt''\ H(t')H(t'')U(t'', t_{init}). \tag{1.1.6}$$

Doing this *ad infinitum*, and relabeling the times by numerical indices $(t_1, t_2, \ldots)$, we immediately have

$$U(t, t_{init}) = \sum_{n=0}^{\infty} \left(\prod_{i=1}^{n} \left(\frac{1}{i\hbar}\right) \int_{t_{init}}^{t_{i-1}} dt_i\ H(t_i) \right), \tag{1.1.7}$$

where $t_0 \equiv t$. We now have U in terms of an infinite series which depends only on the Hamiltonian which we know. Eventually, we will invoke perturbation theory to show that we can learn an incredible amount even from the first few terms. To work toward this goal, we can do a few things to make this expression even nicer. It would be convenient if all of the upper limits were the same, so that manipulating the integrals was less cumbersome. This can always be done by extending the limits of integration, and then introducing heaviside step functions into the integrand to restrict the integration range. Rather then going into it in great detail, we will just state the final result, and we encourage you to check that it is equivalent to the previous formulation. Consider a term

$$\int_{t_{init}}^{t} dt_1 \cdots \int_{t_{init}}^{t_{n-1}} dt_n\ H(t_1) \cdots H(t_n). \tag{1.1.8}$$

We claim that it is equal to

$$\frac{1}{n!} \int_{t_{init}}^{t} dt_1 \cdots \int_{t_{init}}^{t_{n-1}} dt_n \mathrm{T}\left[H(t_1) \cdots H(t_n)\right], \tag{1.1.9}$$

where T is the time-ordering operator, which is defined such that "operators at earlier times go to the right of operators at later times." For example, if $A(t)$ is some operator, and $t_2 > t_3 > t_1$, then the action of the time ordering operator is

$$\mathrm{T}\left[A_1(t_1)A_2(t_2)A_3(t_3)\right] = A_2(t_2)A_3(t_3)A_1(t_1). \tag{1.1.10}$$

In order to avoid thinking about case work for all possible orderings of times, we can instead use the heaviside function $\theta(t)$ to enumerate these cases as

$$\begin{aligned}\mathrm{T}\left[A_1(t_1)A_2(t_2)A_3(t_3)\right] = A_1(t_1)A_2(t_2)A_3(t_3)\theta(t_1-t_2)\theta(t_2-t_3)\\ + \text{permutations of 1,2,3}.\end{aligned} \tag{1.1.11}$$

From here, one can use this type of reasoning to compactly write the series expansion for the unitary evolution operator as

$$\boxed{U(t,t_{init}) = \mathrm{T}\sum_{n=0} \frac{1}{n!}\left(\frac{1}{i\hbar}\int_{t_{init}}^{t} dt'\ H(t')\right)^n = \mathrm{T}\ \exp\left[-\frac{i}{\hbar}\int_{t_{init}}^{t} dt'\ H(t')\right].} \tag{1.1.12}$$

The right-hand side is called the *time-ordered exponential*. It is important to note that so far, we have made *no approximations*. In the formal sense, this series solution for the time evolution operator is exact. This series representation of the time-evolution operator is a simple result with a myriad of useful applications, and is applied throughout almost the entirety of the text.

Simplifications of the time-ordered exponential

Before applying this expression to derive perturbation theory, we should briefly mention two special cases of this expression. First, consider the case in which the Hamiltonian *commutes with itself at later times*: $[H(t), H(t')] = 0$ for all t, t' (this is not common for time-dependent Hamiltonians). In that case, it follows that the time-ordering is ineffectual: all orderings of the Hamiltonian operators are exactly the same. Another way to say this is that the time-ordering operator is the identity, and can thus be ignored. The unitary time-evolution operator is then

$$U(t,t_{init}) = \exp\left[-\frac{i}{\hbar}\int_{t_{init}}^{t} dt'\ H(t')\right]. \tag{1.1.13}$$

The second important case is that in which the Hamiltonian is *time-independent*. Then, the time-ordered exponential reduces to the well-known expression

$$U(t,t_{init}) = \exp\left[-\frac{iH(t-t_{init})}{\hbar}\right]. \tag{1.1.14}$$

The interaction picture

We should mention yet another useful representation of the results developed above. Suppose we express the Hamiltonian in the form $H = H_0 + V$, where H_0 is some Hamiltonian for which we know the corresponding unitary time-evolution operator U_0, and V is a Hamiltonian we know less about. This situation comes up centrally in *perturbation theory*, which we take up in the next section. We may then write the time-dependent Schrodinger equation for the unitary time-evolution operator as

$$i\hbar\partial_t U = (H_0 + V)U, \tag{1.1.15}$$

where we now omit the time-labels, leaving them implicit. Now, let us factor the evolution operator as $U = U_0 U_I$, where $i\hbar\partial_t U_0 = H_0 U_0$, and U_I will be called the *interaction picture time-evolution operator*. It follows immediately that

$$i\hbar\partial_t U_I = U_0^\dagger V U_0 U_I \equiv V_I U_I, \tag{1.1.16}$$

where V_I is the V operator in the so-called *interaction picture*. It should be clear that because this equation is the same as the one we started with in the beginning of this section, the solution is:

$$U_I = \mathrm{T}\exp\left[-\frac{i}{\hbar}\int dt'\ V_I(t')\right]. \tag{1.1.17}$$

With these fundamentals established, we can move on to develop a key analytical tool of quantum mechanics: *time-dependent perturbation theory*.

1.1.1 Time-dependent perturbation theory

The quantum dynamics of most Hamiltonians cannot be solved for anlytically. Therefore, we must turn to approximate techniques to study the dynamics of quantum systems. An extremely powerful and versatile technique to approximate the dynamics of quantum systems is time-dependent perturbation theory, which allows us to solve for the time-dynamics of a system approximately, provided that the Hamiltonian can be decomposed into the sum of an exactly solvable part plus a small correction. While this may sound artificial, it is fortunately not, and perturbation theory is perhaps one of the most useful tools in quantum mechanics. The premise of perturbation theory is simple, and the time-ordered exponential has perfectly set the stage for this development. We learned from the last section that the unitary time-evolution operator for a general quantum system with Hamiltonian $H = H_0 + V$ can be written as

$$U(t,t_0) = U_0(t,t_0)U_I(t,t_0) = U_0(t,t_0) \times \mathrm{T}\ \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} dt'\ V_I(t')\right]. \tag{1.1.18}$$

We will often call H_0, U_0, and the associated eigenstates of H_0 *unperturbed* quantities. The utility of the interaction picture is that it isolates the part of the Hamiltonian which we still need to understand the effects of. The associated probability that the system is in some eigenstate $|f\rangle$ of the unperturbed system at time t is then simply

$$|\langle f|U(t,t_0)|i\rangle|^2 = |\langle f|U_I(t,t_0)|i\rangle|^2, \tag{1.1.19}$$

since the action of U_0 on $|f\rangle$ is simply to produce a phase. In many problems in perturbation theory, we are interested in *scattering probabilities*, which tell us the probability that a system in state $|i\rangle$ has changed, or "scattered", into state $|f\rangle$. We quickly note an important additional piece of terminology, which is that U_I is often called the "S matrix" or "scattering matrix", and its matrix elements are called S-matrix elements. We will use this terminology almost exclusively.

For physical context, we list a few examples of processes which can be described this way

- An excited atom or molecule relaxes to a lower energy level, producing a photon
- A photon incident on an atom or molecule is scattered into a different direction
- An electron in a semiconductor absorbs a photon, exciting the electron from the valence band into the conduction band

We also often formulate this problem in terms of *transition rates*, which tells us the rate at which these scattering probabilities change. In other words, we consider some physical process defined by initial and final states, and then compute the rate at which this process occurs.

The program of perturbation theory for computing these rates is then simple: we Taylor-expand the time-ordered exponential, and find transition rates at whatever order is needed to accurately describe them. In practice, orders higher than two (counting from zero) are rarely considered, as most processes happen to leading order at first or second order in the Taylor expansion. And if higher orders are still needed, it is either for extremely precise predictions (in excess of 8 decimal places of accuracy, which is outside of our scope) or a different method should be found.

First-order scattering amplitude and transition rate

First, we discuss first-order perturbation theory – in other words, processes described by the first order term in the time-ordered exponential expansion. Consider a system starting in an eigenstate $|i\rangle$ of the unperturbed system. At first-order in the Taylor expansion, the S-matrix element describing the state $|i\rangle$ scattering into an orthogonal final state $|f\rangle$ is given by

$$S_{fi} = -\frac{i}{\hbar}\int_{-T}^{T} dt' \; \langle f|V_I(t')|i\rangle = -\frac{iV_{fi}}{\hbar}\int_{-T}^{T} dt' \; e^{i\omega_{fi}t} = -\frac{iV_{fi}}{\hbar}\left(2T\text{sinc}\left(\omega_{fi}T\right)\right). \qquad (1.1.20)$$

Regarding the limits of integration, we have simply redefined t such that $t - t_0 = 2T$, where $2T$ is *the interaction time interval*, and shifted the origin of time so that this interval is centered around time zero. Recall that the sinc function $\text{sinc}(\alpha x) \equiv \frac{sin(\alpha x)}{\alpha x}$ is extremely sharply peaked around $x = 0$ for large α (and $\text{sinc}(0) = 1$). For very large times then, the only probabilities that are significant are energy-conserving ones: $\omega_f = \omega_i$. Another point to mention is that $\frac{\alpha}{\pi}\int_{-\infty}^{\infty} dx \; \text{sinc}(\alpha x) = 1$. Therefore, in the limit of long times, which is of most interest $T \gg \frac{1}{\omega_{fi}}$, we may say that $2T\text{sinc}(\omega_{fi}T) \to 2\pi\delta(\omega_{fi})$.

Squaring the S-matrix to obtain a probability, we have that the transition probability, P_{fi} satisfies:

$$P_{fi} \equiv |S_{fi}|^2 = \frac{|V_{fi}|^2}{\hbar^2}(2\pi)^2\delta^2(\omega_{fi}) = \frac{|V_{fi}|^2}{\hbar^2}(2\pi)^2\delta(\omega_{fi})\delta(0), \qquad (1.1.21)$$

where we have used the delta function identity $\delta(x-a)\delta(f(x)-b) = \delta(x-a)\delta(f(a)-b)$, where $f(x) = x$. If you've never seen $\delta(0)$ before, don't freak out. Remember how we got the delta function: from the integral of an exponential over *finite* limits of integration. In other words, $\delta(0)$ should be understood as

$$\delta(0) \to \int_{-T}^{T} \frac{dt}{2\pi} e^{i\omega_{fi}0} = \frac{2T}{2\pi}. \tag{1.1.22}$$

You should not be too stressed about the fact that we used a delta-function identity for something that wasn't really a delta function due to finite limits of integration. That identity generally sharply peaked functions. We will do these kinds of manipulations often, so we encourage you to try this with the sinc functions directly and convince yourself it works out the same way in the desired limit.

With those disclaimers out of the way, the transition probability is given by

$$P_{fi} = (2T)\frac{2\pi}{\hbar^2}|V_{fi}|^2\delta(\omega_{fi}). \tag{1.1.23}$$

The transition probability is directly proportional to the interaction time, $2T$. We define the average transition rate as $\Gamma_{fi} = \frac{P_{fi}}{2T}$. Finally, we are often not only interested in the rate of transitions into one final states, but all possible final states, denoted Γ_i. This is often called the *decay rate* or *transition rate* of the state i. We note that it is conventional to drop the i subscript, as it can be inferred from context which state is the initial state from the matrix element. Noting that $\Gamma = \sum_f \Gamma_{fi}$, we have that

$$\boxed{\Gamma = \frac{2\pi}{\hbar^2}\sum_f |V_{fi}|^2\delta(\omega_{fi}).} \tag{1.1.24}$$

This formula is called *Fermi's golden rule*, and is perhaps one of the most used formulae in quantum mechanics. It is a workhorse formula in atomic and optical physics, condensed matter physics, quantum field theory, and many other areas that rely on quantum mechanics.

Before moving on to second-order scattering probabilities and transition rates, we should quickly mention a corollary of the considerations of this section. What if our initial state is not prepared in an eigenstate of the Hamiltonian, but is instead prepared in a superposition of eigenstates $|i\rangle = \sum_k c_k |k\rangle$? The associated scattering probability to a final state f is then given by:

$$S_{fi} = \sum_k c_k S_{fk}. \tag{1.1.25}$$

As probabilities are the squares of these quantities, it is immediately clear that there is a possibility for different terms to interfere via cross-terms.

Second-order scattering amplitude and transition rates

A number of important physical processes are described at leading order in second-order perturbation theory. Examples of such processes include the scattering of light by electrons (Rayleigh, Thomson, and Compton scattering), as well as two-photon absorption and emission processes, which are fundamental processes of nonlinear optics. The evaluation of a scattering probability in second-order perturbation theory is in principle a straightforward extension of the considerations of the previous section: we simply expand the unitary evolution operator U_I to second-order. There are a few new steps which are involved, so we outline them here.

The S-matrix element S_{fi}, assuming an initial eigenstate $|i\rangle$, and a final eigenstate $|f\rangle$, of the unperturbed Hamiltonian, is given by

$$S^{(2)}_{fi} = \frac{1}{2}\left(-\frac{i}{\hbar}\right)^2 \int_{-T}^{T} dt' dt'' \, \langle f|\mathrm{T}\left[V_I(t')V_I(t'')\right]|i\rangle. \tag{1.1.26}$$

The time-ordering can be expressed equivalently (by virtue of its definition) as

$$S^{(2)}_{fi} = \frac{1}{2}\left(-\frac{i}{\hbar}\right)^2 \int_{-T}^{T} dt' dt'' \, \langle f|\theta(t'-t'')V_I(t')V_I(t'') + \theta(t''-t')V_I(t'')V_I(t')|i\rangle. \tag{1.1.27}$$

We focus on the first of the two terms, as the second is evaluated in the same way. To put the expression into a convenient form, it is useful to insert a complete set of eigenstates of the unperturbed Hamiltonian, so that we instead evaluate

$$\frac{1}{2}\sum_n \left(-\frac{i}{\hbar}\right)^2 \int_{-T}^{T} dt' dt'' \, \theta(t'-t'')\langle f|V_I(t')|n\rangle\langle n|V_I(t'')|i\rangle. \tag{1.1.28}$$

If the unperturbed Hamiltonian is time-independent, the time-dependence of the matrix element reduces the previous expression to

$$\frac{1}{2}\sum_n \left(-\frac{i}{\hbar}\right)^2 \int_{-T}^{T} dt' dt'' \, \theta(t'-t'')V_{fn}V_{ni}e^{i\omega_{fn}t' + i\omega_{ni}t''}. \tag{1.1.29}$$

We see that the integral is something like a Fourier transform of the Heaviside step function. This integral may be evaluated by means of a famous formula which is the contour integral representation of the step function.

$$\theta(t'-t'') = -\lim_{\eta\to 0}\int \frac{d\omega}{2\pi i}\, \frac{e^{-i\omega(t'-t'')}}{\omega + i\eta}. \tag{1.1.30}$$

Plugging this formula in, and extending the limits of integration from $-\infty$ to ∞ yields

$$i\pi \sum_n \left(-\frac{i}{\hbar}\right)^2 \frac{V_{fn}V_{ni}}{\omega_{in} + i\eta}\delta(\omega_{fi}). \tag{1.1.31}$$

It is simple to verify that the second term in the time-ordering is identical. Therefore, the S-matrix element at second order is given by

$$S^{(2)}_{fi} = 2\pi i \left(-\frac{i}{\hbar}\right)^2 \sum_n \frac{V_{fn}V_{ni}}{\omega_{in} + i\eta}\delta(\omega_{fi}). \tag{1.1.32}$$

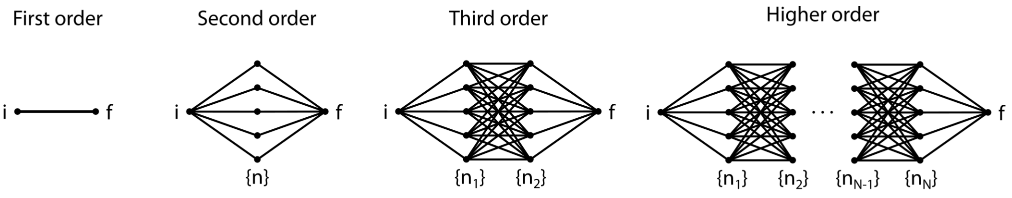

Figure 1.1: Schematic of perturbation theory at first, second, third, and N-th order.

Squaring the S-matrix element to obtain a transition probability, handling $\delta(0)$ the same way as in the previous section, and summing over final states, immediately yields Fermi's Golden Rule at second order:

$$\boxed{\Gamma = \frac{2\pi}{\hbar^4}\sum_f \Big|\sum_n \frac{V_{fn}V_{ni}}{\omega_{in}+i\eta}\Big|^2 \delta(\omega_{fi}).} \tag{1.1.33}$$

The limit $\eta \to 0$ is implicit. You might wonder why the denominator is being made slightly complex. It is to handle an important case of second-order perturbation theory: resonance, i.e., when for some *intermediate state* or *virtual state* n, $\omega_{ni} = 0$ (and by energy conservation $\omega_{fn} = 0$). We will not consider this case here. We will simply content ourselves by mentioning that when resonance happens, the decay rate is essentially that of two sequential first-order processes: from i to n at first order, and then from n to f at first order. This is important in the consideration of elementary physical processes such as resonance flourescence and radiative cascade.

Energy shifts in time-dependent perturbation theory

In the previous two sections, we looked at S-matrix elements between different final states. This leads to a natural question: what about when the two states are the same? It turns out that these elements of the S-matrix lead to energy shifts. You may remember from an elementary quantum mechanics course that energy shifts are typically evaluated in time-independent perturbation theory. We will now show how to evaluate them in time-dependent perturbation theory, and that this yields the same results as from time-independent perturbation theory. The main advantage of evaluating energy shifts in time-dependent perturbation theory is economy of formalism: we can now use a single method (time-dependent perturbation theory) to evaluate all perturbation theory quantities of interest.

To see that elements like S_{ii} are related to energy shifts, consider $S_{ii}(T, -T)$ up to second-order in perturbation theory, a la Equations (15) and (27). Restoring the zeroth order contribution, we can write

$$S_{ii}(T,-T) \approx 1 - \frac{iV_{ii}}{\hbar}(2T) - \frac{i}{\hbar}\sum_n \frac{V_{in}V_{ni}}{\hbar\omega_{in}+i\hbar\eta}(2T) \equiv 1 - \frac{i\delta E(2T)}{\hbar}, \tag{1.1.34}$$

where we define an energy shift δE as

$$\delta E = V_{ii} + \sum_n \frac{V_{in}V_{ni}}{\hbar\omega_{in}+i\hbar\eta}. \tag{1.1.35}$$

Noting that for small changes in energy, $1 - \frac{i\delta E(2T)}{\hbar} \approx e^{-\frac{i\delta E(2T)}{\hbar}}$, and recalling that the S-matrix represents time-evolution *in addition* to the unperturbed Hamiltonian, we see that in that case, the evolution of the initial state can then be approximated by $e^{-\frac{i(E_i+\delta E)(2T)}{\hbar}}$. We may then claim that the effect of the perturbation is to shift the energy of the state $|i\rangle$ by an amount given by Equation (35). You may recognize that that energy shift is exactly the one derived through non-degenerate time-independent perturbation theory. There is one additionally interesting thing to note. In the second-order contribution to the energy shift, we again see the possibility of resonance for some intermediate state $|f\rangle$. Evaluating its contribution to the energy shift by contour integration will yield a complex energy, whose imaginary part is given by (half) the decay rate given by Fermi's Golden Rule at first order in perturbation theory. In other words, decay leads to "complex energies", very roughly speaking.

Eigenfunction shifts in time-dependent perturbation theory

You may remember that in time-independent perturbation theory, shifts in the eigenfunctions can also be calculated. We can also do it in time-dependent perturbation theory. Consider a state which starts at time $-T$ in an eigenstate $|n\rangle$ of H_0 and a perturbation V is turned on. We will assume there is no degeneracy between discrete states. The resulting state at first order is

$$|\psi(t)\rangle = U_0(t,t_0)\left(1 + \frac{1}{i\hbar}\int_{-T}^{t} dt' V_I(t')\right)|n\rangle \tag{1.1.36}$$

Expressing $V_I = U_0^\dagger V U_0$, and inserting a complete set of states, we have that

$$|\psi(t)\rangle = e^{-i\omega_n t}|n\rangle + \frac{1}{i\hbar}U_0(t,t_0)\int_{-T}^{t}\sum_m e^{i\omega_{mn}t}V_{mn}|m\rangle. \tag{1.1.37}$$

Regulating the interaction by turning it on slowly with a time-dependence $e^{-\eta|t|}$, with η infinitesimal, we have:

$$|\psi(t)\rangle = e^{-i\omega_n(t+T)}\left(1 - \frac{iV_{nn}}{\hbar}(t+T)\right)|n\rangle - e^{i\omega_m(t+T)}\sum_{m\neq n}\frac{V_{mn}}{\hbar\omega_{mn}}|m\rangle. \tag{1.1.38}$$

Where wehave dropped the complex infinitesimal in the denominator on the assumption of non-degeneracy. The third term follows from the considerations of the previous section. Approximating the terms in parentheses as an exponential as in the previous subsection, we have

$$|\psi(t)\rangle = e^{-i\left(\omega_n + \frac{V_{nn}}{\hbar}\right)(t+T)}|n\rangle + e^{i\omega_m(t+T)}\sum_{m\neq n}\frac{V_{mn}}{\hbar\omega_{nm}}|m\rangle. \tag{1.1.39}$$

The first term is the initial state with the first-order energy shift. The second term is the static eigenfunction shift from first-order time-independent perturbation theory.

1.1.2 Worked examples of transition rates

In this section, we will do a couple of examples of transition rate problems, which will (a) give you a clearer idea of how the formulae developed here are applied, (b) be of great relevance later in the text, and (c) impress upon you that some very important phenomena can be explained as decays.

Quantum theory of friction (two-level system coupled to harmonic oscillators)

Let's consider a two-level system which is coupled to many harmonic oscillators all of mass m. This problem comes up a lot in the quantum theory of damping (friction), as well as in atomic physics, when considering spontaneous emission by atoms. Let us assume that the two-level system has an energy difference between the excited and ground states of $\hbar\omega_0$. Let us also assume that the oscillators are labeled by a one-dimensional continuous index k, and that the oscillators have a continuum of frequencies ω_k. Let us further assume that the interaction is between the σ_x operator of the two-level system and the position operator of each of the oscillators, with an overall coupling scale α_j, such that the Hamiltonian for this system is:

$$H = \frac{1}{2}\hbar\omega_0\sigma_z + \sum_k \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right) + \sum_k \alpha_j \sqrt{\frac{\hbar}{2m\omega_k}} (a_k + a_k^\dagger)\sigma_x. \tag{1.1.40}$$

We may readily observe that the first two terms of the Hamiltonian correspond to a system which we may readily diagonalize. The eigenstates are of the form

$$|g\rangle|n_1 n_2 \cdots\rangle, |e\rangle|n_1 n_2 \cdots\rangle, \tag{1.1.41}$$

with corresponding energies

$$-\frac{1}{2}\hbar\omega_0 + \sum_k \hbar\omega_k \left(n_k + \frac{1}{2} \right), \frac{1}{2}\hbar\omega_0 + \sum_k \hbar\omega_k \left(n_k + \frac{1}{2} \right) \tag{1.1.42}$$

Note that as the zero of energy may be shifted arbitrarily, we can shift every state down by $\sum\limits_k \frac{1}{2}\hbar\omega_k$, even though for a continuum, this is infinite. We thus identify the first two terms of the Hamiltonian as H_0, the unperturbed Hamiltonian. The perturbation, V, is simply the third term. It's effect vanishes when $\alpha_j = 0$ for all j.

Suppose the initial state of the system at time 0 is $|e\rangle|0 \cdots 0\rangle$. In other words, the two-level system is in the excited state, and the harmonic oscillators are all in the ground state. To determine possible decay pathways at first order, we ask: what states can the interaction Hamiltonian take the initial state to. Apply V to this state. σ_x flips $|e\rangle$ to $|g\rangle$. The sum of creation and annihilation operators promotes the vacuum of oscillators to a superposition of states where each state individually has an excitaton of the oscillator. Therefore, a suitable basis of final states is of the form

$$|f\rangle = |g\rangle|0_1 \cdots 0_{j-1} 1_j 0_{j-1} \cdots\rangle. \tag{1.1.43}$$

Simply transcribing equation (24), and evaluating the matrix elements of the harmonic oscillator, we see that the transition rate is

$$\Gamma = \frac{2\pi}{\hbar} \sum_j \frac{\alpha_j^2}{2m\omega_j} \delta(\omega_{eg} - \omega_j). \tag{1.1.44}$$

The continuous sum can also be written as an integral using the notion of *density of states*. The density of states $\rho(\omega) = \frac{dN}{d\omega}$ represents the number of states dN in an interval of energies $\hbar d\omega$ centered around energy $\hbar\omega$. It's integral represents the total number of states. The decay rate may then be written as

$$\Gamma = \frac{2\pi}{\hbar}\rho(\omega_0)\frac{\alpha^2(\omega_0)}{2m\omega_0}. \tag{1.1.45}$$

Single photon spontaneous emission

Here, we go through a fundamentally important calculation, the single photon spontaneous emission rate in vacuum. Say we have an atom in an excited state. As time passes, fluctuations of the electromagnetic field can cause the electron to relax to a lower energy level, and spontaneously emit a photon. We would like to calculate the rate at which this process occurs, or equivalently, how long the excited state will live before relaxing to a lower state. To do this calculation, we will use Fermi's Golden rule at first order, which states the following: if the interaction Hamiltonian H_{int} causes an initial state $|i\rangle$ to transition into a final state $|f\rangle$, then the rate of transition between these states, denoted $\Gamma_{i\to f}$, is given by

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}|\langle f|H_{\text{int}}|i\rangle|^2\delta(E_f - E_i). \tag{1.1.46}$$

For the case of spontaneous emission for an electron bound in vacuum, the Hamiltonian of interaction is given by $H_{\text{int}} = \mathbf{d}\cdot\mathbf{E}$, where $\mathbf{d} \equiv e\mathbf{r}$ is the dipole operator for the elctron, e is the electron charge, and $\mathbf{E}$ is the operator for the quantized electric field. We can express this quantized electric field operator as a sum over the modes of the electromagnetic environment

$$\mathbf{E} = i\sum_{\hat{e},\mathbf{k}}\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\epsilon_0 V}}\left(\hat{e}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}\hat{a}_{\mathbf{k}} - \hat{e}^*_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}\hat{a}^\dagger_{\mathbf{k}}\right), \tag{1.1.47}$$

where we have been extremely explicit to note that we have to sum over wavevectors $\mathbf{k}$ as well as both polarizations $\hat{e}$. Furthermore, we have the creation and annihilation operators which satisfy the commutation relation $[a_{\mathbf{k}}, a^\dagger_{\mathbf{k}'}] = \delta_{\mathbf{k}\mathbf{k}'}$, and are also normalized such that $\langle \mathbf{k\oe}|\mathbf{k}'\sigma'\rangle = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'}$. Here we are being painfully explicit in the notation regarding polarizations and wavevectors. In many cases, the notation will not be so explicit, and instead a non-vectorized mode label k will be used to denote both the wavevector and polarization simultaneously. We of course also have $a^\dagger_k|0\rangle = |k\rangle$, and $a_k|0\rangle = 0$.

To calculate the spontaneous emission rate, we will go through the following steps:

1. Parameterize the initial and final states of the system $|i\rangle$ and $|f\rangle$.
2. Calculate the matrix element $\langle f|H_{\text{int}}|i\rangle$ using these states and the interaction Hamiltonian.
3. Sum over all possible final states to get the total decay rate.

Setting up the calculation

To describe the state of the system, we need to denote the state of the atom, as well as the state of the electromagnetic field. In other words, a state is characterized by knowing the energy level of the atom, and knowing how many photons there are in each mode. For a single photon relaxation process, we have the initial state as $|i\rangle = |e, 0\rangle$, and $|f\rangle = |g, k\rangle$, where e and g are the excited and ground states of the atom, and k stands for the wavevector and polarization of the emitted photon.

Calculating the matrix element

We can then consider the matrix element $\langle f|H_{\text{int}}|i\rangle$, where $H_{\text{int}} = \mathbf{d} \cdot \mathbf{E}$. This gives us

$$\langle f|H_{\text{int}}|i\rangle = \langle g, k|\, \mathbf{d} \cdot \mathbf{E}\, |e, 0\rangle \tag{1.1.48}$$

$$= -i \sum_{k'} \sqrt{\frac{\hbar\omega_{k'}}{2\epsilon_0 V}}\, \langle g, k|\, \mathbf{d} \cdot \left(\hat{e}_{k'} e^{i\mathbf{k}'\cdot\mathbf{r}} \hat{a}_{k'} - \hat{e}^*_{k'} e^{-i\mathbf{k}'\cdot\mathbf{r}} \hat{a}^\dagger_{k'}\right) |e, 0\rangle \tag{1.1.49}$$

$$= i \sum_{k'} \sqrt{\frac{\hbar\omega_{k'}}{2\epsilon_0 V}}\, \langle g, k|\, \mathbf{d} \cdot \hat{e}^*_{k'} e^{-i\mathbf{k}'\cdot\mathbf{r}}\, |e, k'\rangle \tag{1.1.50}$$

$$= i \sum_{k'} \sqrt{\frac{\hbar\omega_{k'}}{2\epsilon_0 V}} \delta_{kk'}\, \langle g|\, \mathbf{d} \cdot \hat{e}^*_{k'} e^{-i\mathbf{k}'\cdot\mathbf{r}}\, |e\rangle \tag{1.1.51}$$

$$= i \sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}}\, \langle g|\, \mathbf{d} \cdot \hat{e}^*_k e^{-i\mathbf{k}\cdot\mathbf{r}}\, |e\rangle\,. \tag{1.1.52}$$

There are a few things to note. The annihilation operator term kills the zero photon state, and thus does not participate in the calculation. The creation operator $a^\dagger_{k'}$ creates a photon $|k'\rangle$ with the excite atomic state. Then the inner product $\langle k|k'\rangle$ results in a delta function, which collapses the sum into a single term which contains only the photonic state k, which is the assumed final state of the radiation. What we have at the end is then a normalization factor multiplied by a matrix element between the initial and final atomic states. We now make an approximation, which is that the wavelength of the emitted radiation is very large compared to the size of the atom. In other words, $\mathbf{k} \cdot \mathbf{r}$ is very small, so we can neglect higher order terms of the exponential $e^{-i\mathbf{k}\cdot\mathbf{r}}$, and say that this is 1. Doing this removed the k-dependence from the matrix element, which makes the rest of the calculation analytically tractable. This approximation has addition significance which we will discuss in detail later. Inserting the matrix element into Fermi's Golden rule, we now have

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} \left| i\sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}} \hat{e}^*_k \cdot \langle g|\, \mathbf{d}\, |e\rangle \right|^2 \delta(E_f - E_i). \tag{1.1.53}$$

As a brief note, the delta function at the end of this expression enforces energy conservation. In other words, the difference in total energies between the initial and final states of the system must be zero. If the excited and ground states of the atom have energy E_e and E_g respectively, and the emitted photon has energy $\hbar\omega_k$, then the delta function can be written as $\delta(E_e - E_g - \hbar\omega_k)$. In other words, the energy of the emitted photon must be equal to the atomic energy level difference $E_{eg} \equiv E_e - E_g$, which is expected for single photon spontaneous emission. It is often convenient to write the delta function in frequency variables instead by removing $\hbar$. Defining $\omega_{eg} \equiv E_{eg}/\hbar$ as the atomic transition frequency, we can write $\delta(E_{eg} - \hbar\omega_k) = \frac{1}{\hbar}\delta(\omega_{eg} - \omega_k)$.

Sum over all possible final states

Equation 1.1.53 gives the rate of transition from a given initial state $|i\rangle$ to a particular final state $|f\rangle$, which is the tensor product of an atomic ground state for the electron, and a photon of specific wavevector and polarization for the photon. If we don't care about the final state of the photon and just want the rate of transition into any photon, then we need to take this rate and sum over all possible final photon states. Summing over final photon states k is equivalent to summing over wavevectors $\mathbf{k}$ and both polarizations $\hat{\epsilon}$. The wavevector sum can be carried out as a continuum integral, so for three dimensions we have the general rule

$$\sum_k \to \sum_{\hat{\epsilon}} \sum_{\mathbf{k}} \to V \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \sum_{\hat{\epsilon}} \tag{1.1.54}$$

Using substitution we can now write an expression for the total rate of spontaneous emission Γ of the excited state $|e\rangle$ into the ground state $|g\rangle$ and any photonic state:

$$\Gamma = \sum_k \Gamma_{i\to f} = V \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \sum_{\hat{\epsilon}} \frac{2\pi}{\hbar^2} \left| i\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\epsilon_0 V}} \hat{\epsilon}^*_{\mathbf{k}} \cdot \langle g| \mathbf{d} |e\rangle \right|^2 \delta(\omega_{eg} - \omega_{\mathbf{k}}). \tag{1.1.55}$$

Before we go on to evaluate this expression, there are a few things we can note. First, the volume factor which comes from integrating over wavevectors will cancel the volume factor that comes from the electromagnetic mode normalization in the definition of $\mathbf{E}$. This is expected (and required), as the spontaneous emission rate should be independent of the imaginary large box of volume V in which we place the system. Second, the delta function over frequency should simplify the evaluation of the $\mathbf{k}$ integral, as the magnitude of the emitted wavevector, denoted $|\mathbf{k}|$, must satisfy the free-space dispersion $\omega_{\mathbf{k}} = c|\mathbf{k}|$. This means that the only remaining degrees of freedom of the emitted photon are its direction and polarization, which are a geometric issue rather than a fundamental one.

Polarization Sums

We now take a quick diversion to explain the easiest way to sum over photon polarizations $\hat{\epsilon}_{\mathbf{k}}$. The way this is done often seems like magic at first, but is actually very simple. The part of Equation 1.1.55 which involves the photon polarization is $\sum_{\hat{\epsilon}} |\hat{\epsilon}^*_{\mathbf{k}} \cdot \langle g|\mathbf{d}|e\rangle|^2$. Using the notation $\mathbf{d}^{ge} \equiv \langle g|\mathbf{d}|e\rangle$ for the matrix element, and using repeated index notation, we can write this as

$$\sum_{\hat{\epsilon}} |\hat{\epsilon}^*_{\mathbf{k}} \cdot \mathbf{d}^{ge}|^2 = \sum_{\hat{\epsilon}} \hat{\epsilon}^*_i d_i^{(ge)} \hat{\epsilon}_j d_j^{*(ge)}. \tag{1.1.56}$$

Note that the vector label $\mathbf{k}$ has been suppressed because there are already too many hats, subscripts, and superscripts. We now appeal to a simple but important fact about photon polarizations in free space. A photon propagating in vacuum with wavevector $\mathbf{k}$, has two possible basis polarizations which we will denote $\hat{\epsilon}^{(1)}$ and $\hat{\epsilon}^{(2)}$. Both of these polarizations are orthogonal to the direction of propagation $\hat{\mathbf{k}}$, and they are also orthogonal to each other. This means that the set of vectors $\left\{\hat{\epsilon}^{(1)}, \hat{\epsilon}^{(2)}, \hat{\mathbf{k}}\right\}$ forms an orthonormal basis for 3 dimensional space. By completeness, this means that

$$\hat{\epsilon}_i^{*(1)} \hat{\epsilon}_j^{(1)} + \hat{\epsilon}_i^{*(2)} \hat{\epsilon}_j^{(2)} + \hat{k}_i^* \hat{k}_j = \delta_{ij}. \tag{1.1.57}$$

We can now note that the first two terms of the LHS of this completeness relation are equivalent to the sum over two polarizations that we need to perform. Moving the third term over to the RHS and using polarization sum notation gives the relation

$$\sum_{\hat{\epsilon}} \hat{\epsilon}_i^* \hat{\epsilon}_j = \delta_{ij} - \hat{k}_i \hat{k}_j. \tag{1.1.58}$$

Conjugation has been removed from $\hat{k}_i^*$ since all wavevectors we will consider are real. Using this relation, we can complete the polarization sum as

$$\begin{aligned}
\sum_{\hat{\epsilon}} \hat{\epsilon}_i^* d_i^{(ge)} \hat{\epsilon}_j d_j^{*(ge)} &= d_i^{(ge)} d_j^{*(ge)} \sum_{\hat{\epsilon}} \hat{\epsilon}_i^* \hat{\epsilon}_j && (1.1.59)\\
&= d_i^{(ge)} d_j^{*(ge)} \left(\delta_{ij} - \hat{k}_i \hat{k}_j \right) && (1.1.60)\\
&= |\mathbf{d}^{(eg)}|^2 - (d_i^{(ge)} \hat{k}_i)(d_j^{*(ge)} \hat{k}_j) && (1.1.61)\\
&= |\mathbf{d}^{(eg)}|^2 (1 - \cos^2\theta) && (1.1.62)\\
&= |\mathbf{d}^{(eg)}|^2 \sin^2\theta && (1.1.63)
\end{aligned}$$

where θ is the angle between $\hat{k}$ and $\mathbf{d}$. This already tells us something important about the angular distribution of radiation that results from spontaneous emission: the strength of emission will depend on the angle between the dipole transition element $\mathbf{d}^{(ge)}$ and the outgoing wavevector $\mathbf{k}$, and will be zero if they are parallel, and maximal if they are orthogonal.

Final sum over wavevectors

Now that we have summed over polarizations, we just need to do a trivial delta function over final wavevectors, taking care to keep track of factors and variable transformations carefully. Using the polarization sum result, we can write Equation 1.1.55 as

$$\begin{aligned}
\Gamma &= \frac{2\pi |\mathbf{d}^{(ge)}|^2}{\hbar^2} \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \left(\frac{\hbar \omega_{\mathbf{k}}}{2\epsilon_0} \right) \sin^2\theta \delta(\omega_{eg} - \omega_{\mathbf{k}}) && (1.1.64)\\
&= \frac{2\pi |\mathbf{d}^{(ge)}|^2}{2\epsilon_0 \hbar} \frac{1}{(2\pi)^3} \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} \mathrm{d}\theta \sin\theta \sin^2\theta \int_0^{\infty} \mathrm{d}k \, k^2 \omega_{\mathbf{k}} \delta(\omega_{eg} - \omega_{\mathbf{k}}). && (1.1.65)
\end{aligned}$$

The first integral gives a trivial factor of 2π, and the second evaluates to $4/3$. The k-integral can be evaluated by considering the dispersion $\omega_{\mathbf{k}} = c|\mathbf{k}|$. We denote this transformation by $\omega = ck$, and $\mathrm{d}k = \mathrm{d}\omega/c$, which gives

$$\int_0^{\infty} \mathrm{d}k \, k^2 \omega_{\mathbf{k}} \delta(\omega_{eg} - \omega_{\mathbf{k}}) = \int_0^{\infty} \frac{\mathrm{d}\omega}{c} \left(\frac{\omega}{c} \right)^2 \omega \delta(\omega_{eg} - \omega) = \left(\frac{\omega_{eg}}{c} \right)^3. \tag{1.1.66}$$

It is equally valid to evaluate this integral by transforming the delta function into one over k. Putting all of this together gives the final result

$$\Gamma = \frac{\omega_{eg}^3 |\mathbf{d}^{(ge)}|^2}{3\pi \epsilon_0 \hbar c^3} = \frac{4\alpha \omega_{eg}^3 |\mathbf{r}^{(ge)}|^2}{3c^2}, \tag{1.1.67}$$

where α is the fine structure constant and $\mathbf{r}^{(ge)} \equiv \langle g|\mathbf{r}|e\rangle$ is the position matrix element (serving the same purpose as the dipole element but without the charge factor, which has been absorbed into the fine structure constant). The form of the rate in terms of the fine structure constant makes it very easy to see that this expression has the units of a rate.

Electron-photon scattering and why the sky is blue

This is an example of a problem which can be only described with second-order perturbation theory. We consider a photon with wavevector and polarization $|\mathbf{k}\epsilon\rangle$ incident on an atom/molecule which has some known eigenstates $\{|a\rangle\}$ and eigenenergies $\{\omega_a\}$. In this process, the incident photon is scattered, resulting in an outgoing photon with wavevector and polarization $|\mathbf{k}'\epsilon'\rangle$. Furthermore, we assume that the atom both begins and ends in the ground state $|g\rangle$, and that the interaction between the electron in the atom and the electromagnetic field is given by the dipole Hamiltonian $V_{\text{int}} = \mathbf{d} \cdot \mathbf{E}$, where $\mathbf{d} = e\mathbf{r}$ is the dipole operator, and $\mathbf{E}$ is the second-quantized electromagnetic field in free space.

The initial and final states of the system can be parameterized as $|i\rangle = |g, k\rangle$ and $|f\rangle = |g, k'\rangle$, where the non-vectorized symbol $k^{(')}$ is a label used to represent both the wavevector and the polarization. To start this calculation, we use Fermi's Golden rule at second order in perturbation theory which is shown in Eq. 1.1.33. The first thing to focus on are the matrix elements V_{fn} and V_{ni} in the numerator. To do so, we think about what possible intermediate states $|n\rangle$ can cause the transition from $|i\rangle$ to $|f\rangle$.

First, there will be some intermediate atomic state, which we will denote $|a\rangle$. Since the atom is assumed to begin and end in the ground state, the terms which will contribute contain pairs of dipole matrix elements which will cause the virtual transition sequence $|g\rangle \to |a\rangle \to |g\rangle$. For intermediate photon states, there are two possibilities. First, we remind ourselves that the electric field operator takes the form

$$\mathbf{E} = \sum_k \sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}} \left(\hat{\epsilon}_k e^{i\mathbf{k}\cdot\mathbf{r}} a_k + \hat{\epsilon}_k^* e^{-i\mathbf{k}\cdot\mathbf{r}} a_k^\dagger \right), \tag{1.1.68}$$

where the sum over k is implied to include both the wavevector and polarization degrees of freedom. This operator can only create or destroy one photon at a time, but we get to use it twice to connect the initial state to the final state via an intermediate state. Thus, there are two possibilities for the intermediate states

1. An annihilation operator takes the initial state $|k\rangle$ down to the photonic ground state $|0\rangle$, and then a creation operator creates the final state $|k'\rangle$. In this case the intermediate states take the form $|n\rangle = |a, 0\rangle$.

2. A creation operator takes the initial state $|k\rangle$ to a two-photon state $|kk'\rangle$, and then an annihilation operator kills the initial state $|k\rangle$. In this case, the intermediate states take the form $|n\rangle = |a, kk'\rangle$

As we will see, these contributions are quite symmetric, and the distinction between the two amounts to distinguishing the "order" in which the photons are created and destroyed. The word "order" has been placed in quotes because quantum mechanically, there is no proper sense in which one of these processes happens "before" or "after" the other. Nonetheless, people may still use this type of terminology to describe the ordering of operators.

With this discussion of intermediate states laid out, we are now ready to calculate the interaction matrix elements. We have for the first type of intermediate state

$$\begin{aligned}
V_{ni}^{(1)} &= \langle a,0|V_{\mathrm{int}}|g,k\rangle && (1.1.69)\\
&= \sum_q \sqrt{\frac{\hbar\omega_q}{2\epsilon_0 V}}\,\langle a,0|\,\mathbf{d}\cdot\left(\hat{e}_q e^{i\mathbf{q}\cdot\mathbf{r}}a_q + \hat{e}_q^* e^{-i\mathbf{q}\cdot\mathbf{r}}a_q^\dagger\right)|g,k\rangle && (1.1.70)\\
&= \sum_q \sqrt{\frac{\hbar\omega_q}{2\epsilon_0 V}}\,\langle a,q|\,\mathbf{d}\cdot\hat{e}_q e^{i\mathbf{q}\cdot r}\,|g,k\rangle && (1.1.71)\\
&= \sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}}\mathbf{d}^{ag}\cdot\hat{e}_k. && (1.1.72)
\end{aligned}$$

And for the second type of intermediate state

$$\begin{aligned}
V_{ni}^{(2)} &= \langle a,kk'|V_{\mathrm{int}}|g,k\rangle && (1.1.73)\\
&= \sum_q \sqrt{\frac{\hbar\omega_q}{2\epsilon_0 V}}\,\langle a,kk'|\,\mathbf{d}\cdot\left(\hat{e}_q e^{i\mathbf{q}\cdot\mathbf{r}}a_q + \hat{e}_q^* e^{-i\mathbf{q}\cdot\mathbf{r}}a_q^\dagger\right)|g,k\rangle && (1.1.74)\\
&= \sum_q \sqrt{\frac{\hbar\omega_q}{2\epsilon_0 V}}\,\langle a,kk'|\,\mathbf{d}\cdot\hat{e}_q^* e^{-i\mathbf{q}\cdot r}\,|g,kq\rangle && (1.1.75)\\
&= \sqrt{\frac{\hbar\omega_{k'}}{2\epsilon_0 V}}\mathbf{d}^{ag}\cdot\hat{e}_{k'}^*. && (1.1.76)
\end{aligned}$$

We have used the dipole matrix element notation $\mathbf{d}^{(ag)} = \langle a|\mathbf{d}|g\rangle$, and also made the dipole approximation that $e^{\pm i\mathbf{k}\cdot\mathbf{r}} = 1 \pm i\mathbf{k}\cdot\mathbf{r} + \cdots \approx 1$, since we assume that the wavelength of the incident radiation is substantially larger than the size of the wavefunction of the atom (and hence the electric field can be considered constant over the span of the atom). The other two matrix elements are very similar, and we have

$$\begin{aligned}
V_{fn}^{(1)} &= \langle g,k'|V_{\mathrm{int}}|a,0\rangle && (1.1.77)\\
&= \sqrt{\frac{\hbar\omega_{k'}}{2\epsilon_0 V}}\mathbf{d}^{ga}\cdot\hat{e}_{k'}^*. && (1.1.78)
\end{aligned}$$

and

$$\begin{aligned}
V_{fn}^{(2)} &= \langle g,k'|V_{\mathrm{int}}|a,kk'\rangle && (1.1.79)\\
&= \sqrt{\frac{\hbar\omega_k}{2\epsilon_0 V}}\mathbf{d}^{ga}\cdot\hat{e}_k. && (1.1.80)
\end{aligned}$$

Then, referencing Fermi's golden rule, we have

$$\begin{aligned}
\sum_n \frac{V_{fn}V_{ni}}{\omega_{in}+i\eta} &= \sum_a \left(\frac{V_{fn}^{(1)}V_{ni}^{(1)}}{\omega_{ga}+\omega_k+i\eta} + \frac{V_{fn}^{(2)}V_{ni}^{(2)}}{\omega_{ga}-\omega_{k'}+i\eta}\right) && (1.1.81)\\
&= \frac{\hbar}{2\epsilon_0 V}\sqrt{\omega_k\omega_{k'}}\sum_a\left(\frac{\mathbf{d}^{ga}\cdot\hat{e}_{k'}^*\mathbf{d}^{ag}\cdot\hat{e}_k}{\omega_{ga}+\omega_k+i\eta} + \frac{\mathbf{d}^{ga}\cdot\hat{e}_k\mathbf{d}^{ag}\cdot\hat{e}_{k'}^*}{\omega_{ga}-\omega_{k'}+i\eta}\right), && (1.1.82)
\end{aligned}$$

where now $\sum_a$ is a sum over all of the electronic states of the atom/molecule. Since the exact result of this sum is going to be entirely dependent on the electronic structure of the atom/molecule we are scattering off of, there is not any generally nice way to compute this. However, it would be nice if we were still able to access the key physics of this phenomenon, even if the exact details of the molecule are left as an unknown. We can profit by defining a new object here, called the polarizability tensor:

$$\alpha_{ij}(\omega) \equiv \frac{1}{\hbar}\sum_a \left(\frac{d_i^{ga} d_j^{ag}}{\omega_{ga} + \omega + i\eta} + \frac{d_j^{ga} d_i^{ag}}{\omega_{ga} - \omega + i\eta} \right). \tag{1.1.83}$$

Note that in doing this, we have made the assumption that $\omega_k = \omega_{k'}$, or in other words that the collisions we consider are elastic. This was our intention from the beginning, so there is no issue with making that assumption here. We can now use this polarizability to write

$$\sum_n \frac{V_{fn} V_{ni}}{\omega_{in} + i\eta} = \frac{\hbar^2 \omega_k}{2\epsilon_0 V} \hat{\epsilon}_i \hat{\epsilon}_j'^* \alpha_{ij}(\omega_k), \tag{1.1.84}$$

where for index sanity we are using the notation $\hat{\epsilon}_{k^{(\prime)}} = \hat{\epsilon}^{(\prime)}$. Now we finally have something that we shouldn't be afraid to take the squared magnitude of, and then sum over all possible final states. Doing, this we have

$$\begin{aligned}
\Gamma &= \frac{2\pi}{\hbar^4} \sum_{k'} \left| \frac{\hbar^2 \omega_k}{2\epsilon_0 V} \hat{\epsilon}_i \hat{\epsilon}_j'^* \alpha_{ij}(\omega_k) \right|^2 \delta(\omega_k - \omega_{k'}) && (1.1.85)\\
&= \frac{2\pi}{(2\epsilon_0 V)^2} \alpha_{ij}(\omega_k) \alpha_{lm}^*(\omega_k) \hat{\epsilon}_i \hat{\epsilon}_l^* V \int \frac{d^3\mathbf{k}'}{(2\pi)^3} \omega_{k'}^2 \sum_{\hat{\epsilon}'} \hat{\epsilon}_j'^* \hat{\epsilon}_m' \delta(\omega_k - \omega_{k'}) && (1.1.86)\\
&= \frac{2\pi}{(2\epsilon_0 V)^2} \omega_k^2 \alpha_{ij}(\omega_k) \alpha_{lm}^*(\omega_k) \hat{\epsilon}_i \hat{\epsilon}_l^* V \int \frac{d^3\mathbf{k}'}{(2\pi)^3} \delta(\omega_k - \omega_{k'}) (\delta_{jm} - \hat{k}_j' \hat{k}_m') && (1.1.87)
\end{aligned}$$

This is about as far as we can do without making some assumptions about the nature of the polarizability tensor α_{ij}. To proceed, we make the following assumptions:

1. The polarizability tensor is isotropic and homogeneous, meaning that it has only diagonal components which are all identical. In other words, the molecule is "spherical" in its behavior when fields are applied, in the sense that an incident field from a given direction causes a polarization response in that same direction. Mathematically, this means that the tensor is a multiple of the identity, so can be written $\alpha_{ij}(\omega) = \alpha(\omega)\delta_{ij}$.

2. The polarizability tensor can be taken as a static polarizability. This means that we take $\omega \to 0$. This comes from assuming that the energy of the incident photon is small compared to the energy differences between levels, or in other words that $\omega \ll \omega_{ga}$ in Eq. 1.1.83. Thus we write $\alpha(\omega) = \alpha_0$.

With these simplifications, the geometric factor becomes $(1 - \cos^2\theta)$, and any additional geometric considerations coming from the polarization of incoming radiation are eliminated (since the molecule "looks" the same to radiation coming in from *any* angle). With those concerns out of the way, we can write

$$\Gamma = \frac{\omega_k^2 \alpha_0^2}{(2\pi)^2 (2\epsilon_0)^2 V} \int d\Omega \, \sin^2\theta \int_0^\infty dk' \, k'^2 \delta(\omega_k - \omega_{k'}) \tag{1.1.88}$$

Performing the delta function integral and converting to an angular rate, we have

$$\frac{d\Gamma}{d\Omega} = \frac{\alpha_0^2 \omega_k^4 \sin^2\theta}{16\pi^2 \epsilon_0^2 c^3 V}. \tag{1.1.89}$$

Converting this to an angular cross section (rate per angle per unit flux), we have

$$\frac{d\sigma}{d\Omega} = \frac{V}{c}\frac{d\Gamma}{d\Omega} = \frac{\alpha_0^2 \omega_k^4 \sin^2\theta}{16\pi^2 \epsilon_0^2 c^4}. \tag{1.1.90}$$

Finally, integrating this over all solid angles gives the total scattering cross section

$$\sigma = \int d\Omega \, \frac{d\sigma}{d\Omega} = \frac{\alpha_0^2 \omega^4}{6\pi c^4 \epsilon_0^2}. \tag{1.1.91}$$

The key feature of these cross section expressions is that they have the ω^4 scaling which is characteristic of Rayleigh scattering. Due to this steep frequency dependence, higher frequencies are scattered *much* more than lower frequencies. If we compare how red (700 nm) and blue (400 nm) light scatter, we have $\omega_{\text{blue}}/\omega_{\text{red}} = 700/400 = 1.75$. So then $\sigma_{\text{blue}}/\sigma_{\text{red}} = (1.75)^4 \approx 9$. So blue light is scattered by particles in the atmosphere nearly a factor of 10 more than red light.

2 | OPTICAL RESPONSE OF MATERIALS

Polarization of a quantum system by an external electromagnetic field. Linear response theory. Polarizability, susceptibility, and permittivity. Maxwell's equations in a polarizable medium. Harmonic oscillator and Lorentz oscillator model. Electron gas and Drude model. Plasmons and polaritons.

2.1 OPTICAL RESPONSE OF MATERIALS

After a brief overview of quantum mechanical unitary evolution and perturbation theory, we will now introduce some concept which are important as we begin to think more and more about physical problems. At their core, these notes are about the quantum mechanical interactions of electromagnetism and matter. To this end, we can introduce some of the basic principles which govern this interaction. Doing this will provide an important foundation, and also important context for guiding the questions we will ask later on.

Consider the following experiment: suppose we have a chunk of material and we send a weak optical probe at it (i.e., we shine a laser at it). What happens to the laser after interacting with the material? In particular, how much of it is absorbed? How much of it is scattered? Given the ubiquitous nature of this problem, it is fortunate that we can gain insight into this problem using the tools of the previous chapter on perturbation theory. In particular, to model this experiment, let us ask two questions:

1. How do the charges in a material respond to a weak time-dependent (classical) electric field?
2. How do those charges act back on the electric field to produce the scattered light?

We begin by addressing question 1. Suppose we have a single quantum system, an atom for concreteness, and we subject it to a time-dependent electric field $\mathbf{E}(t)$. Then suppose that this field couples to the atom through the atom's dipole moment $\mathbf{d}$ via the Hamiltonian

$$V = -\mathbf{d} \cdot \mathbf{E}(t). \tag{2.1.1}$$

To understand how light gets scattered, we should ask: what dipole moment is induced in the atom by the field? The reason is that scattering is simply dipole radiation from an induced dipole. The light polarizes the atom, the atom radiates, and that radiated field interferes with the incident field to produce the total observed field. Note that by "induced dipole moment", we mean specifically the change in the expectation value of the dipole moment operator relative to its expectation value in the absence of a driving field. In terms of operators, we want to find the change in expectation value of the dipole operator, which we define as

$$\delta \langle \mathbf{d}(t) \rangle = \langle \psi(t) | \mathbf{d} | \psi(t) \rangle - \langle \psi_0(t) | \mathbf{d} | \psi_0(t) \rangle , \tag{2.1.2}$$

where $|\psi(t)\rangle$ represents the time-dependent wavefunction in the presence of the driving field, and $|\psi_0(t)\rangle$ represents the time-dependent wavefunction in the absence of the driving field. This can be re-expressed in the interaction picture as

$$\delta\left\langle \mathbf{d}(t)\right\rangle = \langle\psi_I(t)|\mathbf{d}_I(t)|\psi_I(t)\rangle - \langle\psi_0|\mathbf{d}_I(t)|\psi_0\rangle\,. \tag{2.1.3}$$

In the situation when the driving field is weak, which is an extremely common scenario, we can calculate the wavefunction in the interaction picture using first-order time-dependent perturbation theory. In particular

$$|\psi_I(t)\rangle = |\psi_0\rangle - \frac{i}{\hbar}\int\limits_{-\infty}^{t} dt'\; V_I(t')|\psi_0\rangle = |\psi_0\rangle + \frac{i}{\hbar}\int\limits_{-\infty}^{t} dt'\; \mathbf{d}_I(t')\cdot\mathbf{E}(t')|\psi_0\rangle. \tag{2.1.4}$$

Plugging this into the expectation value of Equation 2.1.3, we see immediately that the unperturbed expectation value cancels out, and to first-order the change in the dipole moment is

$$\begin{aligned}\delta\left\langle \mathbf{d}(t)\right\rangle &= \frac{i}{\hbar}\int\limits_{-\infty}^{t} dt'\langle\psi_0|[\mathbf{d}_I(t),\mathbf{d}_I(t')\cdot\mathbf{E}(t')]|\psi_0\rangle\\ &= \frac{i}{\hbar}\int\limits_{-\infty}^{\infty} dt'\theta(t-t')\langle\psi_0|[\mathbf{d}_I(t),\mathbf{d}_I(t')]|\psi_0\rangle\cdot\mathbf{E}(t').\end{aligned} \tag{2.1.5}$$

Unsurprisingly, the expectation value of the dipole moment is linear in the perturbing field – this is to be expected at first-order in perturbation theory. This expression can be written as

$$\delta\langle\mathbf{d}(t)\rangle = \int\limits_{-\infty}^{\infty} dt'\;\boldsymbol{\alpha}(t,t')\mathbf{E}(t'), \tag{2.1.6}$$

where the concatenation of bolded symbols denotes a matrix-vector product. The matrix

$$\boldsymbol{\alpha}(t,t') = \frac{i}{\hbar}\theta(t-t')\langle\psi_0|[\mathbf{d}_I(t),\mathbf{d}_I(t')]|\psi_0\rangle \tag{2.1.7}$$

is referred to as the atomic polarizability, and is also called a linear response function, because it encodes how the dipole moment linearly responds to the fields. [1] The first thing to notice is that the polarizability is *causal*, as it should be: there are no contributions to the dipole moment at time t from fields at later times. Notice that the polarizability is *non-instantaneous*, the dipole moment at some time t in fact depends on all previous times. Actually, in an atomic system which the unperturbed system is time-independent, or time-translationally invariant, it turns out that $\alpha(t,t') = \alpha(t-t')$. In other words, the value of the dipole moment at time is only set by how long ago the field

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[1] As a point of terminology, this expression is an instance of a general formula called the *Kubo formula*, and is extremely general for connecting an applied field to a quantum observable through linear response. The Kubo formula answers: given a perturbation $V = BF(t)$, where B is an operator and $F(t)$ is a time-dependent perturbation (force), what is the change in observable A? The answer is $\delta\langle A(t)\rangle = -\frac{i}{\hbar}\int\limits_{-\infty}^{\infty} dt'\;\theta(t-t')[A(t),B(t')]F(t')$.

was applied, not the precise time it was applied. Let us now evaluate the polarizability in terms of the eigenfunctions and eigenvalues of the unperturbed Hamiltonian.

To do so, we will (1) use a complete set of states to simplify the commutator, and (2) use the contour integral representation of the heaviside function. Doing (1) yields

$$\alpha(t-t') = \frac{i}{\hbar}\theta(t-t')\sum_n \left(\langle\psi_0|\mathbf{d}_I(t)|\psi_n\rangle\langle\psi_n|\mathbf{d}_I(t')|\psi_0\rangle - \langle\psi_0|\mathbf{d}_I(t')|\psi_n\rangle\langle\psi_n|\mathbf{d}_I(t)|\psi_0\rangle\right). \tag{2.1.8}$$

Assuming that $|\psi_0\rangle$ is an eigenstate of the unperturbed Hamiltonian, we have that the previous expression reduces to

$$\frac{i}{\hbar}\theta(t-t')\sum_n \mathbf{d}_{0n}\mathbf{d}_{n0}(e^{i\omega_{0n}t - i\omega_{0n}t'} - e^{i\omega_{0n}t' - i\omega_{0n}t}). \tag{2.1.9}$$

Now write the heaviside step function in its contour integral representation. That yields:

$$-\frac{1}{\hbar}\int \frac{d\omega}{2\pi}\frac{e^{i\omega(t-t')}}{\omega+i\eta}\sum_n \mathbf{d}_{0n}\mathbf{d}_{n0}(e^{i\omega_{0n}t - i\omega_{0n}t'} - e^{i\omega_{0n}t' - i\omega_{0n}t}). \tag{2.1.10}$$

This may be cleaned up a little bit and expressed as

$$-\frac{1}{\hbar}\int \frac{d\omega}{2\pi}\sum_n \mathbf{d}_{0n}\mathbf{d}_{n0}\left(\frac{e^{i(\omega+\omega_{0n})(t-t')}}{\omega+i\eta} - \frac{e^{i(\omega-\omega_{0n})(t-t')}}{\omega+i\eta}\right). \tag{2.1.11}$$

In order to make further progress, we can write the time-dependent E-field $\mathbf{E}(t)$ in its Fourier representation $\mathbf{E}(\omega)$ as

$$\mathbf{E}(t) = \int \frac{d\omega}{2\pi}\,\mathbf{E}(\omega)e^{-i\omega t}. \tag{2.1.12}$$

Taking the polarizability, and plugging it back into Equation (7), representing the electric field in its Fourier representation from Eq. 2.1.12, we have that

$$\langle\mathbf{d}(t)\rangle = \int \frac{d\omega}{2\pi}\left[-\frac{1}{\hbar}\sum_n\left(\frac{\mathbf{d}_{0n}\mathbf{d}_{n0}}{\omega-\omega_{n0}+i\eta} - \frac{\mathbf{d}_{0n}\mathbf{d}_{n0}}{\omega+\omega_{n0}+i\eta}\right)\right]\mathbf{E}(\omega)e^{-i\omega t}. \tag{2.1.13}$$

Defining $\langle\mathbf{d}(\omega)\rangle$ to be the Fourier transform of $\langle\mathbf{d}(t)\rangle$, and defining

$$\boldsymbol{\alpha}(\omega) \equiv -\frac{1}{\hbar}\sum_n\left(\frac{\mathbf{d}_{0n}\mathbf{d}_{n0}}{\omega-\omega_{n0}+i\eta} - \frac{\mathbf{d}_{0n}\mathbf{d}_{n0}}{\omega+\omega_{n0}+i\eta}\right), \tag{2.1.14}$$

we have the relation

$$\langle\mathbf{d}(\omega)\rangle = \boldsymbol{\alpha}(\omega)\mathbf{E}(\omega). \tag{2.1.15}$$

We have thus found a general formula that tells us how a quantum system polarizes in the presence of a weak probing electric field. Notably, we see that the polarization response can be the strongest when the frequency of the applied field is near resonance with one of the electronic energy differences ω_{n0}. This is a first critical step in understanding how the microscopic quantum properties of atoms and molecules give rise to macroscopic optical properties. We should now connect this to optics, by showing how these polarizabilities (and the related permittivities) appear in Maxwell's equations for the electromagnetic fields.

2.1.1 Maxwell's equations in the presence of of matter

In the above, we have considered what happens when light interacts quantum mechanically with a single atom. However, materials are commonly comprised of many atoms. With the microscopic basis of optical response established, we will now move on to understand what happens when many particles are together. Consider a system of very many atoms whose *optical response* we have just described through Eq. 1.1.83. Suppose we have N atoms uniformly distributed in a volume V, so that the atoms have a density n. Now let us send a weak probing field, and ask about the polarization of the atoms. Rather then asking about the dipole moment, we will instead ask about the *polarization* $\mathbf{P}$, which is the dipole moment per unit volume, which is simply the dipole moment times the density n. In other words

$$\mathbf{P} = n\mathbf{d}. \tag{2.1.16}$$

We have dropped the explicit expectation value notation, and this is understood to be the case from now on. We know that in the presence of an applied field, these atoms will experience a polarization which is proportional to the electric field. But what electric field? Naively, one might suspect that the induced polarization is proportional to the field of the laser pulse sent at the material, commonly referred to as the *applied field*. However, it turns out to be slightly more complicated. To see why, consider what happens when you have many atoms. Any one atom feels not only the field of the laser pulse, but also the fields associated with the dipoles induced by the laser pulse in nearby atoms. This makes sense descriptively, but we are left with a conundrum: how do we find the dipole moment if we do not know the right field, and how do we find the field, if we don't know the right dipole moment? The answer is through the Maxwell equations, which place constraints on the interactions between charges, currents, and fields. Consider the Maxwell equations

$$\nabla \cdot \mathbf{E}(\mathbf{r},t) = \frac{\rho(\mathbf{r},t)}{\epsilon_0} \tag{2.1.17}$$

$$\nabla \cdot \mathbf{B}(\mathbf{r},t) = 0 \tag{2.1.18}$$

$$\nabla \times \mathbf{E}(\mathbf{r},t) = -\partial_t \mathbf{B}(\mathbf{r},t) \tag{2.1.19}$$

$$\nabla \times \mathbf{B}(\mathbf{r},t) = \mu_0 \mathbf{J}(\mathbf{r},t) + \frac{1}{c^2}\partial_t \mathbf{E}(\mathbf{r},t), \tag{2.1.20}$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields, and ρ and $\mathbf{J}$ are the charge and current densities. Writing the equations in frequency domain is much more convenient for analysis, as we'll soon appreciate. In frequency domain, the equations are

$$\nabla \cdot \mathbf{E}(\mathbf{r},\omega) = \frac{\rho(\mathbf{r},\omega)}{\epsilon_0} \tag{2.1.21}$$

$$\nabla \cdot \mathbf{B}(\mathbf{r},\omega) = 0 \tag{2.1.22}$$

$$\nabla \times \mathbf{E}(\mathbf{r},\omega) = i\omega \mathbf{B}(\mathbf{r},\omega) \tag{2.1.23}$$

$$\nabla \times \mathbf{B}(\mathbf{r},\omega) = \mu_0 \mathbf{J}(\mathbf{r},\omega) - \frac{i\omega}{c^2}\mathbf{E}(\mathbf{r},\omega). \tag{2.1.24}$$

Let us assume that there are no *free* charges and currents, only *bound* ones, associated with polarization induced by the driving field. Then, as you may remember from electromagnetism, the bound charge is related to the polarization by $\rho = -\nabla \cdot \mathbf{P}$, while the bound current is related to the polarization by $\mathbf{J} = -i\omega\mathbf{P}$ in frequency domain. In that case, we may then write the first Maxwell equation as

$$\nabla \cdot (\epsilon_0 \mathbf{E} + \mathbf{P}) = 0. \tag{2.1.25}$$

But in the presence of the matter, we know that $\mathbf{P}(\omega) = n\alpha(\omega)\mathbf{E}(\omega) \equiv \epsilon_0 \chi(\omega)\mathbf{E}(\omega)$, where χ is called the *electric susceptibility*. Another definition to know is that we define $\epsilon = (1+\chi)$, where ϵ is called the *relative permittivity*. Finally, the *index of refraction* is defined to be $\sqrt{\epsilon}$. Don't be alarmed, these are all just terms for the same thing, but they all get used quite interchangeably. In terms of the permittivity, we may write the first Maxwell equation as

$$\nabla \cdot \epsilon_0 \epsilon(\omega)\mathbf{E}(\mathbf{r},\omega) = 0. \tag{2.1.26}$$

Similarly, for the fourth Maxwell equation, we may write

$$\nabla \times \mathbf{B}(\mathbf{r},\omega) = -\frac{i\omega\epsilon(\omega)}{c^2}\mathbf{E}(\mathbf{r},\omega). \tag{2.1.27}$$

Thus far, we have made the simple assumption that the density, and thus the permittivity, is uniform in space. There's no fundamental need to make that assumption, and in general, it is a function of position and frequency so that $\epsilon = \epsilon(\mathbf{r},\omega)$.

The key observation to make is that we solved the problem of chicken and egg: we originally didn't know the dipole moment or the field, but we can in fact solve for both in Maxwell's equations, because the polarization was ultimately self-consistently determined by the fields. We now move to discuss the physics of the dielectric function, using perhaps one of the most famous examples, the *Lorentz oscillator*.

2.1.2 Lorentz oscillator

The Lorentz oscillator permittivity can be derived by considering the polarizability of a three-dimensional harmonic oscillator

$$H = \sum_{i=1}^{3} \hbar\omega_i a_i^\dagger a_i. \tag{2.1.28}$$

Remembering that the coordinate operator for an oscillator is given by $x_i = \sqrt{\frac{\hbar}{2m\omega_i}}(a_i + a_i^\dagger)$, an immediate evaluation of the polarizability yields that it is diagonal, and that the diagonal components are given by

$$\alpha_{ii}(\omega) = \frac{e^2}{m}\frac{1}{\omega_i^2 - \omega^2 - 2i\omega\eta}. \tag{2.1.29}$$

For a uniform density n of such oscillators, the permittivity is simply

$$\epsilon_{ii}(\omega) = 1 + \frac{ne^2}{m\epsilon_0}\frac{1}{\omega_i^2 - \omega^2 - 2i\omega\eta}. \tag{2.1.30}$$

Let us discuss the various regimes of this equation to give you a sense of the different characteristic behaviors of the dielectric function.

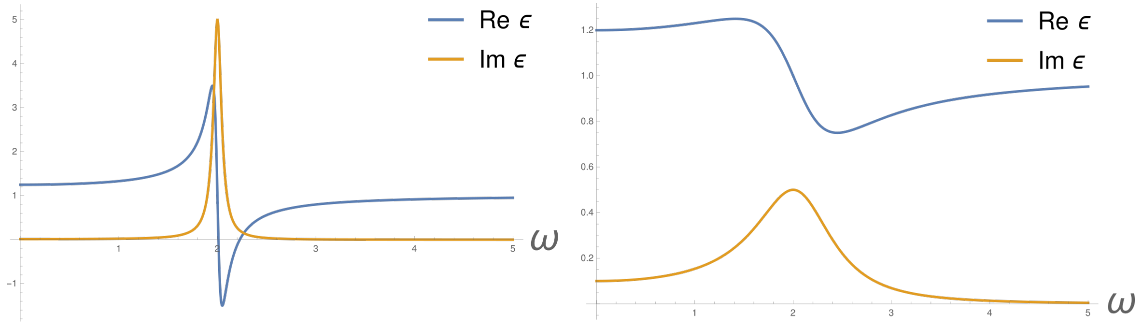

Figure 2.1: Permittivity of a Lorentzian with $\omega_i = 2$ for small η (left) and large η (right). The plasma frequency $\omega_p = \sqrt{ne^2/m\epsilon_0} = 1$.

1. Suppose $\omega \approx 0$. Then the permittivity is simply $1 + \frac{ne^2}{m\epsilon_0\omega_i^2}$ and is roughly constant.
2. Suppose $\omega \gg \omega_i$. Then the permittivity is approximately $1 - \frac{ne^2}{2m\epsilon_0\omega^2}$. For very large frequency, the dielectric constant is extremely close to 1. This result holds generally for all dielectric functions. Beyond the highest resonance, materials are basically incapable of responding to light.
3. Suppose $\omega \approx \omega_i$. Then the real part changes sign as we cross ω_i, and its peak absolute value is limited only by η. Similarly, the imaginary part of the permittivity is sharply peaked, with a height proportional to $1/\eta$ and a width proportional to η. Strictly, η was infinitesimal, but it turns out that if these levels have any kind of decay (including spontaneous emission decay), η can be identified as half of that decay rate.
4. You can also see from Figure 1 that the real part of the permittivity, away from resonance, is roughly constant, and we call these *non-dispersive regions*.

Aside: the imaginary part of the permittivity

You might wonder what it means for the permittivity to have an imaginary part, as when you first learned about dielectric constants, and indices of refraction, they were always real. The short answer is that the imaginary part represents transfer of energy (dissipation), in which the fields do work on the dipoles, and transfer their energy to the dipoles. We can show this quite directly. Physically, this dissipation means that when we send in light, some amount of it gets absorbed.

The work per unit time done by an electric field on a dipole of some frequency is given by

$$P = \frac{\omega}{2}\mathrm{Im}\,\left[\mathbf{d}(\omega)\cdot\mathbf{E}^*(\omega)\right]. \tag{2.1.31}$$

Plugging in the relation between dipole and field, one immediately finds that

$$P = \frac{\omega}{2}\mathbf{E}^*(\omega)\cdot\mathrm{Im}\,\boldsymbol{\alpha}(\omega)\cdot\mathbf{E}(\omega). \tag{2.1.32}$$

One sees immediately that the dissipation is related to the imaginary part of the polarizability, which is, by the definitions above, proportional to the imaginary part of the permittivity.

The imaginary part of the polarizability can be immediately determined from Equation (14) to be

$$\mathrm{Im}\,\alpha = \frac{\pi}{\hbar}\sum_n \mathbf{d}_{0n}\mathbf{d}_{n0}\left(\delta(\omega-\omega_{n0})-\delta(\omega+\omega_{n0})\right), \tag{2.1.33}$$

and the corresponding rate of energy dissipation is given by

$$P = \frac{\pi\omega}{2\hbar}\sum_n |\mathbf{d}_{n0}\cdot\mathbf{E}|^2\left(\delta(\omega-\omega_{n0})-\delta(\omega+\omega_{n0})\right). \tag{2.1.34}$$

Notice two things. (1) Power is dissipated ($P > 0$) when $\omega = \omega_{n0}$, i.e., when the atom *absorbs* light to go from 0 to n. Power is generated ($P > 0$), when $\omega = -\omega_{n0}$, i.e., when the atom *stimulatedly emits* light to go from n to 0. Therefore, the physics of the imaginary part of the permittivity simply corresponds to emission and absorption. This further strengthens our understanding of how electronic energy levels and transitions in atoms govern properties of light-matter interaction which are observable on a macroscopic scale. (2) The rate of power dissipation matches exactly that predicted from Fermi's Golden Rule. Try and verify that.

2.1.3 Polaritons

To conclude this chapter, we now want to ask: given a permittivity $\epsilon(\mathbf{r},\omega)$, which we have either measured or calculated from an underlying microscopic model, what electromagnetic waves can be sustained by the medium in the absence of free charges and free currents. This is a key first step in understanding problems of quantum optics in material media. To answer this question, we need to solve Maxwell's equations for electromagnetic waves. To get Maxwell's equations into a useful form for analysis, we take the curl of Faraday's law, and plug in the Ampere law. That leads to

$$\nabla\times\nabla\times\mathbf{E}(\mathbf{r},\omega) = \epsilon(\mathbf{r},\omega)\frac{\omega^2}{c^2}\mathbf{E}(\mathbf{r},\omega). \tag{2.1.35}$$

We will call this the *wave equation*. Solving this equation, making sure that the constraint $\nabla\cdot\epsilon(\mathbf{r},\omega)\mathbf{E}(\mathbf{r},\omega) = 0$, tells us what electric fields are sustained in a material medium. If we need the magnetic field, we can find it by taking the curl of the electric field, as per Faraday's law.

Let us consider the simplest case of no material whatsoever. Therefore, the polarizability and susceptibility are zero, while the permittivity is 1. It is simple to see that a plane-wave solves these equations.

$$\mathbf{E}(\mathbf{r},\omega) = \epsilon_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.1.36}$$

where $\epsilon_{\mathbf{k}}$ is the polarization vector. The Gauss law constraint tells us that the polarization is transverse to the wavevector. In particular:

$$\mathbf{k}\cdot\epsilon_{\mathbf{k}} = 0. \tag{2.1.37}$$

Plugging this plane wave back into the wave equation, recalling that $\mathbf{k}\times(\mathbf{k}\times\mathbf{A}) = \mathbf{k}(\mathbf{k}\cdot\mathbf{A}) - k^2\mathbf{A}$, we see that the condition needed for the plane wave to be a solution of Maxwell's equations is

$$\omega = ck, \tag{2.1.38}$$

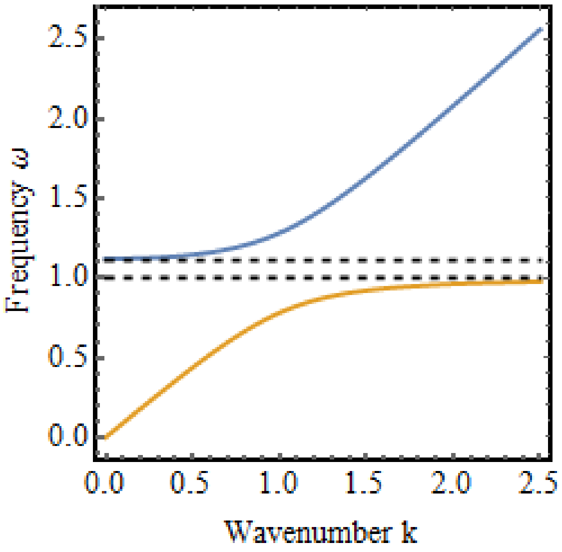

Figure 2.2: Dispersion of polariton modes in a Lorentz oscillator. The plasma frequency $\omega_p = \sqrt{ne^2/m\epsilon_0} = 0.5$, while the transition frequency ω_0 is 1.

which is the famous *dispersion relation* for light in vacuum. Generalizing these considerations to light in a uniform medium of permittivity $\epsilon(\omega)$, we see that the dispersion relation then satisfies the implicit equation

$$\omega = \frac{ck}{\sqrt{\epsilon(\omega)}}. \tag{2.1.39}$$

Let us consider the case of light propagating in a Lorentz oscillator medium. The dispersion relation then satisfies (ignoring dissipation)

$$\left(\omega^2 + \frac{ne^2}{m\epsilon_0}\frac{\omega^2}{\omega_0^2 - \omega^2}\right) = c^2k^2. \tag{2.1.40}$$

We can immediately determine $k(\omega)$ from this equation, though it is more conventional to consider $\omega(k)$. Labeling $\omega_p^2 = \frac{ne^2}{m\epsilon_0}$ for convenience, and re-arranging the equation to have ω only in the numerator gives

$$\omega^2\omega_0^2 - \omega^4 + \omega_p^2\omega^2 = c^2k^2\omega_0^2 - c^2k^2\omega^2 \implies \omega^4 - \omega^2(\omega_p^2 + c^2k^2 + \omega_0^2) + c^2k^2\omega_0^2 = 0. \tag{2.1.41}$$

Therefore

$$\omega^2(k) = \frac{1}{2}\left((\omega_p^2 + c^2k^2 + \omega_0^2) \pm \sqrt{(\omega_p^2 + c^2k^2 + \omega_0^2)^2 - 4c^2k^2\omega_0^2}\right). \tag{2.1.42}$$

As can be seen from the dispersion plot, what one sees is that

1. The dispersion has two branches. The small k part of the lower branch and the large k part of the upper branch satisfy approximately $\omega = ck$. We call that the light-like part of the dispersion.

2. The small k part of the upper branch and the large k part of the lower branch are asymptotic to a fixed frequency. We call that the matter-like part of the dispersion.

3. We call the solutions of Maxwell's equations *polaritons*, because they are essentially excitations whose dispersion is a combination of "half-light", "half-matter". This intuition will be fleshed out in later chapters.

4. There is a region where there are no real solutions for the frequency. We call this band of frequencies the Reststrahlen band. If you send in light into a thick slab of this material at a frequency in the Reststrahlen band, the light cannot enter the material, because there is no energy-conserving state that the light can occupy. Thus, it must be fully reflected.

This kind of dispersion is typical for a material which can have a negative real-part of its permittivity at some point.

2.1.4 General aspects of linear response theory

Often times in physics, we wish to know how changing some input quantity will affect the behavior of some output quantity. Perhaps just as often, the underlying dynamics of the system in question are exactly, or approximately, described by a linear differential equation. Here, we will introduce the concept of a *linear response function* both in time and frequency spaces. We will eventually reveal that these linear response functions are also the Green's functions of the underlying differential equation.

To guide our discussion, we will use the example of the simple harmonic oscillator. Given some driving force $F(t)$, we would like to know the trajectory $x(t)$ which satisfies the differential equation

$$\ddot{x}(t) + \Gamma\dot{x}(t)\omega_0^2 x(t) = F(t). \tag{2.1.43}$$

Taking the Fourier transform of both sides gives

$$x(\omega) = \frac{F(\omega)}{\omega_0^2 - \omega^2 - i\omega\Gamma}, \tag{2.1.44}$$

where $F(\omega) = \int dt\, e^{i\omega t} F(t)$ of course encodes the frequency content of the driving force. In frequency space, the solution to this differential equation takes an easy multiplicative form, and we see that $x(\omega)$ is linearly proportional to $F(\omega)$. We will give this constant of proportionality a symbol,

$$\chi(\omega) = \frac{1}{\omega_0^2 - \omega^2 - i\omega\Gamma}, \tag{2.1.45}$$

and a name: the *linear response function*. One may also notice that $\chi(\omega)$ above bears a close resemblance to the Lorentz oscillator polarizability derived above using the Kubo formula. This is no coincidence, as they are really the same model. In fact, this quick calculation is in fact often presented as the derivation for the Lorentz oscillator model. All that's needed to complete the task is to interpret the force $F(t)$ as a force which arises from a charge in an electric field, and then reason about the extension to many charges over a volume as was done in the quantum derivation. The matching of these derivations tells us that the dynamics captured through the quantum calculation of the polarizability are essentially the same as the dynamics associated with a damped simple harmonic oscillator with an applied force. This is not terribly surprising, linear response theory in quantum mechanics is really about expectation values of operators, which are known to obey classical equations of motion. However, the quantum model has the benefit of making the origins of resonance and decay extremely clear.

We would ideally like to know the time dynamics $x(t)$, so we can take the inverse Fourier transform of the relation $x(\omega) = \chi(\omega)F(\omega)$ to give

$$x(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} \chi(\omega) F(\omega). \tag{2.1.46}$$

Then, we can write the fourier transform of a product of terms as a convolution of their fourier transforms, giving the very important result

$$x(t) = \int dt' \, \chi(t-t') F(t'). \tag{2.1.47}$$

Now, the trajectory $x(t)$ is connected to the applied force $F(t)$ through convolution with the linear response function in time domain, which is given in integral form as

$$\chi(t-t') = \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \chi(\omega) = \int \frac{d\omega}{2\pi} \frac{e^{-i\omega(t-t')}}{\omega_0^2 - \omega^2 - i\omega\Gamma}. \tag{2.1.48}$$

If we look at Eq. 2.1.47, we can see that it looks an awful lot like a solution to a differential equation in the form of a Green's function – in fact, it is exactly that. In the time domain, the linear response function $\chi(t-t')$ is actually just a solution to the harmonic oscillator equation with a delta function source

$$\left(\partial_t^2 + \Gamma \partial_t + \omega_0^2\right) \chi(t-t') = \delta(t-t'). \tag{2.1.49}$$

In other words, $\chi(t-t')$ tells us the trajectory of the equation which results from a delta function impulse at time t'. Note that χ is a function of the time difference $t-t'$. This makes perfect sense: since the differential operator for the harmonic oscillator has no explicit time dependence, the solution which results from an impulse can depend only on the time elapsed since the impulse, and not on any absolute time. Another feature we should expect to see in $\chi(t-t')$ is the preservation of causality – the impulse should have no effect on the trajectory until the time of the impulse. As we will see soon, this aspect will manifest itself mathematically through a heaviside function $\chi(t-t') \propto \theta(t-t')$ which guarantees that the sacred principle of causality is respected.

With this general discussion out of the way, we can proceed with the explicit evaluation of Eq. 2.1.48. With contour integration, the evaluation is quite straightforward. The Fourier representation of Eq. 2.1.48 has a denominator which can be factored into roots as

$$\chi(t-t') = \int \frac{d\omega}{2\pi} \frac{e^{-i\omega(t-t')}}{(\omega-\omega_+)(\omega-\omega_-)}, \tag{2.1.50}$$

where we define $\omega_\pm \equiv -\frac{i\Gamma}{2} \pm \sqrt{\omega_0^2 - (\Gamma/2)^2} \equiv -\frac{i\Gamma}{2} \pm \omega_r$. Note that for notational simplicity we will sometimes use ω_r to refer to the loss-shifted resonance frequency. Additionally, from now on, we will assume that the system is underdamped – in other words, that the loss parameter Γ is sufficiently small that ω_r is real. The response function can be evaluated with contour integration, provided that a path is chosen so that the Fourier exponential decays at the infinite bounds of the path. If $t - t' > 0$, then a semi-circle in the lower half plane can be used. If $t - t' < 0$, then a semi-circle in the upper half plane will be used. Since both poles $\omega_\pm$ lie in the lower half plane, an integral in the upper half plane will be zero, and an integral in the lower half plane will acquire residue at both of these poles. The origin of the causality requirement described above is now manifest, and the integral is evaluated with resides as

$$
\begin{aligned}
\chi(t-t') &= i\theta(t-t')\left(\frac{e^{-i\omega_+(t-t')}}{\omega_+ - \omega_-} - \frac{e^{-i\omega_-(t-t')}}{\omega_- - \omega_+}\right) && (2.1.51)\\
&= \theta(t-t')\frac{e^{-\frac{\Gamma}{2}(t-t')}}{\omega_r}\frac{1}{2i}\left(e^{i\omega_r(t-t')} - e^{-i\omega_r(t-t')}\right) && (2.1.52)\\
&= \theta(t-t')\frac{e^{-\frac{\Gamma}{2}(t-t')}}{\omega_r}\sin\left[\omega_r(t-t')\right]. && (2.1.53)
\end{aligned}
$$

This is a clean result with exactly the features one would expect. When the harmonic oscillator system is given a delta function kick, the system begins oscillating, and then eventually decays with a rate set by Γ. Importantly, the system cannot move until the kick has been given, and so only the time difference $t - t'$ is relevant to the behavior. While the discussion here has been in the context of the extremely familiar harmonic oscillator, the physics and mathematical techniques which underpin this discussion are both general and fundamental.

3 MAXWELL'S EQUATIONS IN MATERIALS

Maxwell's equations in polarizable media. Scalar and vector potentials. Maxwell equations as eigenvalue problems. Green's functions (general). Green's functions for the Maxwell equations. Green's functions in terms of mode expansions. Electromagnetic energy in nondispersive and dispersive electromagnetic media.

3.1 MAXWELL'S EQUATIONS IN MATERIALS

The goal of any problem in classical electrodynamics is to find the time-evolution of the electromagnetic fields under a prescribed distribution of charges and currents. The time-evolution is governed by the Maxwell equations. In frequency-domain, the equations take a much simpler form, which we will almost exclusively use. As you saw in the previous section, the Maxwell equations in frequency domain are given by

$$\nabla \cdot \epsilon(\mathbf{r},\omega)\mathbf{E}(\mathbf{r},\omega) = \frac{\rho(\mathbf{r},\omega)}{\epsilon_0} \tag{3.1.1}$$

$$\nabla \cdot \mathbf{B}(\mathbf{r},\omega) = 0 \tag{3.1.2}$$

$$\nabla \times \mathbf{E}(\mathbf{r},\omega) = i\omega\mathbf{B}(\mathbf{r},\omega) \tag{3.1.3}$$

$$\nabla \times \mathbf{H}(\mathbf{r},\omega) = \mathbf{J}(\mathbf{r},\omega) - i\omega\epsilon_0\epsilon(\mathbf{r},\omega)\mathbf{E}(\mathbf{r},\omega), \tag{3.1.4}$$

where $\epsilon(\mathbf{r},\omega)$ is the frequency-dependent permittivity of the previous chapter. ρ and $\mathbf{J}$ are *free* charge and current densities. Bound charges and currents, as we discussed in the previous section, are captured by the permittivity. As a warning, we will often leave out position and frequency functional dependences. They are implicit.

3.1.1 Maxwell's equations for the potentials

When we formulate quantum electrodynamics for electrons interacting with quantized fields in materials, we will go through the vector and scalar potential, as it makes evident the number of dynamical degrees of freedom needed to describe the electromagnetic field. Therefore, we shall formulate Maxwell's equation for the potentials, as well as introduce the so called *generalized Coulomb gauge*, which is key to the quantization of electromagnetic fields in media. Recall that in electromagnetism, we can define a vector potential $\mathbf{A}$ and a scalar potential ϕ such that $\mathbf{E} = -\nabla\phi - \partial_t\mathbf{A}$ and $\mathbf{B} = \nabla \times \mathbf{A}$. In frequency domain, $\partial_t\mathbf{A} \to -i\omega\mathbf{A}$. The Maxwell equations for the potentials in frequency domain then read:

$$\nabla \cdot (-i\omega\epsilon(\mathbf{r},\omega)\mathbf{A}(\mathbf{r},\omega) + \epsilon(\mathbf{r},\omega)\nabla\phi(\mathbf{r},\omega)) = -\frac{\rho(\mathbf{r},\omega)}{\epsilon_0} \tag{3.1.5}$$

$$\nabla \times \nabla \times \mathbf{A}(\mathbf{r},\omega) = \mu_0\mathbf{J}(\mathbf{r},\omega) - \frac{i\omega}{c^2}\epsilon(\mathbf{r},\omega)\left(i\omega\mathbf{A}(\mathbf{r},\omega) - \nabla\phi(\mathbf{r},\omega)\right). \tag{3.1.6}$$

You will see that the second and third Maxwell equations are trivially satisfied and require no additional effort on our part. We may omit them. Next, we shall make use of *gauge invariance* of Maxwell's equations. In particular, if we perform the following transformations on the potentials: $\phi \to \phi - i\omega\chi$ and $\mathbf{A} \to \mathbf{A} - \nabla\chi$, the electric and magnetic fields remain unaffected. Thus, the electric and magnetic fields are the "physical" fields. Thus, we can choose any gauge that makes convenient the solution of the remaining equations. We will make use of the *generalized Coulomb gauge* $\nabla \cdot \epsilon\mathbf{A} = 0$. You are encouraged to prove that one may always find a gauge transformation to satisfy this condition, provided that the gauge function satisfies $\nabla \cdot \epsilon\nabla\chi = 0$. In this gauge, the remaining Maxwell equations, after some re-arrangement, satisfy:

$$\nabla \cdot \epsilon(\mathbf{r},\omega)\nabla\phi(\mathbf{r},\omega) = -\frac{\rho(\mathbf{r},\omega)}{\epsilon_0} \tag{3.1.7}$$

$$\left(\nabla \times \nabla \times -\epsilon(\mathbf{r},\omega)\frac{\omega^2}{c^2}\right)\mathbf{A}(\mathbf{r},\omega) = \mu_0\mathbf{J}(\mathbf{r},\omega) + \frac{i\omega}{c^2}\epsilon(\mathbf{r},\omega)\nabla\phi(\mathbf{r},\omega). \tag{3.1.8}$$

I will comment that an advantage of these equations is that it is clear that there are only three degrees of freedom needed to describe the electromagnetic fields: one scalar potential, and *two* components of the vector potential. The third component of the vector potential is determined from the other two by the generalized Coulomb gauge condition. But the information in these equations is equivalent to the information in the Maxwell equations for the fields. For example we can easily get the electric field from these previous two equations. Plugging in $\mathbf{A} = \frac{\mathbf{E}+\nabla\phi}{i\omega}$, we see that

$$\left(\nabla \times \nabla \times -\epsilon(\mathbf{r},\omega)\frac{\omega^2}{c^2}\right)\mathbf{E}(\mathbf{r},\omega) = i\omega\mu_0\mathbf{J}(\mathbf{r},\omega). \tag{3.1.9}$$

The magnetic field is simply $\frac{\nabla\times\mathbf{E}}{i\omega}$. Let us now understand the general properties of the solutions to these equations.

3.1.2 General properties of Maxwell's equations in the absence of sources

Consider Maxwell's equations in the absence of sources: $\mathbf{J} = 0$ and $\rho = 0$. The scalar potential equation is solved by $\phi = c$ with c a constant. As we can always perform a gauge transformation that removes this constant, we may simply say $\phi = 0$. Thus, the only equation of interest is that for the vector potential, which simplifies to

$$\nabla \times \nabla \times \mathbf{A}(\mathbf{r},\omega) = \epsilon(\mathbf{r},\omega)\frac{\omega^2}{c^2}\mathbf{A}(\mathbf{r},\omega) \tag{3.1.10}$$

The equation for the vector potential on the other hand does have non-zero solutions for $\omega \neq 0$. For example, if $\epsilon = 1$, then a plane transverse wave of wavevector magnitude k satisfies this equation when $\omega = ck$. In what follows, we will consider a *non-dispersive*, but *inhomogeneous* dielectric medium, so that $\epsilon(\mathbf{r},\omega) = \epsilon(\mathbf{r})$. We will also only consider *lossless* media for the present, such that ϵ is real-valued. A number of powerful general results emerge simply in this case. The resulting equation is a *generalized eigenproblem*, in which an operator ($\nabla \times \nabla\times$), acting on a (vector) function ($\mathbf{A}$), gives that same function, up to an eigenvalue ($\frac{\omega^2}{c^2}$), and a function (ϵ). In the absence of this additional function, this would be a standard eigenproblem. Nevertheless, many results from standard eigenproblems carry over with minimal modification. Here, we enumerate the basic properties of this generalized eigenproblem, and its consequences. These consequences will be critical in the quantization of the electromagnetic field.

To derive basic properties of the Maxwell eigenproblem, we will need to define an inner product between vector functions. In particular, we define

$$\langle \mathbf{X}, \mathbf{Y} \rangle \equiv \int d^3r \; \mathbf{X}^* \cdot \mathbf{Y}. \tag{3.1.11}$$

You are encouraged to confirm that this inner product satisfies the axioms of inner-product spaces. Given this inner product, we may now simply prove (the first two of) the following properties of the Maxwell equations, its eigenfunctions (or eigenmodes) $\mathbf{F}_n(\mathbf{r}) \equiv \mathbf{A}(\mathbf{r}, \omega_n)$, and its corresponding eigenfrequencies ω_n:

1. **The eigenproblem is Hermitian.** In particular $\langle \mathbf{X}, \nabla \times \nabla \times \mathbf{Y} \rangle = \langle \nabla \times \nabla \times \mathbf{X}, \mathbf{Y} \rangle$. To prove this: let us start on the right side of the equality and integrate-by-parts our way over to the left hand side. Recall that $\int d^3r \; \mathbf{A} \cdot \nabla \times \mathbf{B} = -\oint dS \; \hat{n} \cdot (\mathbf{A} \times \mathbf{B}) + \int d^3r \; (\nabla \times \mathbf{A}) \cdot \mathbf{B}$. In everything we will be doing, we will take boundary conditions at infinity such that either: the fields vanish, or they are periodic at the boundary. In either case, this makes the boundary term zero. Thus, we may focus only on the second term. The integration by parts then tells us that the curl moves over (with no change in sign, due to the antisymmetric properties of cross products). Thus, the second curl also moves over for free, and it is then clear that $\langle \mathbf{X}, \nabla \times \nabla \times \mathbf{Y} \rangle = \langle \nabla \times \nabla \times \mathbf{X}, \mathbf{Y} \rangle$, which means $\nabla \times \nabla \times$ is a Hermitian operator.

2. **The eigenvalues are real if ϵ is positive.** Consider $\langle \mathbf{F}_n, \nabla \times \nabla \times \mathbf{F}_n \rangle = \frac{\omega_n^2}{c^2} \langle \mathbf{F}_n, \epsilon \mathbf{F}_n \rangle$. By integration by parts, we may write the left-hand side as $\langle \nabla \times \mathbf{F}_n, \nabla \times \mathbf{F}_n \rangle = \int d^3r \; |\nabla \times \mathbf{F}_n|^2 > 0$. If $\epsilon \geq 0$, then $\langle \mathbf{F}_n, \epsilon \mathbf{F}_n \rangle > 0$, $\omega_n^2 > 0$, and thus ω_n is real. Both positive and negative roots are valid solutions, and correspond to positive and negative frequencies in the frequency-domain Fourier expansion of the electromagnetic field we considered at the beginning of the lecture.

3. **The eigenfunctions can be made orthonormal according to a modified inner product**. Eigenfunctions of different eigenvalues are manifestly orthogonal (and then normalized to be orthonormal) with respect to a new inner product $(\mathbf{X}, \mathbf{Y}) \equiv \int d^3r \; \epsilon \mathbf{X}^* \cdot \mathbf{Y}$. To see this, simply consider the following inner product:

$$\langle \mathbf{F}_m, \nabla \times \nabla \times \mathbf{F}_n \rangle = \frac{\omega_n^2}{c^2} \langle \mathbf{F}_m, \epsilon \mathbf{F}_n \rangle = \frac{\omega_n^2}{c^2} \langle \epsilon \mathbf{F}_m, \mathbf{F}_n \rangle. \tag{3.1.12}$$

By Hermiticity under the standard inner product, it is the case that this must also equal

$$\langle \nabla \times \nabla \times \mathbf{F}_m, \mathbf{F}_n \rangle = \frac{\omega_m^2}{c^2} \langle \epsilon \mathbf{F}_m, \mathbf{F}_n \rangle. \tag{3.1.13}$$

It is thus immediately seen that if $\omega_m \neq \omega_n$, then $(\mathbf{F}_m, \mathbf{F}_n) = \int d^3r \; \epsilon \mathbf{F}_m^* \cdot \mathbf{F}_n = 0$. Degenerate eigenfunctions can be made orthonormal by the Gram-Schmidt procedure, just as in quantum mechanics.

4. **The eigenfunctions span the space of divergenceless functions.** Proving this requires functional analysis, so we will invoke the result instead. Consider a divergenceless (transverse) function $\mathbf{X}$, such that $\nabla \cdot \mathbf{X} = 0$. Then it may be expanded in terms of the eigenfunctions of the Maxwell's equations, up to a factor of ϵ, via:
$$\mathbf{X} = \sum_n c_n \epsilon \mathbf{F}_n, \tag{3.1.14}$$
with c_n the expansion coefficients, given by $c_m = \int d^3r\, \epsilon \mathbf{F}_m^* \cdot \mathbf{F}_n$. You can see that the divergence of each individual term is zero (from the generalized Coulomb gauge condition), so that the divergence of the overall function is zero.

It then follows that we may write an any time-dependent vector potential in the generalized Coulomb gauge by using a mode expansion, as

$$\mathbf{A}(\mathbf{r}, t) = \frac{1}{2} \sum_n \alpha_n \mathbf{F}_n(\mathbf{r}) e^{-i\omega_n t} + \alpha_n^* \mathbf{F}_n^*(\mathbf{r}) e^{i\omega_n t}, \tag{3.1.15}$$

where α_n are arbitrary coefficients. In writing this form, we have explicitly separated positive and negative frequencies. We have also defined the expansion coefficients with a factor of one-half, so that the right-hand side may also be written as $\mathrm{Re}\left[\sum_n \alpha_n \mathbf{F}_n(\mathbf{r}) e^{-i\omega_n t}\right]$. Keep in mind the expansion of Equation 3.1.15, as it will be the central object of study in the canonical quantization of the electromagnetic field. Before moving on, note that for the electric field, one has the exact same eigenproblem in the absence of currents and charges, and the corresponding modes have the same properties (as they are the same modes).

Now that we have a framework for working with the modes of Maxwell's equations in arbitrary media, we can consider how these fields are produced in the first place – through currents and charges. This will reveal the important phenomenon of *radiation*, which we will treat primarily through the method of *Green's functions*.

3.1.3 Maxwell's equations in the presence of charges and currents

In the presence of charges and currents, we must revert back to Equations 3.1.7 and 3.1.8. We require additional mathematical formalism to proceed, namely the method of Green's functions, which we now introduce.

3.1.4 Green's functions

Consider an arbitrary linear differential equation of the form:

$$(\mathcal{D} f) = S(\mathbf{r}), \tag{3.1.16}$$

where $\mathcal{D}$ is a differential operator. $S(\mathbf{r})$ is a source. We have written the equation as a scalar equation, but the general considerations here extend to vector and tensor equations. Examples of a differential operator would be ∇^2, $\nabla^2 + c^2$, with c a constant, ∇^4, $\frac{d}{dx}$, $f(x)\frac{d}{dx}$, etc. The differential operators we'll apply these considerations to are $\nabla \cdot \epsilon \nabla$ and $\nabla \times \nabla \times -\epsilon \frac{\omega^2}{c^2}$. Suppose we now consider the case where the source is a delta function:

$S(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$. We call the corresponding solution of the inhomogeneous equation the Green's function $G(\mathbf{r}, \mathbf{r}')$:

$$(\mathcal{D}G) = \delta(\mathbf{r} - \mathbf{r}'). \tag{3.1.17}$$

If we know the Green's function, then we may solve the differential equation for any source $S(\mathbf{r})$ using linearity. In particular, the solution $f(\mathbf{r})$ can be expressed as an integral of the Green's function with the source as

$$f(\mathbf{r}) = \int d^3r'\; G(\mathbf{r}, \mathbf{r}')S(\mathbf{r}'). \tag{3.1.18}$$

One can easily see why this works by plugging this solution back into Eq. 3.1.16 which gives

$$\mathcal{D}f(\mathbf{r}) = \int d^3r'\; \mathcal{D}G(\mathbf{r}, \mathbf{r}')S(\mathbf{r}') = \int d^3r'\; \delta(\mathbf{r} - \mathbf{r}')S(\mathbf{r}') = S(\mathbf{r}), \tag{3.1.19}$$

where we have only used the defining Green's function property of Eq. 3.1.17. This means that if we can find the Green's function by solving a differential equation with a delta function source, then we can construct the solution to any source by integrating this source against the Green's function. This is a powerful tool of differential equations in both mathematics and physics.

We now turn to how Green's functions can be used to write solutions to Maxwell's equations. We focus first on the defining equations, and then show how the Green's functions can be expressed in terms of eigenmode expansions. By taking Eq. 3.1.7 and replacing source term on the right hand side with a delta function, we can write the equation which defined the Green's function $G_\phi(\mathbf{r}, \omega)$ of the scalar potential as

$$\nabla \cdot \epsilon(\mathbf{r}, \omega)\nabla G_\phi(\mathbf{r}, \omega) = \delta(\mathbf{r} - \mathbf{r}'). \tag{3.1.20}$$

If the solution for $G_\phi(\mathbf{r}, \omega)$ is known, then the scalar potential can be expressed in terms of the charge sources as

$$\phi(\mathbf{r}, \omega) \equiv -\frac{1}{\epsilon_0} \int d^3r'\; G_\phi(\mathbf{r}, \mathbf{r}', \omega)\rho(\mathbf{r}', \omega). \tag{3.1.21}$$

Similarly, replacing the right hand side of Eq. 3.1.8 with a delta function, we see that the Green's function $\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega)$ should satisfy

$$\left(\nabla \times \nabla \times -\epsilon(\mathbf{r}, \omega)\frac{\omega^2}{c^2}\right)\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}')I. \tag{3.1.22}$$

Unlike the equation for the scalar potential, this is a vector equation with a vector source. As such, the Green's function $\mathbf{G}(\mathbf{r}, \mathbf{r}', \omega)$ is necessarily a tensor, and the curls are understood to act on the first index (and first position argument) of the tensor. For this reason, the object $\mathbf{G}$ is often referred to as the *dyadic Green's function*. Consequently, the right hand side is the tensor $\delta(\mathbf{r} - \mathbf{r}')I$, where I is the 3-by-3 identity matrix.

The dyadic Green's function can then be used to write a solution for the vector potential in terms of the current source and scalar potential as

$$\mathbf{A}(\mathbf{r}, \omega) \equiv \int d^3r'\; \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega) \cdot \left(\mu_0\mathbf{J}(\mathbf{r}', \omega) + \frac{i\omega}{c^2}\epsilon(\mathbf{r}', \omega)\nabla\phi(\mathbf{r}', \omega)\right). \tag{3.1.23}$$

Note here that since $\mathbf{G}$ is a 3-by-3 matrix and the dot here means matrix-vector multiplication. As we will rely on it heavily in the next section, we also want the electric field in terms of Green's functions. Since Eq. 3.1.9 expresses the electric field in terms of the same operator, we can easily write

$$\mathbf{E}(\mathbf{r},\omega) = i\omega\mu_0 \int d^3r' \, \mathbf{G}(\mathbf{r},\mathbf{r}',\omega) \cdot \mathbf{J}(\mathbf{r}',\omega). \tag{3.1.24}$$

We are now ready to derive an expression for the Green's function in terms of the eigenmodes $\mathbf{F}_n$ of the source-free problem. This is done by solving Equations 3.1.7 and 3.1.8 individually, finding the result when the current is a delta function, and combining them to get the electric field. This will enable us to infer the Green's function.

We start with the vector potential. Suppose that the vector potential can be expanded in the basis of modes of the Maxwell eigenproblem, so that

$$\mathbf{A}(\mathbf{r},\omega) = \sum_n A_n(\omega)\mathbf{F}_n(\mathbf{r}). \tag{3.1.25}$$

By plugging this into Equation (8), we can immediately see that the left-hand side

$$\sum_n \frac{1}{c^2}\left(\omega_n^2 - \omega^2\right) A_n(\omega)\epsilon(\mathbf{r},\omega)\mathbf{F}_n(\mathbf{r}) \tag{3.1.26}$$

is divergence-less (transverse), as it should be. This transverse left-hand side is being expanded in a complete set of transverse functions $\epsilon\mathbf{F}_n$, as asserted in the previous section. The right-hand side, being transverse, can be expanded similarly as

$$\sum_n c_n(\omega)\epsilon(\mathbf{r},\omega)\mathbf{F}_n(\mathbf{r}). \tag{3.1.27}$$

Taking inner products reveals an expression for the coefficients $c_n(\omega)$ as

$$c_n(\omega) = \int d^3r \; \mathbf{F}_n^*(\mathbf{r}) \left(\mu_0\mathbf{J}(\mathbf{r},\omega) + \frac{i\omega}{c^2}\epsilon(\mathbf{r},\omega)\nabla\phi(\mathbf{r},\omega)\right) = \mu_0 \int d^3r \; \mathbf{F}_n^*(\mathbf{r})\mathbf{J}(\mathbf{r},\omega). \tag{3.1.28}$$

The second term is zero. That is because it is the integral of a product of a divergenceless function and a curl-less function. Solving for A_n, we find that the vector potential is given by

$$\mathbf{A}(\mathbf{r},\omega) = \mu_0 c^2 \sum_n \frac{\int d^3r' \; \mathbf{F}_n^*(\mathbf{r}') \cdot \mathbf{J}(\mathbf{r}',\omega)}{\omega_n^2 - \omega^2}\mathbf{F}_n(\mathbf{r}). \tag{3.1.29}$$

Now let's discuss the scalar potential. The scalar potential is simply

$$\phi(\mathbf{r},\omega) = -\frac{1}{\epsilon_0}\int d^3r' \; G_\phi(\mathbf{r},\mathbf{r}',\omega)\rho(\mathbf{r}',\omega). \tag{3.1.30}$$

Combining these together, the electric field is given by

$$\mathbf{E}(\mathbf{r},\omega) = i\omega\mu_0 c^2 \sum_n \frac{\int d^3r' \; \mathbf{F}_n^*(\mathbf{r}') \cdot \mathbf{J}(\mathbf{r}',\omega)}{\omega_n^2 - \omega^2}\mathbf{F}_n(\mathbf{r}) + \frac{1}{\epsilon_0}\int d^3r' \; \nabla G_\phi(\mathbf{r},\mathbf{r}',\omega)\rho(\mathbf{r}',\omega) \tag{3.1.31}$$

To construct the Green's function, we need to find the electric field produced by a delta-function current source of frequency ω and oriented along the j direction, so that $\mathbf{J}(\mathbf{r},\omega) = \hat{e}_j\delta(\mathbf{r}-\mathbf{r}')$. Then we need to divide by $i\omega\mu_0$. For the first term, it is clear what to do. For the second, we need to know what charge density corresponds to a delta function current density, revealing clearly that the charge distribution corresponding to a delta function current is a dipole. From the continuity equation, we see that

$$\rho(\mathbf{r},\omega) = \frac{1}{i\omega}\nabla\cdot\mathbf{J}(\mathbf{r},\omega) \implies \rho_j(\mathbf{r},\omega) = \frac{1}{i\omega}\partial_j\delta(\mathbf{r}-\mathbf{r}'). \tag{3.1.32}$$

It is given by a derivative of a delta function. It follows that

$$\mathbf{G}(\mathbf{r},\mathbf{r}',\omega) = c^2\sum_n \frac{\mathbf{F}_n(\mathbf{r})\mathbf{F}_n^*(\mathbf{r}')}{\omega_n^2-\omega^2+i0^+} + \frac{c^2}{\omega^2-i0^+}\nabla\nabla' G_\phi(\mathbf{r},\mathbf{r}',\omega). \tag{3.1.33}$$

The infinitesimal imaginary parts in the denominators arise from asking: what happens if $\omega = \omega_m$ [1]? It looks like the Green's function diverges. However, in any realistic situation, the divergence is regularized by the fact that any system has at least infinitesimal dissipation. This is called the *principle of limiting absorption*. To apply it, we take $\omega \to \omega - i0^+$, similarly to what we did when studying perturbation theory in quantum mechanics.

3.2 ENERGY IN DIELIECTRICS

3.2.1 Energy in nondispersive dielectrics

The Poynting vector is given as $\mathbf{S} = \mathbf{E}\times\mathbf{H}$. By conservation of energy, the change in energy density per unit time is given by

$$\frac{\partial u}{\partial t} = -\nabla\cdot\mathbf{S}. \tag{3.2.1}$$

Using the expression for the Poynting vector in terms of the fields $\mathbf{E}$ and $\mathbf{H}$, we calculate the divergence of the Poynting flux as

$$\begin{aligned}\nabla\cdot\mathbf{S} &= \nabla\cdot(\mathbf{E}\times\mathbf{H}) && (3.2.2)\\ &= \mathbf{H}\cdot(\nabla\times\mathbf{E}) - \mathbf{E}\cdot(\nabla\times\mathbf{H}) && (3.2.3)\\ &= -\left(\mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t} + \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t}\right). && (3.2.4)\end{aligned}$$

Hence we can write an expression for the energy change as

$$\frac{\partial u}{\partial t} = -\nabla\cdot\mathbf{S} = \mathbf{E}\cdot\frac{\partial\mathbf{D}}{\partial t} + \mathbf{H}\cdot\frac{\partial\mathbf{B}}{\partial t} = \epsilon_0\epsilon\mathbf{E}\cdot\frac{\partial\mathbf{E}}{\partial t} + \mu_0\mu\mathbf{H}\cdot\frac{\partial\mathbf{H}}{\partial t} \tag{3.2.5}$$

It is easy to check that this is satisfied by

$$u = \frac{1}{4}\left(\epsilon_0\epsilon\mathbf{E}\cdot\mathbf{E} + \mu_0\mu\mathbf{H}\cdot\mathbf{H}\right) = \frac{1}{2}\left(\epsilon_0\epsilon|\mathbf{E}|^2 + \mu_0\mu|\mathbf{H}|^2\right), \tag{3.2.6}$$

where in the second form we have accounted for the fact that the fields may be taken to be complex. This is the familiar formula for the electromagnetic energy density in a nondispersive medium.

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[1] or $\omega = 0$, but we're never interested in this situation

4 QUANTUM ELECTRODYNAMICS

Lagrangian and Hamiltonian formulation of classical electrodynamics in material media. Mode expansion of the Lagrangian and Hamiltonian of the electromagnetic field. Canonical quantization of the electromagnetic field. Long-wavelength approximation. Goeppert-Mayer transformation and dipole Hamiltonian. Cancellation of the dipole self-energy with the Coulomb interaction with induced charges. Power-Zienau-Wooley transformation.

4.1 LAGRANGIAN AND HAMILTONIAN FORMULATION OF CLASSICAL ELECTROMAGNETISM

In the previous chapter, we studied the description of the classical electromagnetic field. We reformulated Maxwell's equations in dielectric media in terms of the vector and scalar potential. As argued from the previous section, this reformulation is helpful because it reveals in a transparent way the number of degrees of freedom needed to describe the electromagnetic field. In this chapter, we will *quantize* the combined system of charges and electromagnetic fields. To quantize the system means essentially to turn all observable quantities describing the system into operators. Thus, the positions and velocities of the matter (charges) become operators, as do the electric and magnetic fields. Additionally, we will need to find a Hamiltonian operator which generates the time-evolution of the light-matter system.

We already know how to quantize the charges, as this is just conventional quantum mechanics – thus the essential new element is the quantization of the electromagnetic field. We will see that each mode of the electromagnetic field is associated with a harmonic oscillator.

In general, the strategy to answering these questions is as follows:

1. Start from a Lagrangian whose equations of motion (Euler-Lagrange equations) are classical equations that we already know (the Maxwell equations for the fields, the Newton equations for the charges)

2. Turn the Lagrangian into a Hamiltonian through the standard Legendre transform

3. For matter described by positions and velocities, we quantize as usual, converting the position into the position operator, and the momentum into the momentum operator $\mathbf{p} = -i\hbar\nabla$. For fields, which possess an infinite number of degrees of freedom (to describe the field at all points in space), we will find that degrees of freedom of the EM field can be conveniently cast in terms of the amplitudes of the normal modes of the field. We will find that the independent field modes act as independent harmonic oscillators, which lead then to a simple and straightforward quantization.

Let us start by finding the Lagrangian of the system of matter and fields. We will do this in three steps: we will first introduce the Lagrangian of a system of matter in an external electromagnetic field. Then, we will introduce the Lagrangian of the electromagnetic field in the absence of charges. Finally, we will derive the Lagrangian describing the interaction between the charges and the fields.

4.1.1 Lagrangian of matter in an external field

We start by considering the Lagrangian describing a single particle in an external field, described by the scalar potential $\phi(\mathbf{r}, t)$ and the vector potential $\mathbf{A}(\mathbf{r}, t)$. We are looking to find a Lagrangian $L(\mathbf{r}(t), \dot{\mathbf{r}}(t), t)$ (dots here denote time-derivative) such that when the associated action functional

$$S[\mathbf{r}(t), \dot{\mathbf{r}}(t); t_i, t_f] \equiv \int_{t_i}^{t_f} dt\ L(\mathbf{r}(t), \dot{\mathbf{r}}(t), t) \tag{4.1.1}$$

is stationary, it reproduces the Newtonian equation of motion for the particle in an external electromagnetic field. By stationary, we mean with respect to a change of the functions $\mathbf{r}(t), \dot{\mathbf{r}}(t)$ To minimize the action, let us consider a small variation of the trajectory $\mathbf{r}(t) \to \mathbf{r}(t) + \delta\mathbf{r}(t)$, where $|\delta\mathbf{r}| \ll |\mathbf{r}|$. We can expand the action in this small variation as

$$\begin{aligned} S[\mathbf{r}(t) + \delta\mathbf{r}(t), \dot{\mathbf{r}}(t) + \delta\dot{\mathbf{r}}(t); t_i, t_f] &= \int_{t_i}^{t_f} dt\ L(\mathbf{r}(t) + \delta\mathbf{r}(t), \dot{\mathbf{r}}(t) + \dot{\delta\mathbf{r}}(t), t) \\ &\approx \int_{t_i}^{t_f} dt\ \left(L(\mathbf{r}(t), \dot{\mathbf{r}}(t), t) + \delta\mathbf{r} \cdot \nabla_{\mathbf{r}} L + \delta\dot{\mathbf{r}} \cdot \nabla_{\dot{\mathbf{r}}} L\right). \end{aligned} \tag{4.1.2}$$

The corresponding change in the action is then

$$\delta S = \int_{t_i}^{t_f} dt\ \left(\delta\mathbf{r} \cdot \nabla_{\mathbf{r}} L + \delta\dot{\mathbf{r}} \cdot \nabla_{\dot{\mathbf{r}}} L\right). \tag{4.1.3}$$

To simplify this further, expressing everything in terms of the change in $\mathbf{r}$, we may use the fact that $\dot{\delta\mathbf{r}} = \delta\dot{\mathbf{r}}$, and perform integration by parts to get

$$\delta S = \delta\mathbf{r} \cdot \nabla_{\dot{\mathbf{r}}} L \Big|_{t_i}^{t_f} + \int_{t_i}^{t_f} dt\ \delta\mathbf{r} \cdot \left(\nabla_{\mathbf{r}} L - \frac{d}{dt} \nabla_{\dot{\mathbf{r}}} L\right). \tag{4.1.4}$$

The equations would simplify greatly if the boundary terms vanished. In fact, they do. The reason is that the way the action principle is formulated, the trajectory that makes the action stationary must respect the boundary conditions of the problem: that we know the position and velocity at the initial and final times. Therefore, if the stationary trajectory respects these boundary conditions, the variation in the trajectory must be zero so that any variation also respects the boundary conditions. Stated mathematically: $\delta\mathbf{r}(t_i) = \delta\mathbf{r}(t_f) = 0$. For

$$0 = \int_{t_i}^{t_f} dt\, \delta\mathbf{r} \cdot \left(\nabla_{\mathbf{r}} L - \frac{d}{dt} \nabla_{\dot{\mathbf{r}}} L \right). \tag{4.1.5}$$

This equation must hold for *any* variation $\delta\mathbf{r}$. The only way this is possible is if the integrand is zero throughout the integration domain. To see this, consider $\delta\mathbf{r} = (1,0,0)\delta(t-t_0)$, with $t_i < t_0 < t_f$. Then we get $0 = \partial_x L(t_0) - \frac{d}{dt}\partial_{\dot{x}} L(t_0)$. This holds for any time, and also for a y or z-directed unit vector weighting the delta function. Therefore,

$$\nabla_{\mathbf{r}} L = \frac{d}{dt} \nabla_{\dot{\mathbf{r}}} L, \tag{4.1.6}$$

which is the Euler-Lagrange equation.

To find the Lagrangian of a given system is essentially trial-and-error: guess a Lagrangian and show that the Euler-Lagrange equations result in the equations of motion for the system. While this may sound circular, the purpose of finding a Lagrangian here is to allow us to find the Hamiltonian which lies at the heart of the quantum description of the system. Thus, Lagrangians give a principled way to determine quantized theories of classical systems.

The Lagrangian for a single particle of charge q and mass m in an electromagnetic field can be found to be

$$L = \frac{1}{2} m \dot{\mathbf{r}}^2 - q\phi(\mathbf{r}(t)) + q\mathbf{A}(\mathbf{r}(t), t) \cdot \dot{\mathbf{r}}. \tag{4.1.7}$$

To show this is the correct Lagrangian, let us evaluate the corresponding Euler-Lagrange equation, showing that it reduces to the Newtonian equation of motion for a charged particle subject to the Lorentz force law. The left-hand side of the Euler-Lagrange equation is simply

$$\nabla_{\mathbf{r}} L = -q\nabla\phi + q(\nabla_{\mathbf{r}} \mathbf{A}) \cdot \dot{\mathbf{r}}, \tag{4.1.8}$$

where it is understood that the dot-product refers to the indices of $\mathbf{A}$ and $\mathbf{r}$. The right-hand side of the Euler-Lagrange equation is given by

$$\frac{d}{dt} \nabla_{\dot{\mathbf{r}}} L = m\ddot{\mathbf{r}} + \frac{d}{dt} \mathbf{A}(\mathbf{r}(t), t) \cdot \nabla_{\dot{\mathbf{r}}} \dot{\mathbf{r}} \tag{4.1.9}$$

which, by application of the chain-rule, gives

$$\frac{d}{dt} \nabla_{\dot{\mathbf{r}}} L = m\ddot{\mathbf{r}} + q\partial_t \mathbf{A} + q(\dot{\mathbf{r}} \cdot \nabla)\mathbf{A}, \tag{4.1.10}$$

where we have omitted the functional dependence of $\mathbf{A}$, as we will not need to think about it anymore. We can very clearly see how the electric field arises in this equation, given that $\mathbf{E} = -\nabla\phi - \partial_t \mathbf{A}$. We need to however expose the dependence on the magnetic field. Let us look at the term $q(\nabla_{\mathbf{r}} \mathbf{A}) \cdot \dot{\mathbf{r}}$ in more detail. Writing the i-component of this in repeated index notation, we have that

$$q(\nabla_{\mathbf{r}} \mathbf{A}) \cdot \dot{\mathbf{r}} = q(\partial_i A_j - \partial_j A_i)\dot{r}_j + q(\partial_j A_i)\dot{r}_j. \tag{4.1.11}$$

The combination $\partial_i A_j - \partial_j A_i$ appears to be a curl of the vector potential, a magnetic field. To proceed, it is useful to cast the term we want $(\dot{\mathbf{r}} \times (\nabla \times \mathbf{A}))_i$ in a form that resembles what we have just derived. We may write

$$\begin{aligned}(\dot{\mathbf{r}} \times (\nabla \times \mathbf{A}))_i &= \epsilon_{ijk}\dot{r}_j\epsilon_{klm}\partial_l A_m \\ &= \epsilon_{kij}\epsilon_{klm}\dot{r}_j\partial_l A_m \\ &= (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl})\dot{r}_j\partial_l A_m \\ &= \dot{r}_j(\partial_i A_j - \partial_j A_i), \end{aligned} \tag{4.1.12}$$

exactly equal to a term we got from the Euler-Lagrange equation. Therefore $q(\nabla_{\mathbf{r}}\mathbf{A}) \cdot \dot{\mathbf{r}} = q\dot{\mathbf{r}} \times \mathbf{B} + q(\dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}})\mathbf{A}$. Equating the left and right hand sides of the Euler-Lagrange equations then yields

$$m\ddot{\mathbf{r}} = q(\mathbf{E} + \dot{\mathbf{r}} \times \mathbf{B}), \tag{4.1.13}$$

as desired.

In many cases, we have not just one particle, but many (N), in external electromagnetic fields. The arguments of this section can easily be generalized to show that the Euler-Lagrange equations still apply for each particle independently, and that the Lagrangian is the sum of the Lagrangians of each individual particle. In other words

$$L = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\mathbf{r}}_i^2 - q_i\phi(\mathbf{r}_i, t) + q_i\mathbf{A}(\mathbf{r}_i, t) \cdot \dot{\mathbf{r}}_i \tag{4.1.14}$$

4.1.2 Lagrangian of the fields without sources

We now move to derive the Lagrangian of the free electromagnetic field. Let us consider for simplicity the electromagnetic field in the absence of sources. Unlike matter, which have well-defined locations, fields are spread out over all space. As a result, the Lagrangian of some field, ϕ, is typically expressed in terms of a Lagrangian density, $\mathcal{L}$ via

$$L[\phi] = \int d^3r \ \mathcal{L}[\phi(\mathbf{r}, t), \partial_\mu\phi(\mathbf{r}, t)], \tag{4.1.15}$$

where we have taken the field to be in three spatial dimensions, as is the most common scenario. We have assumed the Lagrangian to be a function of both the field itself and its derivatives, labeling a generic derivative (time or space), as $\partial_\mu\phi$. The corresponding action is expressed as

$$S[\phi] = \int d^4x \ \mathcal{L}[\phi(\mathbf{r}, t), \partial_\mu\phi(\mathbf{r}, t)], \tag{4.1.16}$$

with $d^4x \equiv d^3r dt$. Fields, like matter, are also subject to a principle of stationary action. Thus, the field is that which leads to $\delta S = 0$. Let us consider an arbitrary variation of the field $\phi \to \phi + \delta\phi$. The action can then be expanded in this variation to first order as

$$\begin{aligned} S[\phi + \delta\phi] &= \int d^4x \ \mathcal{L}[\phi(\mathbf{r}, t) + \delta\phi, \partial_\mu\phi(\mathbf{r}, t) + \delta(\partial_\mu\phi)] \\ &\approx S[\phi] + \int d^4x \left(\delta\phi\frac{\partial\mathcal{L}}{\partial\phi} + \delta(\partial_t\phi)\frac{\partial\mathcal{L}}{\partial(\partial_t\phi)} + \delta(\nabla_{\mathbf{r}}\phi) \cdot \frac{\partial\mathcal{L}}{\partial(\nabla_{\mathbf{r}}\phi)}\cdot\right), \end{aligned} \tag{4.1.17}$$

where

$$\frac{\partial\mathcal{L}}{\partial(\nabla_{\mathbf{r}}\phi)} \equiv \left(\frac{\partial\mathcal{L}}{\partial(\partial_x\phi)}, \frac{\partial\mathcal{L}}{\partial(\partial_y\phi)}, \frac{\partial\mathcal{L}}{\partial(\partial_z\phi)}\right) \tag{4.1.18}$$

in Cartesian coordinates. To proceed, we need to consider boundary conditions for the fields. Regarding spatial boundary conditions, let us assume that the fields either vanish at infinity, or that the fields are enclosed in a large box with periodic boundary conditions. Similarly, we will apply the same temporal boundary conditions. Whether the fields vanish or are periodic, one can show that the boundary terms in the integration by parts vanish. Therefore, it immediately follows that the variation in the action is

$$\delta S = \int d^4x \; \delta\phi \left(\frac{\partial \mathcal{L}}{\partial \phi} - \partial_t \frac{\partial \mathcal{L}}{\partial(\partial_t \phi)} - \nabla_{\mathbf{r}} \cdot \frac{\partial \mathcal{L}}{\partial(\nabla_{\mathbf{r}}\phi)}. \right) \tag{4.1.19}$$

By an argument similar to the one used to derive the Euler-Lagrange equations for matter, it follows that for the action to be stationary for *any* $\delta\phi$, it must be that

$$\frac{\partial \mathcal{L}}{\partial \phi} - \nabla_{\mathbf{r}} \cdot \frac{\partial \mathcal{L}}{\partial(\nabla_{\mathbf{r}}\phi)} = \partial_t \frac{\partial \mathcal{L}}{\partial(\partial_t \phi)}, \tag{4.1.20}$$

which is the Euler-Lagrange equation for fields.

Let us now apply this to the case of electromagnetism in (non-magnetic, non-dispersive) material media. The Lagrangian of the electromagnetic field, described by a scalar and vector potential, turns out to be

$$L[\phi, \mathbf{A}, \partial_\mu \mathbf{A}] = \frac{\epsilon_0}{2} \int d^3r \; \epsilon \mathbf{E}^2 - c^2 \mathbf{B}^2 = \frac{\epsilon_0}{2} \int d^3r \; \epsilon (\nabla\phi + \partial_t \mathbf{A})^2 - c^2 (\nabla \times \mathbf{A})^2. \tag{4.1.21}$$

This Lagrangian looks considerably more complicated than the one we derived above for a single-component field due to the dependence on multiple fields $(\phi, \mathbf{A})$, as well as due to the vectorial nature of the vector potential. However, from the standpoint of the derivation of the Euler-Lagrange equation, all that has happened is that the number of degrees of freedom is larger. We can think of the Lagrangian as

$$L[\phi, \partial_\mu \phi, A_x, \partial_\mu A_x, A_y, \partial_\mu A_y, A_z, \partial_\mu A_z]. \tag{4.1.22}$$

And the Euler-Lagrange equations will apply separately to ϕ, A_x, A_y, A_z.

First, let's find the equation for the scalar potential. Noticing that the Lagrangian does not depend on ϕ or $\partial_t\phi$, but does depend on its spatial gradient, we see that the Euler-Lagrange equation generated from the potential is

$$\nabla \cdot \epsilon \nabla \phi + \partial_t \nabla \cdot (\epsilon \mathbf{A}) = 0, \tag{4.1.23}$$

which is in agreement with Eq. (3.1.7) in the absence of sources.

Now, we need to obtain the equations from differentiation with respect to the vector potential and its derivatives. There is no dependence on the vector potential itself, only its derivatives. Differentiating with respect to the time-derivative of A_s, the s-component of $\mathbf{A}$, gives

$$\frac{\partial \mathcal{L}}{\partial(\partial_t A_s)} = \epsilon_0 \epsilon (\partial_t A_s + \partial_s \phi) = -\epsilon_0 \epsilon E_s = -D_s, \tag{4.1.24}$$

with $\mathbf{D}$ the displacement field.

Now, we must differentiate the Lagrangian with respect to the spatial derivatives, which is complicated by the presence of curls. The term to evaluate for the equation for A_s is

$$\partial_r \frac{\partial \mathcal{L}}{\partial(\partial_r A_s)}. \tag{4.1.25}$$

In repeated-index notation, the term in the Lagrangian density associated with the magnetic field (modulo $\epsilon_0 c^2$) is

$$-\frac{1}{2}\epsilon_{ijk}\epsilon_{ilm}(\partial_j A_k)(\partial_l A_m). \tag{4.1.26}$$

Noting that the $\partial_i A_j$ are independent degrees of freedom, it follows that $\frac{\partial(\partial_i A_j)}{\partial(\partial_r A_s)} = \delta_{ir}\delta_{js}$. It follows that the derivative (Eq. 5.1.25) of Eq. (5.1.26) is simply

$$\epsilon_{sri}\epsilon_{ilm}\partial_r\partial_l A_m = (\nabla \times \nabla \times \mathbf{A})_s. \tag{4.1.27}$$

Therefore, the equation for the vector potential is

$$\nabla \times \nabla \times \mathbf{A} + \frac{\epsilon}{c^2}\left(\partial_t^2 \mathbf{A} + \nabla\partial_t\phi\right) = 0, \tag{4.1.28}$$

which is Eq. (3.1.8) in the absence of sources. We have thus proven that the Lagrangian of Eq. 5.1.21 is in fact the correct Lagrangian of the field.

4.1.3 Interaction Lagrangian

Now let's consider the influence of interactions between matter and light. Actually, there's not much to consider. In Section 5.1.1, we derived the Lagrangian describing matter in electromagnetic fields, thus implicitly taking into account the interactions between matter and fields. The only real change is one of perspective: the fields are now degrees of freedom, rather than fixed, external entities, and therefore are subject to time-evolution. The Lagrangian of a system of N matter in an electromagnetic field is thus

$$\boxed{L = \sum_{i=1}^{N} \frac{1}{2}m_i\dot{\mathbf{r}}_i^2 - q_i\phi(\mathbf{r}_i, t) + q_i\mathbf{A}(\mathbf{r}_i, t)\cdot\dot{\mathbf{r}}_i + \frac{\epsilon_0}{2}\int d^3r\ \epsilon(\nabla\phi + \partial_t\mathbf{A})^2 - c^2(\nabla \times \mathbf{A})^2}. \tag{4.1.29}$$

This Lagrangian does not change the equations of motion for the matter, as the field Lagrangian does not depend on the particle degrees of freedom. However, the term representing the interaction between matter and fields: $-q_i\phi(\mathbf{r}_i, t) + q_i\mathbf{A}(\mathbf{r}_i, t)\cdot\dot{\mathbf{r}}_i$ do change the equation for the fields. To find the change to the field equations however, we need to find the Lagrangian density associated with the interaction terms, and cast these terms as integrals. This is done by introducing integrals, so that the interaction terms become

$$\begin{aligned}&\int d^3r - q_i\phi(\mathbf{r}_i, t)\delta(r - r_i(t)) + q_i\mathbf{A}(\mathbf{r}_i, t)\cdot\dot{\mathbf{r}}_i\delta(r - r_i(t))\\ &= \int d^3r\ -\rho(\mathbf{r}, t)\phi(\mathbf{r}, t) + \mathbf{j}(\mathbf{r}, t)\cdot\mathbf{A}(\mathbf{r}, t),\end{aligned} \tag{4.1.30}$$

where we have introduced the charge and current densities.

Differentiating the Euler-Lagrange equations for the fields gives

$$\nabla\cdot\epsilon\nabla\phi + \partial_t\nabla\cdot(\epsilon\mathbf{A}) = -\rho/\epsilon_0 \tag{4.1.31}$$

for the scalar potential equation and

$$\nabla \times \nabla \times \mathbf{A} + \frac{\epsilon}{c^2}\left(\partial_t^2 \mathbf{A} + \nabla \partial_t \phi\right) = -\mu_0 \mathbf{j} \tag{4.1.32}$$

for the vector potential equation. These are exactly the same as the Maxwell equations with sources that we derived earlier. With this, we have the full *Maxwell-Newton-Lorentz* system of equations that classically describes light and matter

$$\begin{aligned} m\ddot{\mathbf{r}} &= q(\mathbf{E} + \dot{\mathbf{r}} \times \mathbf{B}) \\ \nabla \cdot \epsilon \nabla \phi + \partial_t \nabla \cdot (\epsilon \mathbf{A}) &= -\rho/\epsilon_0 \\ \nabla \times \nabla \times \mathbf{A} + \frac{\epsilon}{c^2}\left(\partial_t^2 \mathbf{A} + \nabla \partial_t \phi\right) &= -\mu_0 \mathbf{j}. \end{aligned} \tag{4.1.33}$$

4.1.4 Hamiltonian of the matter and the fields

As our ultimate goal is a quantum theory of matter and electromagnetic fields, as because the Hamiltonian is the central quantity of that theory, we must derive the Hamiltonian corresponding to this Lagrangian. As you will remember from mechanics, the Hamiltonian $H(p, q)$ corresponding to a Lagrangian $L(q, \dot{q})$ is obtained by the Legendre transform:

$$H = p\dot{q} - L, \tag{4.1.34}$$

where p, the canonical momentum, is defined as

$$p = \frac{\partial L}{\partial \dot{q}}. \tag{4.1.35}$$

For the matter, the canonical momentum can easily be seen to be

$$\mathbf{p} = m\mathbf{v} + q\mathbf{A}. \tag{4.1.36}$$

Meanwhile, for the fields, the canonical momentum is

$$\mathbf{\Pi}(\mathbf{r}) = \frac{\partial L}{\partial \dot{\mathbf{A}}} = -\mathbf{D}. \tag{4.1.37}$$

The Hamiltonian then follows immediately as

$$H = \sum_{i=1}^{N} \frac{(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_i))^2}{2m_i} + q_i \phi(\mathbf{r}_i, t) + \frac{\epsilon_0}{2} \int d^3 r \, \frac{\mathbf{\Pi}^2}{\epsilon} + c^2 (\nabla \times \mathbf{A})^2. \tag{4.1.38}$$

While this answer looks quite clean, there is a serious complication associated with it. It has to do with the fact that matter and field degrees of freedom are mixed together. For example, the vector and scalar potentials in Eq. (5.1.33) are mixed together. Additionally, the Hamiltonian of the field mixes the scalar and vector potentials through Π. This complicates analysis greatly, and thus we at this stage make a choice of gauge that eliminates this mixing.

From now on, we will assume to be in the *generalized Coulomb gauge* introduced in Chapter, 3 so that

$$\boxed{\nabla \cdot \epsilon \mathbf{A} = 0}. \tag{4.1.39}$$

This choice of gauge leads to two major simplifications. The first is that the scalar potential is completely determined by the matter (as there are no homogeneous solutions to $\nabla \cdot \epsilon \nabla \phi = -\rho/\epsilon_0$ that carry an electric field). Therefore, the scalar potential is actually a particle degree of freedom. The scalar potential is given in terms of the Green's function of the Laplace equation as

$$\phi(\mathbf{r}) = -\frac{1}{\epsilon_0} \sum_{i=1}^{N} q_i G_\phi(\mathbf{r}, \mathbf{r}_i) \tag{4.1.40}$$

The second thing is that we can define the canonical field momentum without the scalar potential. This is because the canonical field momentum came from deriving a term like

$$\int d^3r \; \epsilon((\partial_t \mathbf{A})^2 + 2\mathbf{A} \cdot \nabla\phi + (\nabla\phi)^2). \tag{4.1.41}$$

But, if $\nabla \cdot \epsilon \mathbf{A} = 0$, then $\int d^3r \; \epsilon \mathbf{A} \cdot \nabla\phi = 0$ because it is an integral of a dot product between a curl-less and divergence-less function. Meanwhile, we can write the third term as

$$\int d^3r \; \epsilon \nabla\phi \cdot \nabla\phi = \int d^3r \; -\phi \nabla \cdot \epsilon \nabla \phi = \int d^3r \; \rho\phi. \tag{4.1.42}$$

Therefore, re-defining the canonical momentum for the field as $\mathbf{\Pi} = \epsilon_0 \epsilon(\partial_t \mathbf{A})$, we can write the Hamiltonian as:

$$H = \sum_{i=1}^{N} \frac{(\mathbf{p}_i - q_i \mathbf{A}_i(\mathbf{r}_i))^2}{2m_i} - \frac{1}{2\epsilon_0} \sum_{i,j=1}^{N} q_i q_j G_\phi(\mathbf{r}_i, \mathbf{r}_j) + \frac{\epsilon_0}{2} \int d^3r \; \frac{\mathbf{\Pi}^2}{\epsilon} + c^2 (\nabla \times \mathbf{A})^2. \tag{4.1.43}$$

This is the final form of the Hamiltonian of light and matter. As a note, while the Hamiltonian "should" be written in terms of position and momenta, as we have above, it is very common to see the Hamiltonian with the field momentum expressed in terms of the vector potential, in order to keep a small number of variables in the Hamiltonian. Thus, the form we will state in practice is

$$\boxed{H = \sum_{i=1}^{N} \frac{(\mathbf{p}_i - q_i \mathbf{A}_i(\mathbf{r}_i))^2}{2m_i} - \frac{1}{2\epsilon_0} \sum_{i,j=1}^{N} q_i q_j G_\phi(\mathbf{r}_i, \mathbf{r}_j) + \frac{\epsilon_0}{2} \int d^3r \; \epsilon (\partial_t \mathbf{A})^2 + c^2 (\nabla \times \mathbf{A})^2}. \tag{4.1.44}$$

4.1.5 Electromagnetic modes as degrees of freedom of the radiation

The Hamiltonian form of classical electrodynamics exposes that the non-redundant degrees of freedom are the system are the positions and momenta of the matter, the vector potential, and its time-derivative. The vector potential carries an infinite number of degrees of freedom, as a result of the fact that the fields are defined at every point in space. This is cumbersome, and it would be ideal to have a simpler (but still infinite) set of degrees of freedom by which to describe the electromagnetic field. The mode expansion technique of Chapter 3 provides us with just that.

Recall that: for a time-dependent potential satisfying the generalized Coulomb gauge condition, we may expand the potential in terms of the modes of the source-free Maxwell equations as:

$$\mathbf{A}(\mathbf{r}, t) = \sum_n A_n(t) \mathbf{F}_n(\mathbf{r}). \tag{4.1.45}$$

Here, we will take $A_n(t)$ to be purely real coefficients, and $\mathbf{F}_n(\mathbf{r})$ to be real-valued modes. This can be done without loss of generality in lossless non-magnetic systems[1] Later, we will show that this assumption was unnecessary, and that everything we will derive will hold for complex modes as well. But this makes the initial derivations very easy.

Let us see how the Lagrangian and Hamiltonian of the electromagnetic field without sources looks like under this mode expansion. Plugging this into the Lagrangian, and using orthonormality, we immediately find that:

$$L = \frac{\epsilon_0}{2} \sum_n \left(\dot{A}_n^2 - \omega_n^2 A_n^2 \right) . \tag{4.1.46}$$

The second term arose from moving one of the curls to the other side and making use of the Maxwell eigenproblem. The Lagrangian has now been recast as a function of A_n and $\dot{A}_n$,, suggesting that the mode coefficients, A_n, are the canonical coordinates of the electromagnetic field. For each n, then we have as the corresponding Euler-Lagrange equation:

$$\ddot{A}_n + \omega_n^2 A_n = 0, \tag{4.1.47}$$

The corresponding Hamiltonian is:

$$H = \frac{\epsilon_0}{2} \sum_n \left(\dot{A}_n^2 + \omega_n^2 A_n^2 \right) . \tag{4.1.48}$$

Expressing H in terms of the canonical position A_n and momentum $\epsilon_0 \dot{A}_n$, we have that

$$H = \sum_n \left(\frac{p_n^2}{2\epsilon_0} + \frac{1}{2} \epsilon_0 \omega_n^2 q_n^2 \right) . \tag{4.1.49}$$

This is clearly the Hamiltonian of a set of harmonic oscillators associated with each mode. The frequencies of the oscillators are the modal frequencies ω_n and a “mass” ϵ_0.

The result we arrived at, although very simple, is extremely important. It says: **The time-dependent amplitudes of the modes behave in exactly the same way as a harmonic oscillator. In the quantum theory, the mode amplitudes act as independent quantum harmonic oscillators.**

This point holds not just for electromagnetism, but other wave equations, such as acoustic wave equations, hydrodynamic wave equations, and relativistic wave equations for fundamental particles. In fact, the statement in the box is the fundamental principle of quantum field theory.

4.2 QUANTIZATION OF THE ELECTROMAGNETIC FIELD IN THE ABSENCE OF CHARGES

We have shown at least classically that the free electromagnetic field is dynamically equivalent to a set of harmonic oscillators. Therefore, we quantize it in the same way we

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[1] It is a consequence of ϵ being real that all of the modes can be chosen *real*. It can be immediately seen that if $\mathbf{F}$ is a mode of Maxwell's equations with frequency ω, it is also the case that $\mathbf{F}^*$ is also a mode with the same frequency, meaning that $\mathbf{F} \pm \mathbf{F}^*$ are both modes, which are purely real. This also means that for a non-degenerate mode, it is real. While for a complex mode, it must have a degenerate partner which is its conjugate. This situation also happens in the Schrodinger equation.

quantize a particle on a spring. The canonical position and momenta of the different modes are promoted to Hermitian operators satisfying a canonical commutation relation where $[p_m, q_n] = i\hbar\delta_{mn}$. In quantum field theory, it is not common to make too much reference to this commutator. Instead, it is more useful to recast this commutator as one in terms of creation and annihilation operators. Then the canonical commutation relation will be formulated as the usual $[a_m, a_n^\dagger] = \delta_{mn}$. Let us define creation and annihilation operators

$$a_n = \sqrt{\frac{\epsilon_0}{2\hbar\omega_n}}\left(\omega_n q_n + \frac{i}{\epsilon_0}p_n\right), \quad a_n^\dagger = \sqrt{\frac{\epsilon_0}{2\hbar\omega_n}}\left(\omega_n q_n - \frac{i}{\epsilon_0}p_n\right). \tag{4.2.1}$$

It follows immediately that

$$q_n = \sqrt{\frac{\hbar}{2\epsilon_0\omega_n}}\left(a_n + a_n^\dagger\right), \quad p_n = -i\sqrt{\frac{\hbar\omega_n\epsilon_0}{2}}\left(a_n - a_n^\dagger\right). \tag{4.2.2}$$

Expressing the canonical degrees of freedom in terms of the creation and annihilation operators, we have that

$$H = \sum_n \frac{\hbar\omega_n}{2}\left(a_n^\dagger a_n + a_n a_n^\dagger\right) = \sum_n \hbar\omega_n\left(a_n^\dagger a_n + \frac{1}{2}\right). \tag{4.2.3}$$

To complete the quantization of the field, the last thing we need to do is write the operator form of the vector potential. That follows from the mode expansion and the fact that $q_n = A_n$. Expressing the q_n in terms of the creation and annihilation operators, we automatically have

$$\mathbf{A} = \sum_n \sqrt{\frac{\hbar}{2\epsilon_0\omega_n}}(a_n + a_n^\dagger)\mathbf{F}_n. \tag{4.2.4}$$

In the quantization of the fields, we assumed that the modes were real. This is not necessary. If we express the vector potential in terms of complex modes, then the Hamiltonian is the same as before (just keeping in mind that the creation and annihilation operators are associated with different modes from before). The vector potential on the other hand, takes the form:

$$\mathbf{A}(\mathbf{r}) = \sum_n \sqrt{\frac{\hbar}{2\epsilon_0\omega_n}}\left(\mathbf{F}_n(\mathbf{r})a_n + \mathbf{F}_n^*(\mathbf{r})a_n^\dagger\right). \tag{4.2.5}$$

To see that this form can be arrived at from an expansion in real modes, consider a case in which the vector potential has two degenerate real modes of frequency ω. As we argued before, since any complex mode has a degenerate partner which is the conjugate, we can always construct two real degenerate modes as the real and imaginary parts of one of the complex modes. Let us call these modes $\mathbf{F}_1$ and $\mathbf{F}_2$, their associated annihilation operators a_1 and a_2 and then consider the contribution of those two modes to the vector potential. Let us now do a change of variables. Let us define two new annihilation operators $b_1 \equiv \frac{a_1 - ia_2}{\sqrt{2}}$ and $b_2 \equiv \frac{a_1 + ia_2}{\sqrt{2}i}$. Let us also define two new modes $\mathbf{G}_1 = \frac{\mathbf{F}_1 + i\mathbf{F}_2}{\sqrt{2}}$ and $\mathbf{G}_2 = \frac{i\mathbf{F}_1 + \mathbf{F}_2}{\sqrt{2}}$. With these definitions, one can show that

$$\omega(a_1^\dagger a_1 + a_2^\dagger a_2) = \omega(b_1^\dagger b_1 + b_2^\dagger b_2) \tag{4.2.6}$$

and

$$(a_1 + a_1^\dagger)\mathbf{F}_1 + (a_2 + a_2^\dagger)\mathbf{F}_2 = \mathbf{G}_1(\mathbf{r})b_1 + \mathbf{G}_1^*(\mathbf{r})b_1^\dagger + \mathbf{G}_2(\mathbf{r})b_2 + \mathbf{G}_2^*(\mathbf{r})b_2^\dagger. \tag{4.2.7}$$

You should convince yourself that based on these observations, it is always possible to go from a purely real form of the mode expansion of the vector potential operator to a complex form. With the field quantized, we now move to the main topic of this “course": the interactions of light and matter according to quantum electrodynamics.

4.2.1 Hamiltonian of quantum electrodynamics for non-relativistic matter

We have now quantized the electromagnetic field in the absence of currents and charges. However, most problems that we will be interested in involve the interaction of bound and free electrons with electromagnetic fields. These bound and free electrons represent free charges and currents (which we call matter), and therefore the electromagnetic field is no longer free. We are therefore interested in the Hamiltonian that describes the interaction of light and matter. To construct it, all we need to do is take the Hamiltonian of Eq. (5.1.44) and replace the free electromagnetic field part by the expansion in Harmonic oscillators. The final Hamiltonian is

$$\boxed{H = \sum_{i=1}^{N} \frac{(\mathbf{p}_i - q_i\mathbf{A}(\mathbf{r}_i))^2}{2m_i} - \frac{1}{2\epsilon_0}\sum_{i,j=1}^{N} q_i q_j G_\phi(\mathbf{r}_i, \mathbf{r}_j) + \sum_n \hbar\omega_n \left(a_n^\dagger a_n + \frac{1}{2}\right)}. \tag{4.2.8}$$

4.2.2 Dipole approximation and dipole Hamiltonian

In many situations in quantum electrodynamics, the wavelength of the photons which the matter interacts with is much larger than the spatial extent of the system of charges. It follows then that the modes of the vector potential vary negligibly over the extent of the electronic wavefunctions. In that case, we may simply replace the $\mathbf{r}_i$ in the vector potential by $\mathbf{r}_0$, which can be thought of as the center of the distribution of charges. This approximation is called the *long-wavelength approximation*, and also the *dipole approximation*, as the result of the approximation is that the interaction between matter and light is well described as an interaction of the quantized electric field with the dipole moment of the system of charges. In this section, we will do a unitary transformation of the Hamiltonian to a much simpler form that is exactly equivalent in the dipole approximation.

Consider the following unitary transformation of the Hamiltonian prescribed by the operator $U = e^{\frac{i}{\hbar}\mathbf{d}\cdot\mathbf{A}(\mathbf{r}_0)}$, where $\mathbf{d} = \sum_{i=1}^{N} q_i\mathbf{r}_i$ is the total dipole moment associated with the charges. We would like to calculate $U^\dagger H U$. To do this, we will make heavy use of the Baker-Campbell-Hausdorff (BCH) formula:

$$e^A B e^{-A} = A + [A, B] + \frac{1}{2!}[A, [A, B]] + \frac{1}{3!}[A, [A, [A, B]]] + \dots. \tag{4.2.9}$$

As usual, the best strategy for evaluating these kinds of things is divide and conquer. Let’s evaluate the unitary rotation of $\mathbf{p}_i$, $\mathbf{A}(\mathbf{r}_i)$, and a_n. No unitary rotation needs to

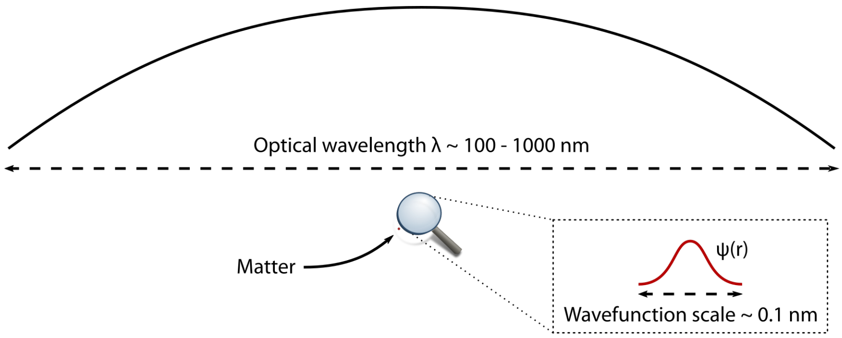

Figure 4.1: The dipole approximation is valid when the relevant optical wavelengths are many times larger than the scale of the matter. When this is the case, many calculations can be simplified by assuming that the electromagnetic field does not vary over the scale of the matter wavefunctions.

be done on the scalar potential terms, as they are functions of the position operators, which commute with the position operators in the argument of the exponential of U. According to BCH, for the kth component of the momentum $\mathbf{p}_i$:

$$U^\dagger p_{ik} U = p_{ik} - \frac{i}{\hbar}\sum_j q_j [r_{jk'} A_{k'}(\mathbf{r}_0), p_{ik}] + \cdots = p_{ik} - \frac{i}{\hbar}\sum_j q_j A_{k'}(\mathbf{r}_0)(i\hbar\delta_{ij}\delta_{kk'}) + \ldots, \tag{4.2.10}$$

where ... denotes the remaining terms of the expansion. We are using repeated index notation. The remaining terms are zero, as the second term is a multiple of the identity in the particle space, which will commute with p_{ik}. Therefore, we have

$$U^\dagger p_{ik} U = p_{ik} + q_i A_k(\mathbf{r}_0). \tag{4.2.11}$$

Now let's look at the unitary rotation of the vector potential.

$$U^\dagger A_k(\mathbf{r}_0) U = A_k(\mathbf{r}_0) - \frac{i}{\hbar}\sum_j q_j [r_{jk'} A_{k'}(\mathbf{r}_0), A_k(\mathbf{r}_0)] + \cdots = A_k(\mathbf{r}_0). \tag{4.2.12}$$

This is obvious, as the terms of vector potential are analogous to the position operator of the harmonic oscillator. And we know that the components of the position operator commute with themselves. Thus, the vector potential is unchanged by the rotation. But if that's the case, then we have that

$$U^\dagger \sum_{i=1}^{N} \frac{(\mathbf{p}_i - q_i \mathbf{A}(\mathbf{r}_0))^2}{2m_i} U = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}. \tag{4.2.13}$$

which is a very nice simplification. To conclude the transformation, we need to transform the creation and annihilation operators. Let's examine the unitary rotation of the creation operator

$$\begin{aligned} U^\dagger a_n^\dagger U &= a_n^\dagger - \frac{i}{\hbar}\sum_j q_j [r_{jk} A_k(\mathbf{r}_0), a_n^\dagger] + \cdots = a_n^\dagger - \frac{i}{\hbar}\sum_j q_j \mathbf{r}_j \sqrt{\frac{\hbar}{2\epsilon_0 \omega_n}} \mathbf{F}_n^*(\mathbf{r}_0) \\ &= a_n^\dagger - \frac{i}{\hbar}\sqrt{\frac{\hbar}{2\epsilon_0\omega_n}} \mathbf{d} \cdot \mathbf{F}_n^*(\mathbf{r}_0). \end{aligned} \tag{4.2.14}$$

Again, the second term is a multiple of the identity (this time on the photon space), and so the other terms in the series are zero. It follows by Hermitian conjugation that

$$U^\dagger a_n U = a_n + \frac{i}{\hbar}\sqrt{\frac{\hbar}{2\epsilon_0\omega_n}}\mathbf{d}\cdot\mathbf{F}_n(\mathbf{r}_0). \tag{4.2.15}$$

The number operator then transforms as

$$U^\dagger a_n^\dagger a_n U = \left(a_n^\dagger - \frac{i}{\hbar}\sqrt{\frac{\hbar}{2\epsilon_0\omega_n}}\mathbf{d}\cdot\mathbf{F}_n^*(\mathbf{r}_0)\right)\left(a_n + \frac{i}{\hbar}\sqrt{\frac{\hbar}{2\epsilon_0\omega_n}}\mathbf{d}\cdot\mathbf{F}_n(\mathbf{r}_0)\right). \tag{4.2.16}$$

Combining this with the $\hbar\omega_n$ and the summation, we have that the free-field Hamiltonian transforms into

$$\hbar\omega_n\left(a_n^\dagger a_n + \frac{1}{2}\right) - \mathbf{d}\cdot\left(i\sum_n\sqrt{\frac{\hbar\omega_n}{2\epsilon_0}}\left(\mathbf{F}_n a_n - \mathbf{F}_n a_n^\dagger\right)\right) + \frac{1}{2\epsilon_0}\sum_n\left|\mathbf{d}\cdot\mathbf{F}_n(\mathbf{r}_0)\right|^2. \tag{4.2.17}$$

Noting that the modal sum in parentheses in the second term is simply the electric field operator $\mathbf{E}(\mathbf{r}_0)$, we may write the QED Hamiltonian as

$$\begin{aligned} H = &\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} - \frac{1}{2\epsilon_0}\sum_{i,j=1}^N q_i q_j G_\phi(\mathbf{r}_i,\mathbf{r}_j) + \sum_n \hbar\omega_n\left(a_n^\dagger a_n + \frac{1}{2}\right) \\ &- \mathbf{d}\cdot\mathbf{E}(\mathbf{r}_0) + \frac{1}{2\epsilon_0}\sum_n\left|\mathbf{d}\cdot\mathbf{F}_n(\mathbf{r}_0)\right|^2 \end{aligned} \tag{4.2.18}$$

There are several main advantages of the dipolar Hamiltonian with respect to the Hamiltonian written in terms of the momentum. For one, the quadratic term in the vector potential has gone, leading to only a single interaction term between light and matter, in terms of the physical electric field. Another major advantage of this Hamiltonian relates to the meanings of the various operators. In particular, in the old frame (called the velocity frame from now on), the velocity is given by $\mathbf{v} = (\mathbf{p} - q\mathbf{A})/m$, meaning that the physical velocity of the particle is tied to the quantized field, making it difficult to interpret. Moreover, the momentum operator does not have a direct physical significance in this gauge. In the dipolar gauge, the velocity transforms to $U^\dagger\mathbf{v}U = \mathbf{p}/m$, making the physical velocity independent of the quantized field – and allowing much simpler and more intuitive interpretation of what the particles do versus what the photons do. There is a third reason, which has to do with the last term in the Hamiltonian, which is called the *dipole self-energy*, which we will elaborate on below.

As a rule then, when the long-wavelength approximation is valid, we will use the dipolar Hamiltonian.

Cancellation of the dipole self-energy with parts of the Coulomb Hamiltonian

In this section, we elaborate on the form of the dipolar self-energy, showing that it is completely cancelled by part of the Coulomb term (the second term) of Eq. 5.2.18. As a result, the final Hamiltonian describing the system of charges in the dipole gauge is

$$\boxed{H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2\epsilon_0}\sum_{i,j=1}^N \frac{q_i q_j}{4\pi\epsilon_0|\mathbf{r}_i - \mathbf{r}_j|} + \sum_n \hbar\omega_n\left(a_n^\dagger a_n + \frac{1}{2}\right) - \mathbf{d}\cdot\mathbf{E}(\mathbf{r}_0)}. \tag{4.2.19}$$

In the remainder of this section, we prove this remarkable simplification. But a reader interested primarily in applying this Hamiltonian to solve problems may skip this section without loss of continuity.

This cancellation implies that there is a connection between the radiation modes **F** and the solutions of the Poisson equation (which are connected to G_ϕ). They are connected by completeness: any radiation field can be expanded in the **F** functions, while any electrostatic field can be expanded in eigenfunctions ϕ of the Laplace equation. Together then, any electric field whatsoever can be expanded in terms of the **F**s and the ϕs. Let's now make this connection more precise.

To this end, let us define two tensorial projection functions, $\mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}'), \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}')$ as

$$\begin{aligned}\mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}') &= \sum_n \epsilon(\mathbf{r}')\mathbf{F}_n^*(\mathbf{r}')\mathbf{F}_n(\mathbf{r}) \\ \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}') &= -\sum_n \epsilon(\mathbf{r}')\nabla'\phi_n^*(\mathbf{r}')\nabla\phi_n(\mathbf{r})/\lambda_n,\end{aligned} \tag{4.2.20}$$

where the functions ϕ_n are eigenfunctions of the Laplace equation in a medium, with eigenvalue λ_n, defined by

$$\nabla\cdot\epsilon\nabla\phi_n = \lambda_n\phi_n \tag{4.2.21}$$

We have defined the second projection function with a minus sign as a matter of convenience. It is easy to show that the Laplace eigenfunctions, for a real permittivity, are orthonormal.

We have referred to these two functions as projection functions. Let us now show that they are. The claim is that $\mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}')$ projects a function onto the space spanned by the radiation modes, while $\mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}')$ projects a function onto the space spanned by the Laplace eigenfunctions. Let us start by projecting $\mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}')$ onto functions like $F_m(\mathbf{r})$ and $\nabla\phi_m(\mathbf{r})$, as follows:

$$\begin{aligned}\int d^3r'\ \mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}')\cdot\mathbf{F}(\mathbf{r}') &= \mathbf{F}_m(\mathbf{r}) \\ \int d^3r'\ \mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}')\cdot\nabla\phi_m(\mathbf{r}') &= 0.\end{aligned} \tag{4.2.22}$$

In the first, we have used the orthonormality of the radiation mode eigenfunctions. In the second, we have used the fact that the dot product of a divergenceless function and a curl-less function integrates to zero.

Meanwhile, projecting $\mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}')$ onto functions like $F_m(\mathbf{r})$ and $\nabla\phi_m(\mathbf{r})$, as follows:

$$\begin{aligned}\int d^3r'\ \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}')\cdot\mathbf{F}(\mathbf{r}') &= 0 \\ \int d^3r'\ \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}')\cdot\nabla\phi_m(\mathbf{r}') &= \nabla\phi_n(\mathbf{r}).\end{aligned} \tag{4.2.23}$$

In the first line, we have used the fact that the dot product of a divergenceless function and a curl-less function integrates to zero. In the second, we have used integration by parts and the orthonormality of the Laplace eigenfunctions. Notice that the minus sign, as well as the division by the eigenvalue were necessary to get the projection to come out to just the gradient of the Laplace eigenfunction. Suppose we decompose the electric field into radiation and electrostatic parts, as:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}^{\epsilon,\perp}(\mathbf{r}) + \mathbf{E}^{\epsilon,||}(\mathbf{r}), \tag{4.2.24}$$

with

$$\begin{aligned} \mathbf{E}^{\epsilon,\perp}(\mathbf{r}) &= \sum_n A_n \mathbf{F}_n(\mathbf{r}) \\ \mathbf{E}^{\epsilon,||}(\mathbf{r}) &= -\sum_n B_n \nabla \phi_n(\mathbf{r}). \end{aligned} \tag{4.2.25}$$

Then it immediately follows from the projection operators above that

$$\begin{aligned} \int d^3r' \ \mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}') \cdot \mathbf{E}^{\epsilon,\perp}(\mathbf{r}') &= \mathbf{E}^{\epsilon,\perp}(\mathbf{r}) \\ \int d^3r' \ \mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}') \cdot \mathbf{E}^{\epsilon,||}(\mathbf{r}') &= 0. \end{aligned} \tag{4.2.26}$$

and

$$\begin{aligned} \int d^3r' \ \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}') \cdot \mathbf{E}^{\epsilon,\perp}(\mathbf{r}') &= 0 \\ \int d^3r' \ \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}') \cdot \mathbf{E}^{\epsilon,||}(\mathbf{r}') &= \mathbf{E}^{\epsilon,||}(\mathbf{r}). \end{aligned} \tag{4.2.27}$$

Of course, from which it follows that

$$\int d^3r' \ (\mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}') + \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}')) \cdot \mathbf{E}(\mathbf{r}') = \mathbf{E}(\mathbf{r}), \tag{4.2.28}$$

meaning that in the space of electric field functions,

$$\mathbf{P}^{\epsilon,\perp}(\mathbf{r},\mathbf{r}') + \mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')I, \tag{4.2.29}$$

with I the 3×3 identity matrix.

To proceed, we need to understand the electrostatic projection function, $\mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}')$, better. It can be immediately shown that

$$\mathbf{P}^{\epsilon,||}(\mathbf{r},\mathbf{r}') = -\epsilon(\mathbf{r}')\nabla\nabla' G_\phi(\mathbf{r},\mathbf{r}'). \tag{4.2.30}$$

To see this, let us consider the defining equation for the Green's function

$$\nabla \cdot \epsilon \nabla G_\phi(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \tag{4.2.31}$$

Let us expand the delta function in terms of the Laplace eigenfunctions, similarly to what we did when finding the mode-expansion of the Green's function of the Maxwell equations in Chapter 3. Suppose we define

$$\begin{aligned} G_\phi(\mathbf{r},\mathbf{r}') &= \sum_n G_n \phi_n(\mathbf{r}) \\ \delta(\mathbf{r}-\mathbf{r}') &= \sum_n \delta_n \phi_n(\mathbf{r}). \end{aligned} \tag{4.2.32}$$

By taking inner products, it can immediately be seen that $\delta_n = \phi_n^*(\mathbf{r}')$. Plugging these expansions into Eq. (5.2.31) yields

$$G_\phi(\mathbf{r},\mathbf{r}') = \sum_n \phi_n^*(\mathbf{r}')\phi_n(\mathbf{r})/\lambda_n, \tag{4.2.33}$$

immediately proving the claim of Eq. (5.2.30).

Let us now consider the implications of Eq. (5.2.30) for Eq. (5.2.29). Eq. (5.2.29) then states

$$\sum_n \epsilon(\mathbf{r}')\mathbf{F}_n^*(\mathbf{r}')\mathbf{F}_n(\mathbf{r}) = \delta(\mathbf{r}-\mathbf{r}')I + \epsilon(\mathbf{r}')\nabla\nabla' G_\phi(\mathbf{r},\mathbf{r}'). \tag{4.2.34}$$

As we see here, the radiation modes are in fact connected to the electrostatic interactions encoded in G_ϕ.

With Eq. (5.2.34) in place, we can now consider the dipole self-energy term. Let us consider it in the context of a neutral system of charges (i.e., no ions) in a region where $\epsilon = 1$, for simplicity. If they are not, then additional complications related to *local field effects* arise. In accord with the long-wavelength approximation, the charges are also assumed to localized around position $\mathbf{R}$ with positions $\mathbf{R} + \mathbf{r}_i$. Defining the dipole moment $\mathbf{d} = \sum_i q_i \mathbf{r}_i$, we have that the dipole self-energy term is

$$\frac{1}{2\epsilon_0}\sum_{i,j} q_i q_j \mathbf{r}_i \cdot \left(\sum_n \mathbf{F}_n^*(\mathbf{R})\mathbf{F}_n(\mathbf{R})\right) \cdot \mathbf{r}_j. \tag{4.2.35}$$

From Eq. (5.34), we see that this term is

$$\frac{1}{2\epsilon_0}\sum_{i,j} q_i q_j \mathbf{r}_i \cdot \left(I\delta(0) + \nabla\nabla' G_\phi(\mathbf{R},\mathbf{R})\right) \cdot \mathbf{r}_j. \tag{4.2.36}$$

The first term is clearly infinite, but also has no dependence on the medium whatsoever. This term thus also appears in the free-space QED Hamiltonian. In the context of the free-space Hamitonian, that this first term is an infinite (non-identity) operator presents a problem, as it shifts the energy levels of the system by different infinite amounts (leading to infinite energy differences between states). This is clearly unacceptable, as is. It is however solvable by the program of *renormalization*, discussed in Chapter **??**. The resolution is that this term, in addition to other infinite contributions, lead to a *slight* change or renormalization of the energy levels of the matter in the absence of the electromagnetic field. Thus, functionally, this term is ignored, and we consider it as slightly changing the energy levels of the unperturbed system.

The second term however, looks quite a lot like another term in the Hamiltonian: the Coulomb interaction, given by

$$V_{\text{coul}} = -\frac{1}{2\epsilon_0}\sum_{i,j=1}^{N} q_i q_j G_\phi(\mathbf{r}_i,\mathbf{r}_j). \tag{4.2.37}$$

In fact, it is tempting to Taylor expand the Green's function, so that

$$V_{\text{coul}} \approx -\frac{1}{2\epsilon_0}\sum_{i,j=1}^{N} q_i q_j (G_\phi(\mathbf{R},\mathbf{R}) + \mathbf{r}_i \cdot \nabla\nabla' G_\phi(\mathbf{R},\mathbf{R}) \cdot \mathbf{r}_j). \tag{4.2.38}$$

The second term would exactly cancel the second term in the dipole self-energy. However, the Green's function has a rapidly varying part like $1/|\mathbf{r}_i - \mathbf{r}_j|$ associated with the free-space Coulomb interaction, making it un-justified to Taylor expand the Green's function this way. To solve this however, we can *split* the Green's function in two parts, as:

$$G(\mathbf{r},\mathbf{r}') = -\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|} + G^{\text{ind}}(\mathbf{r},\mathbf{r}'). \tag{4.2.39}$$

We claim that this second term varies *slowly* over the scale of the system of charges, provided that the system is far from the interface with a medium (compared to the extent of the emitter). This can be understood from the principle of superposition in electrostatics. When we place a charge near a medium, the total electrostatic potential is the sum of the potential of the charge, and the potential of the bound charges in the medium *induced* by the charge. In other words, the field created by a charge of magnitude q at position $\mathbf{r}'$ is

$$\phi = \frac{q}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{s}\,\frac{\rho^{\text{ind}}(\mathbf{s})}{4\pi\epsilon_0|\mathbf{r}-\mathbf{s}|}. \tag{4.2.40}$$

The first term corresponds to the free-space part of the Green's function, while the second corresponds to $G^{\text{ind}}(\mathbf{r},\mathbf{r}')$. Suppose distance of the system of charges to the medium (where induced charges are) is d and the extent of the system of charges is a. Then, it is clear from the previous equation that the potential of the induced charges varies slowly over a provided $a \ll d$, and can thus be Taylor expanded around the center of the system of charges. Therefore, we may write the Coulomb interaction as:

$$V_{\text{coul}} = \sum_{i,j=1}^{N}\frac{q_iq_j}{8\pi\epsilon_0|\mathbf{r}_i-\mathbf{r}_j|} - \frac{1}{2\epsilon_0}\sum_{i,j=1}^{N} q_iq_j(G^{\text{ind}}(\mathbf{R},\mathbf{R}) + \mathbf{r}_i\cdot\nabla\nabla' G^{\text{ind}}(\mathbf{R},\mathbf{R})\cdot\mathbf{r}_j). \tag{4.2.41}$$

For a neutral system of charges, $\sum_i q_i = 0$, simplifying the Coulomb interaction to

$$V_{\text{coul}} = \sum_{i,j=1}^{N}\frac{q_iq_j}{8\pi\epsilon_0|\mathbf{r}_i-\mathbf{r}_j|} - \frac{1}{2\epsilon_0}\sum_{i,j=1}^{N} q_iq_j\mathbf{r}_i\cdot\nabla\nabla' G^{\text{ind}}(\mathbf{R},\mathbf{R})\cdot\mathbf{r}_j. \tag{4.2.42}$$

Meanwhile from Eq. (5.2.36), we get (ignoring the $\delta(0)$ term)

$$\frac{1}{2\epsilon_0}\sum_{i,j} q_iq_j\mathbf{r}_i\cdot\left(-\nabla\nabla'\frac{1}{4\pi|\mathbf{r}-\mathbf{r}'|}\bigg|_{\mathbf{r}=\mathbf{r}'=\mathbf{R}} + \nabla\nabla' G^{\text{ind}}(\mathbf{R},\mathbf{R})\right)\cdot\mathbf{r}_j. \tag{4.2.43}$$

The first term is an infinite self-energy which doesn't depend on the medium, and can also functionally be ignored. The second term however, which is medium-dependent is cancelled by a term of opposite sign in V_{coul}. Therefore, neglecting infinite self-energy terms which don't affect subsequent calculations, the Hamiltonian reduces to:

$$H = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m} + \frac{1}{2\epsilon_0}\sum_{i,j=1}^{N}\frac{q_iq_j}{4\pi\epsilon_0|\mathbf{r}_i-\mathbf{r}_j|} + \sum_n \hbar\omega_n\left(a_n^\dagger a_n + \frac{1}{2}\right) - \mathbf{d}\cdot\mathbf{E}(\mathbf{r}_0), \tag{4.2.44}$$

completing the proof of this remarkable cancellation.

5 QUANTUM RADIATION BY BOUND ELECTRONS

5.1 FIRST-ORDER EMISSION PROCESSES

Let us start our survey of "elementary light-matter interaction processes" by considering processes that happen at first-order in perturbation theory.

5.1.1 Spontaneous emission into an arbitrary medium

We start by considering spontaneous emission of a dipole emitter in a general medium. We will express the rate in terms of general modes, and show then that the emission rate can be fully expressed in terms of the (imaginary part of) Green's function of the medium. We may then express the *spontaneous emission rate enhancement* (or Purcell enhancement) in terms of Green's functions, leading to a standard formula in the literature for the Purcell enhancement factor. We will then consider a special case of Purcell enhancement in a resonant cavity and show that for a cavity of quality factor Q and mode volume V that the enhancement goes like Q/V.

Consider a dipole-allowed transition between matter states e and g. The transition rate for radiative decay from e to g is

$$\Gamma = \frac{2\pi}{\hbar^2}\sum_n \frac{\hbar\omega_n}{2\epsilon_0}\mathbf{d}^{ge*}\cdot\mathbf{F}_n^*(\mathbf{r}_0)\mathbf{F}_n(\mathbf{r}_0)\cdot\mathbf{d}^{ge}\delta(\omega_{eg}-\omega_n). \tag{5.1.1}$$

We see a sum over modes of a dyadic expression in the modes with a delta function. This should be highly reminiscent of the mode expansion of the Green's function that we developed in Lecture 3. Recall that the imaginary part of the Green's function is simply

$$\text{Im }G(\mathbf{r_0},\mathbf{r_0},\omega) = \pi c^2\sum_n \frac{1}{2\omega_n}\mathbf{F}_n^*(\mathbf{r}_0)\mathbf{F}_n(\mathbf{r}_0)\delta(\omega_n-\omega). \tag{5.1.2}$$

Isolating the imaginary part of the Green's function in Equation (1) yields

$$\Gamma = \frac{2\omega_{eg}^2}{\hbar\epsilon_0 c^2}\mathbf{d}^{ge*}\cdot\text{Im }\mathbf{G}(\mathbf{r_0},\mathbf{r_0},\omega_{eg})\cdot\mathbf{d}^{eg}. \tag{5.1.3}$$

Let us remind ourselves about the Green's function of free space. This will serve both as a sanity check of the results derived here, as well as a way to parameterize the enhancement of spontaneous emission relative to free space. In free-space, the imaginary part of the Green's function is simply

$$\text{Im }G(\mathbf{r}_0,\mathbf{r}_0,\omega) = \frac{\pi c^2}{2\omega}\frac{V}{(2\pi)^3}\int d^3k\sum_{\hat{e}_\mathbf{k}}\frac{1}{V}\hat{e}_\mathbf{k}^*\hat{e}_\mathbf{k}\delta(\omega-ck), \tag{5.1.4}$$

which simplifies to

$$\text{Im }G(\mathbf{r}_0,\mathbf{r}_0,\omega) = \frac{\pi c^2}{2\omega}\frac{1}{(2\pi)^3}\int d^3k\ (I-\hat{k}\hat{k})\delta(\omega-ck). \tag{5.1.5}$$

Taking tensor components of this expression, we quickly recognize that the off-diagonal components are zero. Moreover, when doing the angular integrals, we find that all of them are equal. When the dust settles, the final result is

$$\text{Im } G(\mathbf{r}_0, \mathbf{r}_0, \omega) = \frac{\omega}{6\pi c} I. \tag{5.1.6}$$

It is isotropic and homogeneous, just as free space is. Plugging in this Green's function into Equation (3) yields the usual free-space spontaneous emission rate. More interestingly, if we call the spontaneous emission rate in free-space Γ_0, then

$$\frac{\Gamma}{\Gamma_0} = \frac{6\pi c}{\omega} \frac{\mathbf{d}^{*eg}}{|\mathbf{d}^{eg}|} \cdot \text{Im } \mathbf{G}(\mathbf{r}_0, \mathbf{r}_0, \omega_{eg}) \cdot \frac{\mathbf{d}^{eg}}{|\mathbf{d}^{eg}|}. \tag{5.1.7}$$

This expression for the spontaneous emission enhancement is called the *Purcell factor*. This is an extremely general formula for spontaneous emission enhancement in an arbitrary medium, and this formula has been studied extensively by many authors. Importantly, this quantity can be computed completely classically, as it depends only on the direction of the dipole, and the Green's function of the classical Maxwell equations, which can be computed numerically by simulating the Maxwell's equations for an oscillating dipole, and finding the imaginary part of the resulting complex electric field at the location of the dipole. This is often in practice what people do to calculate Purcell factors for most structures, as most structures are not amenable to an analytical treatment of the Green's function. Let us now do another example of the Purcell factor for an atom in a resonant cavity.

Purcell effect in a resonant cavity

Consider a resonant cavity with a single electromagnetic mode at frequency ω_0 and with lifetime γ. The lifetime can be due to either absorptive losses or radiative losses. The effect is the same. Calling the normalized mode $\mathbf{F}(\mathbf{r}_0) \equiv \frac{\mathbf{u}(\mathbf{r}_0)}{\sqrt{V}}$, with V the *mode volume*, the corresponding imaginary part of the Green's function is

$$\pi c^2 \text{Im } \frac{1}{\pi V} \frac{\mathbf{u}(\mathbf{r}_0)\mathbf{u}(\mathbf{r}_0)}{\omega_0^2 - \omega^2 - i\Gamma\omega} = \frac{\pi c^2}{V} \mathbf{u}(\mathbf{r}_0)\mathbf{u}(\mathbf{r}_0) \left(\frac{1}{\pi} \frac{\Gamma\omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega_0^2} \right), \tag{5.1.8}$$

where I've used that $\mathbf{u}$ is necessarily real for a time-reversal symmetric non-degenerate cavity mode (and for degenerate modes can be made real). Plugging in Equation (8) into the Purcell enhancement formula yields

$$\frac{\Gamma}{\Gamma_0} = \frac{6\pi^2 c^3}{\omega V} |\hat{n} \cdot \mathbf{u}(\mathbf{r}_0)|^2 \left(\frac{1}{\pi} \frac{\Gamma\omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2} \right) \tag{5.1.9}$$

where I've defined $\hat{n} = \frac{\mathbf{d}^{eg}}{|\mathbf{d}^{eg}|}$. Let us consider the (optimistic case) when the dipole is parallel to the mode polarization at $\mathbf{r}_0$, and is also on resonance with the cavity $\omega_0 = \omega$. Then the Purcell factor is

$$\frac{\Gamma}{\Gamma_0} = \frac{6\pi c^3}{\omega^2 \Gamma V} |\hat{n} \cdot \mathbf{u}(\mathbf{r}_0)|^2. \tag{5.1.10}$$

Defining the quality factor $Q = \frac{\omega_0}{\Gamma}$, we have

$$\frac{\Gamma}{\Gamma_0} = \frac{3}{4\pi^2} \frac{Q}{(V/\lambda^3)} |\hat{n} \cdot \mathbf{u}(\mathbf{r}_0)|^2. \tag{5.1.11}$$

where we have expressed the frequency in terms of the wavelength. As we see, the Purcell enhancement is related to the quality factor of the mode, as well as the ratio of the mode volume to the "volume of a photon". We see a residual dependence on where exactly the emitter is relative to the cavity mode. If it is placed in a node of the cavity, then the Purcell factor is zero.

Spontaneous emission by line-broadened atoms

In the previous section, we have assumed the electron to have perfectly discrete eigenstates, e and g. By this, we mean for example that if you start the atom in the state $|e\rangle$, as a function of time, it will change only by a time-dependent phase $e^{-i\omega_e t}$. However, for an excited state, this is not truly the case for a number of reasons. For one, the fact that an electron can undergo spontaneous emission means that the probability of the electron remaining in the excited state will decay exponentially as $e^{-\Gamma t}$. From basic principles of Fourier transforms, such a state must have some width in frequency about its center frequency, ω_e, of roughly Γ, implying that the electronic excited state is functionally a continuum of states, rather than a discrete state. We call the atomic state broadened. Mechanisms beyond spontaneous emission also lead to frequency broadening (also called line broadening), such as collisions with other atoms, emission of other particles such as lattice vibrations (for electrons in solids). Another important effect is *inhomogeneous broadening*, which is an effect of having many electrons with slightly different excited state frequencies. In this case, the atomic line is on average broadened into a continuum (assuming one has many atoms), and the net effect happens to be the same. It is called inhomogeneous broadening because the broadening is related to differences between atoms. Broadening mechanisms related to spontaneous emission and collisions are sometimes referred to as homogeneous broadening.

We now want to describe how spontaneous emission occurs in the presence of line broadening. The key observation is that the exponential decay of the excited state in this case is very much like the exponential decay of a photon in an absorbing (lossy) medium. Thus, any source of exponential decay is a type of loss, or damping mechanism, but for electrons instead of photons. For photons, we considered lossy systems through their Green's functions by taking the frequency denominators to be complex. For electrons, we will now do the same. The starting point of our calculation is the general observation, proved in Problem 1 of Chapter 1, that the transition rate induced by a perturbation V, in any quantum system, is given by

$$\Gamma = -\frac{2}{\hbar}\mathrm{Im}\,\langle i|VG(\omega_i)V|i\rangle, \tag{5.1.12}$$

where $G(E) = (H-E)^{-1}$ is the Green's function of the Schrodinger equation. Due to the loss in the electron system, the initial frequency should be taken as $\omega_i - i\gamma/2$, with γ the loss rate, and ω_i the real-valued frequency, just like we did for the lossy cavity in the previous section. The Green's function of the quantum mechanical system, assuming a two-level system coupled to photons, is given by

$$G(\omega_i) = \sum_p \frac{|g,p\rangle\langle g,p|}{E_g + E_p - E_i + i\gamma/2} + \frac{|e,p\rangle\langle e,p|}{E_e + E_p - E_i + i\gamma/2}, \tag{5.1.13}$$

where e, g are the excited and ground states of the two level system, with corresponding real-valued energies $E_{e,g}$ and p denotes states in the photonic Fock space, with corresponding energy E_p. To proceed, we identify that for spontaneous emission, the initial state is $|e, 0\rangle$ and that the perturbation is $-\mathbf{d} \cdot \mathbf{E}$. Assuming that there are no dipole matrix elements between e and e, as well as g and g, the only state that the perturbation can take the initial state to are $|g, n\rangle$, with n denoting a one-photon state in mode n. Taking this into account, we may write for the decay rate

$$\Gamma = -\frac{2}{\hbar^2}\mathrm{Im}\sum_n \frac{|\langle g, n|\mathbf{d}\cdot\mathbf{E}|e, 0\rangle|^2}{\omega_g + \omega_n - \omega_e + i\gamma/2} = \frac{1}{\hbar^2}\sum_n |\langle g, n|\mathbf{d}\cdot\mathbf{E}|e, 0\rangle|^2 \frac{\gamma}{(\omega_g + \omega_n - \omega_e)^2 + \gamma^2/4}. \tag{5.1.14}$$

In keeping with the results of the previous sections, let us express this result in terms of the Green's function of the Maxwell's equations. To do so, we evaluate the matrix elements to get

$$\Gamma = \frac{1}{\hbar^2}\sum_n \frac{\hbar\omega_n}{2\epsilon_0}\mathbf{d}^{ge*}\cdot\mathbf{F}_n^*(\mathbf{r}_0)\mathbf{F}_n(\mathbf{r}_0)\cdot\mathbf{d}^{ge}\frac{\gamma}{(\omega_g + \omega_n - \omega_e)^2 + \gamma^2/4}. \tag{5.1.15}$$

To massage the expression into a form where it may readily be expressed in terms of the imaginary part of the Green's function of the Maxwell equations, we multiply the RHS of the previous equation by $1 = \int_0^\infty d\omega\delta(\omega - \omega_n)$. Doing so, we arrive at

$$\Gamma = \frac{1}{\hbar^2}\sum_n \int_0^\infty d\omega\delta(\omega - \omega_n)\frac{\hbar\omega^2}{2\epsilon_0\omega_n}\mathbf{d}^{ge*}\cdot\mathbf{F}_n^*(\mathbf{r}_0)\mathbf{F}_n(\mathbf{r}_0)\cdot\mathbf{d}^{ge}\frac{\gamma}{(\omega_g + \omega - \omega_e)^2 + \gamma^2/4}, \tag{5.1.16}$$

where I have used the fact that $f(\omega)\delta(\omega - \omega_n) = f(\omega_n)\delta(\omega - \omega_n)$. Using Equation (V.2) for the modal representation of the Maxwell Green's function, we arrive at our final answer for the spontaneous emission rate of a line-broadened electron:

$$\Gamma = \frac{1}{\pi\epsilon_0\hbar c^2}\int_0^\infty d\omega\, \omega^2\mathbf{d}^{ge*}\cdot\mathrm{Im}\,\mathbf{G}(\mathbf{r}_0, \mathbf{r}_0, \omega)\cdot\mathbf{d}^{ge}\frac{\gamma}{(\omega_g + \omega - \omega_e)^2 + \gamma^2/4}. \tag{5.1.17}$$

Let's look at the implications of this for the Purcell effect by considering the emission into a single mode resonant cavity. Using the Green's function from the previous section for a single-mode cavity, we can immediately infer that

$$\Gamma = \frac{1}{\pi\epsilon_0\hbar V}|\mathbf{d}^{ge*}\cdot\mathbf{u}(\mathbf{r}_0)|^2\int_0^\infty d\omega\, \omega^2\frac{\Gamma\omega}{(\omega^2 - \omega_0^2)^2 + \Gamma^2\omega^2}\frac{\gamma}{(\omega_g + \omega - \omega_e)^2 + \gamma^2/4}. \tag{5.1.18}$$

To cast this equation into a more clearly symmetric form, we observe that in most cases of cavity emission, the cavity loss is small, and so the only frequencies in the cavity Lorentzian with a strong response will be concentrated around $\pm\omega_0$. However, only the plus sign is relevant strong response, because we can only get a strong response if ω_0 is near $\omega_e - \omega_g > 0$. Thus, we are interested in $\omega \approx \omega_0$, for which $\omega^2 - \omega_0^2$ may be approximated as $2\omega_0(\omega - \omega_0)$, leading to

$$\Gamma = \frac{1}{4\pi\epsilon_0\hbar\omega_0 V}|\mathbf{d}^{ge*}\cdot\mathbf{u}(\mathbf{r}_0)|^2\int_0^\infty d\omega\, \omega^2\frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2/4}\frac{\gamma}{(\omega_g + \omega - \omega_e)^2 + \gamma^2/4}. \tag{5.1.19}$$

As we see, the integral takes a quite symmetric form, integrating a cavity Lorentzian against a two-level system Lorentzian. As can easily be seen, this integral maximizes when $\omega_0 = \omega_{eg}$, as expected. What is less easy to see is that this integral maximizes when $\gamma = \Gamma$, a condition known as *Q-matching* or *critical coupling*. Two other limits of importance are $\gamma \ll \Gamma$ and $\gamma \gg \Gamma$. The first case corresponds to minimal electronic broadening compared to cavity broadening, and coincides exactly with what was considered in the previous section. The second case corresponds to a quite different limit in which the cavity Lorentzian can be treated as a delta function, yielding

$$\Gamma = \frac{\omega_0}{4\epsilon_0 \hbar V} |\mathbf{d}^{ge*} \cdot \mathbf{u}(\mathbf{r}_0)|^2 \frac{\gamma}{(\omega_g + \omega_0 - \omega_e)^2 + \gamma^2/4}. \tag{5.1.20}$$

On resonance, the rate is

$$\Gamma = \frac{Q_{el}}{\epsilon_0 \hbar V} |\mathbf{d}^{ge*} \cdot \mathbf{u}(\mathbf{r}_0)|^2, \tag{5.1.21}$$

where Q_{el} is the quality factor of the electronic state, defined as ω_0/γ. Like in the case where the cavity was broad but the electron was narrow, we would like to quantify how this rate compares to the rate of emission in free space. Dividing by the rate of free space emission, we have

$$\frac{\Gamma}{\Gamma_0} = \frac{3}{8\pi^2} \frac{Q_{el}}{(V/\lambda^3)} |\hat{n} \cdot \mathbf{u}(\mathbf{r}_0)|^2. \tag{5.1.22}$$

This result is essentially symmetric to the case where the electron was narrow and the cavity was broad, with the electronic quality factor taking the role of the photon quality factor in the previous section.

Spontaneous emission by many atoms: superradiance

Before moving to second-order processes, we would like to discuss an interesting phenomenon of spontaneous emission involving *many atoms* collectively interacting with a single photon mode. This phenomenon is called *superradiance* and refers to a group of atoms emitting much faster than you'd naively expect. For example, let's say we have N atoms, each which can individually do spontaneous emission with rate Γ. And let us suppose that only one of them is excited. Then you would expect that the rate of spontaneous emission is simply Γ. However, there are conditions where it can be $N\Gamma$. Similarly, if there are N excited atoms, there are situations where the decay rate can go as $N^2\Gamma$. Let us try and see how this happens. For simplicity, we will assume all of the atoms are two-level atoms, so that the Hamiltonian is

$$H = \sum_{i=1}^{N} \frac{\hbar\omega_0}{2} \sigma_{z,i} + H_{em} + \sum_{i=1}^{N} \mathbf{d}\sigma_{x,i} \cdot \mathbf{E}(\mathbf{r}_i), \tag{5.1.23}$$

where we have denoted the dipole matrix element of the two-level atoms as $\mathbf{d}$. This matrix element, the Pauli X operators, is the dipole operator of each atom. In what follows, we will also consider another simplification, introduced by Dicke, that the spatial extent of the atoms is much smaller than the wavelength of emitted light, so that the field does not vary over the atomic cloud. This represents in fact an important simplification. That reduces the Hamiltonian to

$$H = \omega_0 J_z + H_{em} + \frac{2\mathbf{d} \cdot \mathbf{E}(\mathbf{r}_0)}{\hbar} J_x, \tag{5.1.24}$$

where $J_z = \frac{\hbar}{2}\sum_{i=1}^{N}\sigma_{z,i}$ and $J_x = \frac{\hbar}{2}\sum_{i=1}^{N}\sigma_{x,i}$ are the total angular momenta in the z and x directions, respectively. We immediately recognize that the total angular momentum in the z-direction is the atomic part of the Hamiltonian, and that the total angular momentum in the x-direction is what couples to the (quantized) electric field. It is clear then that we want to organize the possible states of the atomic cloud into simultaneous eigenstates of J^2 and J_z denoted $|J, M\rangle$, with J the total angular momentum quantum number and M the z-directed angular momentum quantum number. The total z-angular momentum of the system is $\hbar M$. Recall also how addition of angular momentum works. If we have two spin 1/2 systems (e.g., two two-level atoms), then the Hilbert space of the joint system can be decomposed into a direct sum of spaces corresponding to different total angular momenta. For example

$$\frac{1}{2}\otimes\frac{1}{2} = 1\oplus 0, \tag{5.1.25}$$

or

$$\frac{1}{2}\otimes\frac{1}{2}\otimes\frac{1}{2} = \frac{3}{2}\oplus\frac{1}{2}\oplus\frac{1}{2}\oplus 0. \tag{5.1.26}$$

Let us now make the same assumption as Dicke, which is that we prepare the initial state of the atomic cloud so that all of the atoms are initially excited. We will denote this state as $|e\cdots e\rangle$. This state has a total z angular momentum of $\frac{\hbar N}{2}$, with N the number of atoms. As you can see from adding N spin 1/2 systems, the only J corresponding to a total z-angular momentum of $\hbar N/2$ is $\frac{N}{2}$.

If the evolution is according to this Hamiltonian, then the total angular momentum eigenvalue J^2 cannot change, and all evolution moves the state around the set of states $|\frac{N}{2}, M\rangle$. This is because J_z cannot change the total angular momentum, as the $|J, M\rangle$ states are eigenstates of J_z. J_x also cannot change the spin, as it is simply a sum of the raising and lowering operators $J_x = \frac{1}{2}(J_+ + J_-)$. These operators only change the M quantum number. The result of this somewhat complicated reasoning about angular momentum is that the set of atomic states we transition between during spontaneous emission are states of the form $|\frac{N}{2}, M\rangle$. As the transition operator J_x can only change M by ± 1, we have that the initial state of the atomic cloud $|e\cdots e\rangle = |\frac{N}{2}, \frac{N}{2}\rangle$ goes down to the state $|g\cdots g\rangle = |\frac{N}{2}, -\frac{N}{2}\rangle$ by radiative cascade. Before calculating the transition rate, which will now be a simple matter, let us also quickly state that the states in the $J = \frac{N}{2}$ manifold are always *fully symmetric* states with respect to permutations of atoms. This can be derived, but we will simply state it here. For example, the first state below $|e\cdots e\rangle$ is $|\frac{N}{2}, \frac{N}{2}-1\rangle = \frac{1}{\sqrt{N}}(|ge\cdots e\rangle + |ege\cdots e\rangle + \cdots |e\cdots eg\rangle)$. Similarly the state $|\frac{N}{2}, \frac{N}{2}-m\rangle$ can be expressed as $S|g_1\cdots g_m e_1\cdots e_{N-m}\rangle$, where S, the symmetrization operator, simply adds all permutations to this state, and normalizes it. With all that said, let us now find the spontaneous emission rate between two adjacent *superradiant states*. The emission rate between M and $M-1$ is simply

$$\Gamma = \frac{2\pi}{\hbar^2}\frac{4}{\hbar^2}|\langle M-1|J_x|M\rangle|^2\sum_n\frac{\hbar\omega_n}{2\epsilon_0}|\mathbf{d}\cdot\mathbf{F}_n(\mathbf{r}_0)|^2\delta(\omega_0-\omega_n) \tag{5.1.27}$$

Comparing this to the usual rate of spontaneous emission, we see a factor of

$$\frac{4}{\hbar^2}|\langle M-1|J_x|M\rangle|^2 = (J+M)(J-M+1), \tag{5.1.28}$$

where we have used yet another result from the theory of angular momentum. Namely that

$$J_-|J,M\rangle = \hbar\sqrt{(J+M)(J-M+1)}|J,M-1\rangle. \tag{5.1.29}$$

Let's look at a few cases of this. Let's look at the decay from the state $|\frac{N}{2},-\frac{N}{2}+1\rangle$ to $|\frac{N}{2},-\frac{N}{2}\rangle$. The former state has one excitation, symmetrically distributed over the atoms. The latter has all atoms in the ground state. Plugging in numbers, we see that the rate of emission is $N\Gamma_0$, which is N times the amount of radiation expected, given that only one atom is excited! This is sometimes called "the greatest radiation anomaly" inherent in superradiance, and for good reason. Another interesting case is when half of the atoms are excited, corresponding to $M=0$. In that case, the rate of emission goes as $\frac{N}{2}\left(\frac{N}{2}+1\right)\approx\frac{N^2}{4}$ in the large N limit. This is just essentially what we saw in the previous example, except now there are $O(N)$ excitations, leading to $O(N^2)$ radiation.

Absorption and Stimulated emission

We have discussed in quite some detail the quantum theory of spontaneous emission by atoms, in which an excited atom, in the absence of photons, emits a photon. However, it is also possible for an excited atom to emit a photon into some mode while simultaneously in the presence of photons occupying that same mode. In this case, the emission *into the same mode* is enhanced by the number of photons already in the mode, and is thus referred to as *stimulated emission*, because the emission is stimulated by the presence of photons. Of course, what is also possible is that an atom in the ground state can absorb a photon in some mode, reducing the overall number of photons in *that same mode* by one. This is called *absorption*. Occasionally, it is also referred to as stimulated absorption, to maintain parity with stimulated emission. Though of course, unlike the case of emission, there is no analogous spontaneous absorption, as it violates conservation of energy.

Let us now calculate the rate of absorption and stimulated emission. Let's consider stimulated emission, rather than absorption, since its treatment more closely mirrors what we have done for spontaneous emission. A naive formulation of the problem would be to simply take the initial state as $|e,N_k\rangle$, and the final state as $|g,N_k+1\rangle$ with $|e\rangle$ some excited state of the atom, $|g\rangle$ some state of lower energy, and $|N_k\rangle$ a Fock state that has N_k photons in mode k. The problem with this naive formulation is that there is no continuum of final states, and therefore exponential decay from initial to final state is not the expected dynamic. Rather, in the absence of any dissipation (line-broadening), the system, starting in one of those states, would undergo coherent oscillations between the initial and final states with some period determined by the number of photons. These are called *Rabi oscillations*, and will be elucidated in a later section.

This naive formulation of stimulated emission overlooks two important complications that "re-instate" a continuum. For one, the incident electromagnetic field may not be all in a single mode, but instead is spread out over modes in a narrow frequency range that overlaps with the atomic transition. This electromagnetic wavepacket has a continuum of modes in it and therefore there is a continuum of final states associated with which mode in the wavepacket gets stimulatedly emitted. This is a common case, and conceptually is very close to spontaneous emission. However, there is a second way to get a continuum, which is by having the atomic line be broadened (i.e., by having atomic losses). The latter source of a continuum is much more important in applications such as lasers. We will focus solely on this latter case here, leaving the former as an exercise to the reader.

To describe stimulated emission, let us take as the initial state $|e, N_k\rangle$. The transition rate of this system is given in terms of the Schrodinger Green's function as

$$\Gamma = -\frac{2}{\hbar}\text{Im }\langle i|VG(\omega_i)V|i\rangle. \tag{5.1.30}$$

The Green's function of the quantum mechanical system, assuming a two-level system coupled to photons, is given by

$$G(\omega_i) = \sum_p \frac{|g,p\rangle\langle g,p|}{E_g + E_p - E_i + i\gamma/2} + \frac{|e,p\rangle\langle e,p|}{E_e + E_p - E_i + i\gamma/2}, \tag{5.1.31}$$

where e, g are the excited and ground states of the two level system, with corresponding real-valued energies $E_{e,g}$ and p denotes states in the photonic Fock space, with corresponding energy E_p. Taking the light-matter interaction to be described by the dipole Hamiltonian, the transition rate is given by

$$\Gamma = -\frac{2}{\hbar}\text{Im}\left[\frac{(N_k+1)\frac{\hbar\omega_k}{2\epsilon_0}|\mathbf{d}^{ge}\cdot\mathbf{F}_k^*|^2}{E_g + (N_k+1)\hbar\omega_k + i\hbar\gamma/2 - (E_e + N_k\hbar\omega_k)} + \frac{N_k\frac{\hbar\omega_k}{2\epsilon_0}|\mathbf{d}^{ge}\cdot\mathbf{F}_k|^2}{E_g + (N_k-1)\hbar\omega_k + i\hbar\gamma/2 - (E_e + N_k\hbar\omega_k)}\right]. \tag{5.1.32}$$

In deriving the above equation, we have assumed as usual that there is no dipole matrix element between the excited state and itself, and have also used the fact that the electric field operator can only change the photon number by 1. We have also used the algebra of the harmonic oscillator in saying that $a^\dagger|N\rangle = \sqrt{N+1}|N+1\rangle$ and $a|N\rangle = \sqrt{N}|N-1\rangle$. Simplifying further yields

$$\Gamma = \frac{\gamma\omega_k}{2\hbar\epsilon_0}\left[\frac{(N_k+1)|\mathbf{d}^{ge}\cdot\mathbf{F}_k^*|^2}{(\omega_k-\omega_{eg})^2+\gamma^2/4} + \frac{N_k|\mathbf{d}^{ge}\cdot\mathbf{F}_k|^2}{(\omega_{eg}+\omega_k)^2+\gamma^2/4}\right]. \tag{5.1.33}$$

For the typical case of $\gamma \ll \omega_{eg}$, it is clear that when the photon is resonant with the transition, the first term is much larger than the second one (typically by several orders of magnitude). Making this approximation, we have that

$$\Gamma = (N_k+1)\frac{\omega_k}{\hbar\epsilon_0}|\mathbf{d}^{ge}\cdot\mathbf{F}_k^*|^2\frac{\gamma/2}{(\omega_{eg}-\omega_k)^2+\gamma^2/4}. \tag{5.1.34}$$

This is the rate of stimulated emission. When there are no photons initially in the mode, the rate coincides with that of Eq. (V.15). We should discuss the second term that we approximated away, as it on first glance looks odd: it represents the possibility of absorbing a photon, while the atom goes from the excited state to the ground state. This process appears to violate conservation of energy, and if the atom had no losses, it would. This would manifest in Eq. (V.33), as the Lorentzian in the second term would become a delta function $\delta(\omega_{eg}+\omega_k) = 0$. However, when losses are present, part of the excited state technically extends below the ground state (which we assumed here to be perfectly sharp). These states below the ground state could in fact absorb a photon and be promoted to the excited state in an energy conserving way, but for small losses, the fraction of the excited below the ground state is negligible. For the excited state needs to be so broad that a significant part of it is below the ground state. However, when this happens, the low-loss approximation that lead to the specific form of the Green's function we used is violated, and the results of Eq. (V.33) should simply not be trusted.

To conclude this section, we discuss absorption. Taking now the initial state as $|g, N_k\rangle$, and following the same treatment that led to Eq. (V.34), one can easily show that the rate of absorption is given by

$$\Gamma = N_k \frac{\omega_k}{\hbar\epsilon_0} |\mathbf{d}^{ge} \cdot \mathbf{F}_k|^2 \frac{\gamma/2}{(\omega_{eg} - \omega_k)^2 + \gamma^2/4}, \tag{5.1.35}$$

which is effectively the same, except with N_k instead of $N_k + 1$. As expected, when there are no photons present, there is no absorption.

A first look at lasers

5.2 SECOND-ORDER EMISSION PROCESSES

Rayleigh scattering

Now that we have developed a lot more machinery, we can revisit a problem that was described in Chapter 1 in more generality and depth: the problem of a photon scattering off of an atom in the ground state. Such scattering is referred to a Rayleigh scattering, which famously results in blue skies and sunsets. In this process, we consider initial states $|i\rangle = |g, 1_k\rangle$ and final states $|f\rangle = |g, 1_{k'}\rangle$, where g is the atomic ground state, and k (k') is the initial (final) photonic mode. Parameterized this way, we have also assumed that the scattering process is elastic. Since we have assumed the atom returns to the ground state by the end of the interaction, the only way this is possible is if the initial and final photon states have the same frequency ($\omega_k = \omega_{k'}$). To use the second order Fermi Golden Rule in the dipole approximation, we first compute the second order amplitude:

$$\sum_n \frac{V_{fn} V_{ni}}{\omega_{in} + i\eta} = \sum_a \frac{\hbar}{2\epsilon_0} \sqrt{\omega_k \omega_{k'}} \left[\frac{(\mathbf{d}^{ga} \cdot \mathbf{F}^*_{k'}(\mathbf{r}_0))(\mathbf{d}^{ag} \cdot \mathbf{F}^*_k(\mathbf{r}_0))}{\omega_{ga} + \omega_{k'} + i\eta} + \frac{(\mathbf{d}^{ga} \cdot \mathbf{F}_k(\mathbf{r}_0))(\mathbf{d}^{ag} \cdot \mathbf{F}^*_{k'}(\mathbf{r}_0))}{\omega_{ga} - \omega_{k'} + i\eta} \right] \tag{5.2.1}$$

$$= \frac{\hbar^2 \omega_k}{2\epsilon_0} F_i^{(k)} F_j^{(k')*} \alpha_{ij}(\omega_k), \tag{5.2.2}$$

where $\alpha_{ij}(\omega_k)$ is the atomic polarizability as defined in Eq. 1.1.83. By assuming an elastic collision, we can write

$$\Gamma = \frac{2\pi}{\hbar^4} \sum_{k'} \left| \frac{\hbar^2 \omega_k}{2\epsilon_0} F_i^{(k)} F_j^{(k')*} \alpha_{ij}(\omega_k) \right|^2 \delta(\omega_k - \omega_{k'}) \tag{5.2.3}$$

$$= \frac{2\pi}{\hbar^4} \sum_{k'} \left(\frac{\hbar^2 \omega_k}{2\epsilon_0} \right)^2 F_i^{(k)} F_j^{(k')*} F_l^{(k)} F_m^{(k')*} \alpha_{ij}(\omega_k) \alpha^*_{lm}(\omega_k) \delta(\omega_k - \omega_{k'}) \tag{5.2.4}$$

$$= \frac{\omega^3}{\epsilon_0^2 c^2} F_i^{(k)}(\mathbf{r}_0) \alpha_{ij}(\omega) \operatorname{Im} G_{jm}(\mathbf{r}_0, \mathbf{r}_0, \omega) \alpha^*_{lm}(\omega) F_l^{(k)*}(\mathbf{r}_0) \tag{5.2.5}$$

$$= \frac{\omega^3}{\epsilon_0^2 c^2} \mathbf{F}_k(\mathbf{r}_0) \cdot \left[\alpha(\omega) \operatorname{Im} G(\mathbf{r}_0, \mathbf{r}_0, \omega) \alpha^\dagger(\omega) \right] \cdot \mathbf{F}^*_k(\mathbf{r}_0). \tag{5.2.6}$$

where in the last few steps we have started denoting the incoming frequency by ω. We note that the final quantity in brackets is a tensor. Using this equation in the case of free space where $\mathbf{F}_k(\mathbf{r}) = \hat{e}e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$ and assuming an isotropic polarizability very quickly gives

$$\Gamma = \frac{c}{V}\frac{\omega^4|\alpha(\omega)|^2}{6\pi\epsilon_0^2 c^4} = \frac{c}{V}\sigma. \tag{5.2.7}$$

It is worth noting that this calculation can actually be performed much more quickly, leveraging what we already know about linear response and spontaneous emission. Physically, Rayleigh scattering can be interpreted in the following way: an incoming field in mode k interacts with some piece of matter in its ground state; this incoming field, through linear response, induces a dipole moment in the matter at frequency ω_k, with an amplitude determined by the polarizability $\alpha(\omega_k)$; this induced dipole then radiates (through spontaneous emission), into other modes k' in the surroundings, which is the scattered field.

To implement this perspective in the calculation, we begin with the field associated with a single incoming photon in mode k: $E_{k,i} = \sqrt{\hbar\omega_k/2\epsilon_0}F_{k,i}(\mathbf{r}_0)$. Then, the induced dipole is $d_i = \alpha_{ij}E_{k,j} = \sqrt{\hbar\omega_k/2\epsilon}\alpha_{ij}F_{k,j}$. Then, we can use the spontaneous emission formula from a dipole, now replacing the usual spontaneous transition dipole moment with this induced dipole, to obtain:

$$\Gamma = \frac{2\omega^2}{\hbar\epsilon_0 c^2}d_i \operatorname{Im} G_{ij}(\mathbf{r}_0,\mathbf{r}_0,\omega)d_j^* = \frac{\omega^3}{\epsilon_0^2 c^2}\mathbf{F}_k\cdot\left[\alpha(\omega)\operatorname{Im} G(\mathbf{r}_0,\mathbf{r}_0,\omega)\alpha^\dagger(\omega)\right]\cdot\mathbf{F}_k^*. \tag{5.2.8}$$

This exactly matches the formula we obtained through the more cumbersome method. The key takeaway here is that the second order calculation for Rayleigh scattering really just amounts to linear response plus spontaneous emission. Thus, if we have already done the hard work of establishing both of these individually, the answer to the scattering problem drops out almost trivially. This perspective will become relevant again soon, when we look at nonlinear optical processes.

Resonance fluorescence

Let us now move to light-emission processes which can only be described at second-order in perturbation theory. But to warm up to this, let us consider an example "halfway" between first- and second-order perturbation theory. In particular, we start by considering the problem of *resonance fluorescence,* in which an electron in an atom absorbs a photon whose energy is equal (or nearly equal) to a transition energy in the system, and then subsequently re-emits. The initial state of this process is taken to be $|g,m\rangle$, with g the ground state of the atom and m a single-photon state in mode m. The final state of the process is taken to be $|g,n\rangle$, with n a single-photon in a different mode n. The leading-order contribution to this process comes from second-order in perturbation theory. The corresponding transition rate is

$$\Gamma = \frac{2\pi}{\hbar^4}\sum_n\left(\frac{\hbar}{2\epsilon_0}\right)^2\omega_m\omega_n\left|\sum_a\frac{(\mathbf{d}^{ga}\cdot\mathbf{F}_m)(\mathbf{d}^{ag}\cdot\mathbf{F}_n^*)}{\omega_g-\omega_a-\omega_n+i\frac{\Gamma_a}{2}}+\frac{(\mathbf{d}^{ga}\cdot\mathbf{F}_n^*)(\mathbf{d}^{ag}\cdot\mathbf{F}_m)}{\omega_g+\omega_m-\omega_a+i\frac{\Gamma_a}{2}}\right|^2\delta(\omega_m-\omega_n). \tag{5.2.9}$$

As mentioned before, we are particularly interested in the case where the absorption of photon m is nearly resonant with some atomic state b, i.e., $\omega_g + \omega_m = \omega_b$. As we can see from the denominators, the first term in the sum over intermediate states can never have a resonance for finite frequency photons. The second term however can. Let us assume the existence of a state b for which $\omega_g + \omega_m \approx \omega_b$ (to within $\Gamma_b/2$). This term dominates the sum completely, and the resonance fluorescence rate becomes approximately

$$\Gamma = \frac{2\pi\omega_m^2}{4\epsilon_0^2\hbar^2}|\mathbf{d}^{bg}\cdot\mathbf{F}_m|^2\sum_n \frac{|\mathbf{d}^{gb}\cdot\mathbf{F}_n^*|^2}{(\omega_m-\omega_{bg})^2+\frac{\Gamma_b^2}{4}}\delta(\omega_m-\omega_n). \tag{5.2.10}$$

We briefly comment that for the case of N initial photons in mode m, the resonance fluorescence rate is simply scaled by a factor of N. Finally, we note that the sum over modes and delta function can be cast in terms of the imaginary part of the Green's function to give the general formula

$$\Gamma = \frac{\omega^3}{\epsilon_0^2\hbar^2c^2}\frac{|\mathbf{d}^{bg}\cdot\mathbf{F}_m(\mathbf{r}_0)|^2}{(\omega-\omega_{bg})^2+\frac{\Gamma_b^2}{4}}\mathbf{d}^{gb}\cdot\operatorname{Im}G(\mathbf{r}_0,\mathbf{r}_0,\omega)\cdot\mathbf{d}^{bg} \tag{5.2.11}$$

Let us consider the special case of an atom in free space, in which the relevant dipole transition is z-polarized, and the initial photon has frequency ω, and polarization $\hat{\epsilon}$. Then the resonance fluorescence rate (for N photons) is simply given by.

$$\Gamma = \frac{\pi\omega^2}{2\epsilon_0^2\hbar^2}\frac{N}{V}\frac{|d^{bg}|^4\hat{\epsilon}_z^2}{(\omega_m-\omega_{bg})^2+\frac{\Gamma_b^2}{4}}\int\frac{d^3k}{(2\pi)^3}\sum_{\hat{\epsilon}_\mathbf{k}}\hat{\epsilon}_{\mathbf{k}z}^2\delta(\omega-\omega_n) \tag{5.2.12}$$

The sum over polarizations simply reduces to $\sin^2\theta$ as usual. The frequency integral simply yields $\frac{\omega^2}{c^3}$. Defining an angular cross section for resonance fluorescence, $\frac{d\sigma}{d\Omega} = \frac{V}{cN}\frac{d\Gamma}{d\Omega}$, we have that

$$\frac{d\sigma}{d\Omega} = \frac{\omega^4}{16\pi^2\epsilon_0^2c^4\hbar^2}\frac{|d^{bg}|^4\hat{\epsilon}_z^2\sin^2\theta}{(\omega_m-\omega_{bg})^2+\frac{\Gamma_b^2}{4}}, \tag{5.2.13}$$

which is indeed the known result. We can see that the resonance fluorescence cross section shares the $\omega^4\sin^2\theta$ dependence of the Rayleigh scattering process we discussed as an example of perturbation theory. The main difference here is that near-resonance, there is a strong enhancement of the scattering, which is to be expected because the absorption part of the fluorescence process becomes much more efficient near resonance. To complete the discussion of resonance fluorescence, let us consider the magnitude of the total cross section on resonance. To calculate the total cross section, we integrate over solid angles. The angular integral as usual is $\frac{8\pi}{3}$, and the corresponding cross section is

$$\sigma = \frac{\omega^4}{6\pi\epsilon_0^2c^4\hbar^2}\frac{|d^{bg}|^4\hat{\epsilon}_z^2}{(\omega_m-\omega_{bg})^2+\frac{\Gamma_b^2}{4}} = \frac{12\pi c^2\omega^6|d^{bg}|^4}{72\pi^2\epsilon_0^2\hbar^2c^6}\frac{\hat{\epsilon}_z^2}{(\omega_m-\omega_{bg})^2+\frac{\Gamma_b^2}{4}} = \frac{12\pi}{2}\frac{c^2}{\omega^2}\frac{\frac{\Gamma_b^2}{4}}{(\omega_m-\omega_{bg})^2+\frac{\Gamma_b^2}{4}}, \tag{5.2.14}$$

where in the last part of the equality, we have assumed that the lifetime of the state b is purely radiative in nature. On resonance, the cross section becomes

$$\sigma = \frac{3}{2\pi}\lambda^2\hat{\epsilon}_z^2, \tag{5.2.15}$$

with λ the wavelength of the incident radiation. The effort to re-arrange the result in this fashion is well worth it, because it tells us that the effective size of an atom as seen by a resonant photon is *much* larger than the size of the atom. For light of energy 1 eV, the effective size of an atom appears to be on the order of a micron, much larger than its size of angstroms.

Two-photon spontaneous emission

We now move to a more complicated second-order process, namely the simultaneous emission of two-photons by an atom. In particular, we will consider transitions from an initial state $|e, 0\rangle$ to final states of the form $|g, m, n\rangle$. The rate of such a process immediately follows from Fermi's Golden Rule at second order as:

$$\Gamma = \frac{1}{2}\frac{2\pi}{\hbar^4}\sum_{m,n}\left(\frac{\hbar}{2\epsilon_0}\right)^2 \omega_m\omega_n \left|\sum_a \frac{(\mathbf{d}^{ga}\cdot\mathbf{F}_m^*)(\mathbf{d}^{ae}\cdot\mathbf{F}_n^*)}{\omega_e-\omega_a-\omega_n} + \frac{(\mathbf{d}^{ga}\cdot\mathbf{F}_n^*)(\mathbf{d}^{ae}\cdot\mathbf{F}_m^*)}{\omega_e-\omega_a-\omega_m}\right|^2 \delta(\omega_{eg}-\omega_m-\omega_n). \tag{5.2.16}$$

The overall $\frac{1}{2}$ out in front simply indicates that the unconstrained sum over m and n is redundant, as flipping the order of $|m, n\rangle$ and $|n, m\rangle$ are the same state. Let us write the dot product in terms of indices, as well as reverse indices on the second term in order to get

$$\Gamma = \frac{\pi}{4\epsilon_0^2\hbar^2}\sum_{m,n}\omega_m\omega_n\left|\left(\sum_a \frac{d_i^{ga}d_j^{ae}}{\omega_e-\omega_a-\omega_n} + \frac{d_j^{ga}d_i^{ae}}{\omega_e-\omega_a-\omega_m}\right)F_{mi}^*F_{nj}^*\right|^2 \delta(\omega_{eg}-\omega_m-\omega_n) \tag{5.2.17}$$

Like the Rayleigh scattering problem, it is useful to take the complicated sum over intermediate states and give it a name. Let us call it the *transition polarizability*. In other words

$$\alpha_{ij}^{ge}(\omega_m, \omega_n) \equiv \sum_a \frac{d_i^{ga}d_j^{ae}}{\omega_e-\omega_a-\omega_n} + \frac{d_j^{ga}d_i^{ae}}{\omega_e-\omega_a-\omega_m}. \tag{5.2.18}$$

Expanding the square then leads to the emission rate

$$\Gamma = \frac{\pi}{4\epsilon_0^2\hbar^2}\sum_{m,n}\omega_m\omega_n\alpha_{ij}^{ge}(\omega_m, \omega_n)\alpha_{rs}^{ge*}(\omega_m, \omega_n)F_{mi}^*F_{nj}^*F_{mr}F_{ns}\delta(\omega_{eg}-\omega_m-\omega_n). \tag{5.2.19}$$

Let us now express this in terms of Green's functions. The end result will have the imaginary part of the Green's function appear twice. Recalling that the imaginary part of the Green's function has a delta function, we see that we are short a delta function. Let us then multiply the expression by $1 = \int d\omega\ \delta(\omega - \omega_m)$. Doing so (and some additional multiplications by 1), we have

$$\begin{aligned}\Gamma = \frac{1}{\pi\epsilon_0^2\hbar^2c^4}\int_0^{\omega_{eg}} d\omega \sum_{m,n}\omega_m^2\omega_n^2\frac{\pi c^2}{2\omega_m}\frac{\pi c^2}{2\omega_n}\alpha_{ij}^{ge}(\omega_m, \omega_n)\alpha_{rs}^{ge*}(\omega_m, \omega_n)F_{mi}^*F_{nj}^*F_{mr}F_{ns} \\ \times\,\delta(\omega_{eg}-\omega_m-\omega_n)\delta(\omega-\omega_m),\end{aligned} \tag{5.2.20}$$

where we have truncated the limits of integration of the delta function, as $\omega_m > 0$ and if $\omega_m > \omega_{eg}$, energy cannot be conserved and the corresponding contribution to the emission rate is zero anyway. Recognizing that $\delta(\omega_{eg} - \omega_m - \omega_n)\delta(\omega - \omega_m) =$

$\delta(\omega_{eg} - \omega_n - \omega)\delta(\omega - \omega_m)$, and that $\omega_m^2\omega_n^2 = \omega^2(\omega_{eg} - \omega)^2$, we may immediately replace the sum over m and n by delta functions. This yields:

$$\Gamma = \frac{1}{\pi\epsilon_0^2\hbar^2c^4}\int_0^{\omega_{eg}} d\omega\, \omega^2(\omega_{eg}-\omega)^2\alpha_{ij}^{ge}(\omega,\omega_{eg}-\omega)\alpha_{rs}^{ge*}(\omega,\omega_{eg}-\omega) \times \text{Im}\, G_{ir}(\mathbf{r}_0,\mathbf{r}_0,\omega)\text{Im}\, G_{js}(\mathbf{r}_0,\mathbf{r}_0,\omega_{eg}-\omega), \tag{5.2.21}$$

where we have restored the position dependence of the Green's function. To keep the form identical to that in the literature, we note that in a time-reversal symmetric system, the Green's function evaluated at two points is symmetric. Thus we may switch the indices of the Green's function if we want. Judiciously doing so exposes that the matrix structure is that of a trace.

$$\Gamma = \frac{1}{\pi\epsilon_0^2\hbar^2c^4}\int_0^{\omega_{eg}} d\omega\, \omega^2(\omega_{eg}-\omega)^2\text{tr}\Big[\alpha(\omega,\omega_{eg}-\omega)\text{Im}\, G(\mathbf{r}_0,\mathbf{r}_0,\omega_{eg}-\omega) \times \alpha^{ge\dagger}(\omega,\omega_{eg}-\omega)\text{Im}\, G(\mathbf{r}_0,\mathbf{r}_0,\omega)\Big]. \tag{5.2.22}$$

Decay rate of the 2s state in Hydrogen:

The general formula derived for the 2-photon decay rate is a pleasing result, but it would be even more pleasing if we were able to use it to obtain a physical numerical result. To this end, we will discuss the 2s → 1s two-photon transition rate in Hydrogen, which has been experimentally measured at a very slow $\Gamma_{2s\rightarrow 1s} \approx 8.23/\text{s}$, corresponding to a lifetime of 120 milliseconds. The greatest obstacle in performing an exact calculation is the computation of the atomic transition polarizability defined in Eq. 5.2.18. If the transition polarizability is known, then the use of Eq. 5.2.22 is relatively straightforward. With this in mind, we will first manipulate Eq. 5.2.18 into a form which reveals the scaling of the transition rate, and isolates the cumbersome part of the calculation as a dimensionless integral. This will enable us to make an order of magnitude estimation of the 2s decay rate without excessive labor. At the end of the section, the details for exact evaluation of the transition polarizability will be provided, leading to a precise numerical result which matches experimental results.

In free space, the imaginary part of the Maxwell Green function evaluated at two idential points is, as we have shown, given by $\text{Im}\,\mathbf{G}(0,0,\omega) = \frac{\omega}{6\pi c}I$, where I is the 3×3 identity. Since the general expression for 2-photon decay involves an integral over freqeuncies, it is useful to define a differential decay rate per unit frequency, which we will call $d\Gamma/d\omega$. This quantity is dimensionless, and carries information about the rate of photon emission from a particular part of the spectrum. We can then immediately write

$$\frac{d\Gamma}{d\omega} = \frac{1}{\pi\epsilon_0^2\hbar^2c^4}\frac{\omega^3(\omega-\omega_{eg})^3}{(6\pi c)^2}\text{Tr}[\alpha(\omega,\omega_{eg}-\omega)\alpha^\dagger(\omega,\omega_{eg}-\omega)], \tag{5.2.23}$$

where so far we have only assumed that the emission occurs in free space, and have made no assumptions about the emitter's electronic structure. We will now convert the transition polarizability into a dimensionless form factor by identifying appropriate scales. Referring to its definition in Eq. 5.2.18, we see that it has units of dipole moment squared over frequency. The dipole moment scale for simple atoms is ea_0, where a_0 is the Bohr radius, while for the frequency denominator we can use ω_{eg}. This allows us to define a dimensionless polarizability tensor $\tilde{\alpha} \equiv (e^2 a_0^2/\omega_{eg})\alpha$. Making this conversion, simplifying constants, and making groups of the fine structure constant, we can write

$$\frac{d\Gamma}{d\omega} = \frac{4}{9\pi}\alpha^2 \frac{\omega^3(\omega_{eg}-\omega)^3 a_0^4}{\omega_{eg}^2 c^4} \operatorname{Tr}[\tilde{\alpha}(\omega, \omega_{eg}-\omega)\tilde{\alpha}^\dagger(\omega, \omega_{eg}-\omega)]. \tag{5.2.24}$$

We now have a form that is amenable to scaling analysis and numerical estimation. The result is manifestly unitless, and has been sucessfully separated into two parts: one containing relevant scales of the system, and the other a form factor which is complicated, but of order unity. For the 2s to 1s transition in atomic hydrogen, $\omega_{eg} = 1.55 \times 10^{16}$ rad/s. Since the differential decay rate should be symmetrical about $\omega_{eg}/2$, we will estimate it at this point. This estimation yields a final decay rate of $\Gamma_{2s\to 1s} \approx 1.5$ per second, which is not far from the experimental value of 8.23/sec, and indicates that $\tilde{\alpha}$ is correctly performing its role as a form factor. In terms of scaling, there is one more analysis we can make by converting frequency over speed of light into a free space wave vector. This is

$$\frac{d\Gamma}{d\omega} \sim \alpha^2 (ka_0)^4 \operatorname{Tr}[\alpha\alpha^\dagger]. \tag{5.2.25}$$

Here, $k = \omega/c = 2\pi/\lambda_0$ is the free space wavevector, which scales with inverse proportion to the wavelength. With this in mind, we have $(ka_0)^4 \sim (a_0/\lambda_0)^4$ which indicates how the wavelength of emitted radiation compares to atomic size. For this particular transition, the peak of the 2-photon radiation spectrum is around 242 nm, which is more than 4500 times larger than the bohr radius. When discussing single photon spontaneous emission, we saw that in free space, atomic systems make generally poor antennas for emitting radiation. For two photon processes this is still true, but the scaling is even worse. While the free space dipole rate scales as $(ka_0)^2$, here we have $(ka_0)^4$. This analysis is at the heart of the physics which explains why the lifetime of the 2s state in hydrogen (milliseconds) is so large, compared to that of the 2p state (nanoseconds) for instance.

For completeness, we can now analyze the $2s \to 1s$ transition polarizability of hydrogen to obtain a numerically accurate value of the transition rate. All of the key physics has been discussed, so what follows is essentially a mathematical exercise. As a result, this section can be skipped without any loss of continuity.

To start, we turn our attention to Eq. 5.2.18, which after inserting states more explicitly, and converting the frequency denominator into energies with $\hbar$, can be equivalently written as

$$\alpha_{ij}^{ge}(\omega_m, \omega_n) = e^2\hbar \sum_a \frac{\langle g|r_i|a\rangle \langle a|r_j|e\rangle}{E_e - E_a - \hbar\omega_n} + \frac{\langle g|r_j|a\rangle \langle a|r_i|e\rangle}{E_e - E_a - \hbar\omega_m}. \tag{5.2.26}$$

The most foreboding aspect of this expression is that it requires summation over *all eigenstates of Hydrogen*, denoted $|a\rangle$. What's more is that due to the nature of energy differences in the denominator, substantial contributions can arise from high energy eigenstates, including those in the continuum of ionized states with eigenenergies which exceed the binding energy of Hygroden. To do this sum in a way which is more slick, we employ a Green's function trick which we have actually seen already in some form. Recall how in our description of photonic modes in arbitrary media, we use the Maxwell

Green's function to encode sums over states. That way, once the sum over states has been performed once, the Green's function result can be used more broadly in calculations involving light-matter interactions. It turns out we use the same logic for the electronic states. In other words, we will use the Green's function for the Schrodinger equation for hydrogen to perform the sum over intermediate electronic states.

Given a Hamiltonian H, the Schrodinger Green's function $G(E)$ can be defined through an operator equation as

$$(E-H)G(E) = I, \tag{5.2.27}$$

where I is of course the identity operator. Then we can define matrix elements like $G(\mathbf{r},\mathbf{r}',E) \equiv \langle \mathbf{r}|G(E)|\mathbf{r}'\rangle$, which satisfy

$$(E-H)G(\mathbf{r},\mathbf{r}',E) = \delta^{(3)}(\mathbf{r}-\mathbf{r}'). \tag{5.2.28}$$

For now we continue to work abstractly, and we can "solve" Eq. 5.2.27 for $G(E)$ by inversion, and an insertion of a complete set of states $\sum_a |a\rangle\langle a|$, as

$$G(E) = \frac{I}{E-H} = \sum_a \frac{|a\rangle\langle a|}{E-E_a}, \tag{5.2.29}$$

where we have used the fact that $H|a\rangle = E_a|a\rangle$. Note that formally speaking, this sum includes all eigenstates of the Hamiltonian, including both bound and ionized states. Comparing Eq. 5.2.29 with Eq. 5.2.26, we notice a striking similarity. Using this observation, we can express the transition polarizability in terms of the Green's function operator as

$$\begin{align} \alpha_{ij}^{ge}(\omega_m,\omega_n) &= e^2\hbar\left[\langle g|r_i G(E_e-\hbar\omega_n) r_j|e\rangle + \langle g|r_j G(E_e-\hbar\omega_m) r_i|e\rangle\right] \tag{5.2.30} \\ &= e^2\hbar\int d^3r\, d^3r' \left[r_i r'_j \psi_g^*(\mathbf{r})\psi_e(\mathbf{r}')G(\mathbf{r},\mathbf{r}',E_e-\hbar\omega_n) + r_j r'_i \psi_g^*(\mathbf{r})\psi_e(\mathbf{r}')G(\mathbf{r},\mathbf{r}',E_e-\hbar\omega_m)\right], \tag{5.2.31} \end{align}$$

where we have inserted two complete sets of position states to put all states and operators into known functional forms. The formal setup for this calculation is now mostly done – we have expressed the atomic transition polarizability of Hydrogen in terms of the two wavefunctions $\psi_{e,g}(\mathbf{r})$ we are transitioning between, as well as the position-space representation of the Green's function for Hydrogen $G(\mathbf{r},\mathbf{r}',E)$. This Green's function can fortunately be referenced from the literature, and is given as

$$G(\mathbf{r},\mathbf{r}',E) = \frac{m}{4\pi i\hbar^2 k r r'}\sum_{l=0}^{\infty}(2l+1)P_l(\cos\gamma)\Gamma(1+l-i\nu)W_{i\nu}^{l+1/2}\left(-2ikr_>\right)M_{i\nu}^{l+1/2}\left(-2ikr_<\right) \tag{5.2.32}$$

where γ is the angle between $\mathbf{r}$ and $\mathbf{r}'$, $r_>$ and $r_<$ are the larger and smaller of r and r', and we define $k = \sqrt{2mE/\hbar^2}$, $\nu = 1/(ka_0)$, and $a_0 = 4\pi\epsilon_0\hbar^2/(me^2)$. Additionally, W and M are Whittaker functions, which can be defined in terms of hypergeometric functions as

$$\begin{align} M_{i\nu}^{l+1/2}(z) &= e^{-z/2}z^{l+1}{}_1F_1(l+1-i\nu, 2l+2; z) \tag{5.2.33} \\ W_{i\nu}^{l+1/2}(z) &= e^{-z/2}z^{l+1}U(l+1-i\nu, 2l+2; z). \tag{5.2.34} \end{align}$$

While this form of the Green's function is technically correct, it will be more useful to have it represented as an expansion in products of spherical harmonics. This will be particularly convenient since in the most general case, one will need to take angular integrals of the Green's function against the hydrogenic wavefunctions. In order to accomplish this, we will make use of the identity

$$P_l(\cos\gamma) = \frac{4\pi}{2l+1}\sum_{m=-l}^{l} Y_{lm}(\theta,\phi)Y^*_{lm}(\theta',\phi'). \tag{5.2.35}$$

After making this substitution, we can write the whole Green's function as a spherical harmonic expansion

$$G(\mathbf{r},\mathbf{r}',E) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} g_l(r,r',E)Y_{lm}(\theta,\phi)Y^*_{lm}(\theta',\phi'), \tag{5.2.36}$$

where

$$g_l(r,r',E) = \frac{m}{i\hbar^2 krr'}\Gamma(1+l-i\nu)W^{l+1/2}_{i\nu}(-2ikr_>)M^{l+1/2}_{i\nu}(-2ikr_<). \tag{5.2.37}$$

We are now ready to use this to compute the transition polarizability. Since we are only considering s to s transitions, and hydrogen has spherical symmetry, the atomic transition polarizability tensor will be diagonal and isotropic, expressable as $\alpha_{ij}(\omega_n,\omega_m) = \delta_{ij}\alpha(\omega_n,\omega_m)$. In other words, there is only one scalar quantity we need to compute. This means that we can pick any component we want. If we focus on the xx component, this means that $r_x = r\sin\theta\cos\phi$, and likewise for r'_x. The the only part of the expression with angular coordinate dependence can be isolated,

$$\sum_{m=-l}^{l}\left|\int d\Omega\, \sin\theta\cos\phi Y_{lm}(\theta,\phi)\right|^2 = \frac{4\pi}{3}\delta_{l=1}. \tag{5.2.38}$$

which is nonzero only for $l = 1$, and $m = \pm 1$. This means that only g_1 can contribute to the polarizability, forcing $l = 1$ everywhere. This means that both the l and m sums have been taken care of, allowing us to write an integral which is purely radial:

$$\alpha^{ge}(\omega_m,\omega_n) = \frac{4\pi e^2 m_e\Gamma(2-i\nu_n)}{3i\hbar k_n}\int_0^\infty dr\, r^2\int_0^\infty dr'\, r'^2\psi^*_g(r)\psi_e(r')W^{3/2}_{i\nu_n}(-2ik_n r_>)M^{3/2}_{i\nu_n}(-2ik_n r_<) + (n\to m). \tag{5.2.39}$$

Here, $k_n \equiv \sqrt{2m(E_e-\hbar\omega_n)/\hbar^2}$ and similarly $\nu_n = 1/(k_n a_0)$.

The final result is

where $\tilde{\alpha}(\omega,\omega_{eg}-\omega)$ is a dimensionless version of the scalar polarizability, which we can write as

$$\tilde{\alpha}(\omega,\omega_{eg}-\omega) \equiv \frac{4\pi}{27i}\left(\frac{ma_0^2\omega_{eg}^2}{\hbar\omega_{eg}}\right)\times \tag{5.2.40}$$

$$\left[\nu\Gamma(1-i\nu)\int_0^\infty\int_0^\infty du\, du'\, (uu')^2\psi_g(u)\psi_e(u')W^{3/2}_{i\nu_n}(-2iu_>/\nu)M^{3/2}_{i\nu_n}(-2iu_</\nu) + (\omega\to\omega_{eg}-\omega)\right] \tag{5.2.41}$$

So far, the only assumption we have made is that the transition is between s-states, and hence the angular integrals have been completed independently of the wavefunctions

$\psi_{e,g}$. If we consider the 2s → 1s transition in Hydrogen, then we have the dimensionless wavefunctions

$$\psi_{1s}(u) = \frac{1}{\sqrt{\pi}} e^{-u} \tag{5.2.42}$$

$$\psi_{2s}(u) = \frac{1}{4\sqrt{2\pi}} (2-u) e^{-u/2}. \tag{5.2.43}$$

Plugging these in and evaluating the integrals numerically, we can finally find the total differential transition rate. Integrating this curve, we obtain the total decay rate of 8.23/sec which is in excellent agreement with lifetime measurements of the 2s state.

5.3 HIGHER-ORDER EMISSION PROCESSES AND OPTICAL NONLINEARITIES

Nonlinear susceptibility

Let us now consider a single example of a emission process that only occurs at higher order in perturbation theory. The process that we shall consider is *second harmonic generation*. The second harmonic generation process is one in which an electron absorbs two photons of frequency ω and emits a single photon of frequency 2ω. This process is the most elementary process of the field of *nonlinear optics*, the field of optics which concerns itself with induced polarizations that are nonlinear in the field strength. The most elementary (and most relevant) process of second-harmonic generation can be described as a transition of the form $|g, Nq\rangle \to |g,(N-2)q,k\rangle$, where q and k are generic mode labels. As you can see, there two photons are absorbed, and one is emitted. The lowest order at which this process can happen is at third-order in perturbation theory. As a reminder, the expression for the transition rate is

$$\Gamma = \frac{2\pi}{\hbar^6} \sum_f \left| \sum_{n_1,n_2} \frac{V^{f,n_2} V^{n_2,n_1} V^{n_1,i}}{(\omega_i - \omega_{n_1})(\omega_i - \omega_{n_2})} \right|^2 \delta(\omega_{fi}). \tag{5.3.1}$$

We will assume that there are no resonant contributions to the second-harmonic generation (i.e., that the two-photon absorption is merely virtual). This is typically the case anyway. Let us now plug in details relevant to our problem. Let's start with energy conservation. Energy conservation for this problem implies $\omega_k = 2\omega_q$, that the emitted photon is the second harmonic of the first. Now let us consider the sum over intermediate states. The intermediate states correspond to the atom being in different states a, b, as well as different orders of emission and absorption. As the two absorbed photons are identical, there are only three orders for absorption emission, which we can label as (using A for absorption and E for emission): AAE, AEA, EAA. The corresponding terms in the sum over intermediate states are (before squaring)

$$\text{Term 1} = \sum_{a,b} \frac{d_i^{gb} d_j^{ba} d_l^{ag}}{(\omega_g - \omega_a + \omega_q)(\omega_g - \omega_b + 2\omega_q)} \left(\frac{\hbar}{2\epsilon_0}\right)^{3/2} \sqrt{N(N-1)\omega_q^2 \omega_k} F_{k,i}^* F_{q,l} F_{q,j}, \tag{5.3.2}$$

$$\text{Term 2} = \sum_{a,b} \frac{d_j^{gb} d_i^{ba} d_l^{ag}}{(\omega_g - \omega_a + \omega_q)(\omega_g - \omega_b + \omega_q - \omega_k)} \left(\frac{\hbar}{2\epsilon_0}\right)^{3/2} \sqrt{N(N-1)\omega_q^2\omega_k} F_{q,j} F_{k,i}^* F_{q,l}, \tag{5.3.3}$$

$$\text{Term 3} = \sum_{a,b} \frac{d_l^{gb} d_j^{ba} d_i^{ag}}{(\omega_g - \omega_a - \omega_k)(\omega_g - \omega_b + \omega_q - \omega_k)} \left(\frac{\hbar}{2\epsilon_0}\right)^{3/2} \sqrt{N(N-1)\omega_q^2\omega_k} F_{q,l} F_{q,j} F_{k,i}^* \tag{5.3.4}$$

The indices were re-arranged to make all the fields the same, as we did in two-photon emission. We'll also simplify the denominators using the fact that $\omega_k = 2\omega_q$. The three terms then become

$$\text{Term 1} = \sum_{a,b} \frac{d_i^{gb} d_j^{ba} d_l^{ag}}{(\omega_g - \omega_a + \omega_q)(\omega_g - \omega_b + 2\omega_q)} \left(\frac{\hbar}{2\epsilon_0}\right)^{3/2} \sqrt{N(N-1)\omega_q^2\omega_k} F_{k,i}^* F_{q,l} F_{q,j}, \tag{5.3.5}$$

$$\text{Term 2} = \sum_{a,b} \frac{d_j^{gb} d_i^{ba} d_l^{ag}}{(\omega_g - \omega_a + \omega_q)(\omega_g - \omega_b - \omega_q)} \left(\frac{\hbar}{2\epsilon_0}\right)^{3/2} \sqrt{N(N-1)\omega_q^2\omega_k} F_{q,j} F_{k,i}^* F_{q,l}, \tag{5.3.6}$$

$$\text{Term 3} = \sum_{a,b} \frac{d_l^{gb} d_j^{ba} d_i^{ag}}{(\omega_g - \omega_a - 2\omega_q)(\omega_g - \omega_b - \omega_q)} \left(\frac{\hbar}{2\epsilon_0}\right)^{3/2} \sqrt{N(N-1)\omega_q^2\omega_k} F_{q,l} F_{q,j} F_{k,i}^*. \tag{5.3.7}$$

We may then express the sum in the following, following the spirit of the discussions of Rayleigh scattering and two-photon emission.

$$\text{Sum of terms} \equiv \hbar^2 \sqrt{\frac{\hbar\omega_k}{2\epsilon_0}} F_{k,i}^* \alpha_{ijl}^{(2)}(\omega_q, \omega_q; 2\omega_q) E_{q,j} E_{q,l}, \tag{5.3.8}$$

where

$$\begin{aligned} \alpha_{ijl}^{(2)}(\omega_q, \omega_q; 2\omega_q) = & \frac{1}{\hbar^2} \sum_{a,b} \frac{d_i^{gb} d_j^{ba} d_l^{ag}}{(\omega_g - \omega_a + \omega_q)(\omega_g - \omega_b + 2\omega_q)} \\ & + \frac{d_j^{gb} d_i^{ba} d_l^{ag}}{(\omega_g - \omega_a + \omega_q)(\omega_g - \omega_b - \omega_q)} + \frac{d_l^{gb} d_j^{ba} d_i^{ag}}{(\omega_g - \omega_a - 2\omega_q)(\omega_g - \omega_b - \omega_q)} \end{aligned} \tag{5.3.9}$$

and $E_{q,j} \equiv \sqrt{\frac{\hbar\omega_q N}{2\epsilon_0}} F_{q,j}$. In general, we are interested in making contact with the classical limit of second-harmonic generation, in which there many photons in the initial field, and therefore $N \gg 1$ and $N - 1 \approx N$. We have made this approximation. The additional constants were chosen because the quantity $\alpha_{ijk}^{(2)}$ is a known one in nonlinear optics. It is called the *second-order polarizability*. Combining everything together, the rate of emission of photon k is

$$\Gamma = \frac{2\pi}{\hbar^2} \sum_k \frac{\hbar\omega_k}{2\epsilon_0} |\mathbf{d} \cdot \mathbf{F}_k^*|^2 \delta(\omega_k - 2\omega_q), \tag{5.3.10}$$

where we have defined $d_i = \alpha_{ijl}^{(2)} E_{q,j} E_{q,l}$. Look at what just happened. This says that the rate of emission of photons at the second harmonic is just spontaneous emission by a dipole created at frequency 2ω whose amplitude is nonlinear in the strength of the initial field. This is the standard interpretation of nonlinear optical processes.

6 FLUCTUATIONAL ELECTRODYNAMICS

6.0.1 The fluctuation dissipation thoerem

6.0.2 Quantization of the Electromagnetic field in dispersive and absorbing media

In the previous sections, we have quantized the electromagnetic field in dielectric systems, and we made the strong assumption that the dielectric material is both non-dissipative and non-dispersive. This is of course a strong assumption, as it is not true of many materials, especially ones that enable strong interactions between matter and electromagnetic fields, such as metals, which support highly confined plasmons. In the previous sections, we went far without having to deal with material dissipation, predicting spontaneous emission, the Purcell effect, scattering, fluorescence, optical nonlinearities, and the Casimir-Polder force. We were even able to generalize many of our results to absorbing media (or so we claimed) by expressing final answers in terms of Green's functions, a concept which remains valid even in absorbing media, despite that the underlying modes which we expressed the Green's function in terms of are no longer orthonormal and complete. While this method is quite economical, it is not satisfying, and it would be ideal to have a justified formal framework that also more automatically deals with electromagnetic interactions in dissipative media without ever going through modes.

In this section, we quantize the electromagnetic field in linear, absorbing media. Our program for quantizing the field will be to recognize that in any material system, the field is dictated by the polarization currents inside the material. We will thus quantize the currents in an arbitrary material, promoting the currents to bosonic excitations, whose properties will be constrained by the *fluctuation-dissipation theorem*. By forcing the current operator to be consistent with the fluctuation-dissipation theorem, it allows us to quantize any medium in terms of its dielectric permittivity without thinking about the microscopic details of the system, and without thinking about modes. We will then use the Green's function in order to connect the quantized currents to a quantized field operator.

6.0.3 Fluctuation-dissipation theorem

To start carrying out this program, we need to understand the fluctuations of the electromagnetic field in a medium. We can connect these fluctuations ultimately to fluctuations of currents in the medium by the electromagnetic relation

$$\mathbf{E}(\mathbf{r},\omega) = i\omega\mu_0 \int d^3r' \; \mathbf{G}(\mathbf{r},\mathbf{r}',\omega)\mathbf{j}(\mathbf{r}',\omega). \tag{6.0.1}$$

Through this, we may then express field-field correlation functions in terms of current-current correlation functions. This connection motivates us to understand some general properties of correlation functions of physical observables. The general property we would like to develop connects correlation functions to imaginary parts of response functions. This property is called the *fluctuation-dissipation theorem*, and is one of the most important and powerful theorems in the physics of linear systems. What we will now show in particular is that the current-current correlator is proportional to the imaginary part of the dielectric permittivity.

The setup for this theorem is as follows: consider a quantum system whose observables $A_i(\mathbf{r})$ couples to a time-dependent classical field $X_i(\mathbf{r}, t)$ by the interaction Hamiltonian (written in the interaction picture)

$$V_{int} = -\int d^3x \, \mathbf{A}_I(\mathbf{r}, t) \cdot \mathbf{X}(\mathbf{r}, t). \tag{6.0.2}$$

In a system where the observable is electric polarization, the coupling field is simply the electric field, such that $\mathbf{A} = \mathbf{P}$ and $\mathbf{X} = \mathbf{E}$. When the observable is charge density, the coupling field is the electric potential. When the observable is electric current density, the coupling field is the vector potential. When the observable is magnetization density, the coupling field is the magnetic field. Recall from Lecture 2 that if we apply a perturbing field $\mathbf{X}(\mathbf{r}, t) = \int \frac{d\omega}{2\pi} \, e^{-i\omega t} \mathbf{X}(\mathbf{r}, \omega)$, then the Fourier transform of the expectation value of the observable $\mathbf{A}$ in the time-dependent state is given from linear response theory by

$$\langle \mathbf{A}(\mathbf{r}, t) \rangle = \int d^3x' dt' \, \chi^{A,A}(\mathbf{r}, \mathbf{r}', t, t') \mathbf{X}(\mathbf{r}', t'), \tag{6.0.3}$$

where the "AA" susceptibility is given from the Kubo formula by

$$\chi^{A,A}(\mathbf{r}, \mathbf{r}', t, t') = \frac{i}{\hbar} \theta(t - t') \langle [\mathbf{A}(\mathbf{r}, t), \mathbf{A}(\mathbf{r}', t')] \rangle. \tag{6.0.4}$$

This form is slightly more general than the one we worked out for the dipole-dipole susceptibility in Section 2. There, we simply had $\chi^{d,d}(t, t') = -\frac{i}{\hbar} \theta(t - t') \langle [\mathbf{d}(t), \mathbf{d}(t')] \rangle$, and the susceptibility function was simply the atomic polarizability. The only real difference is the position argument in the observables, which is to be expected from the fact that in the Hamiltonian of Equation (275), the perturbing field couples to the quantum observable at every point in space, rather than some specific origin of coordinates, like in the case when the coupling Hamiltonian is simply $-\mathbf{d} \cdot \mathbf{E}$. Therefore, we leave the derivation of Equations (276) and (277) as an exercise in first-order perturbation theory. Note that the expectation value is taken with respect to some state. This state, for a quantum system at zero temperature, is typically the ground state, while for a system at finite temperature, is described (in the canonical ensemble) by a thermal density matrix of the form $\rho = \frac{e^{-\beta H}}{Z} = \sum_m \frac{e^{-\beta E_m}}{Z} |m\rangle\langle m|$, with $\beta = (kT)^{-1}$ the inverse temperature, H the unperturbed Hamiltonian of the quantum system, and $Z = \sum_m e^{-\beta E_m}$ is the partition function. In that case, the expectation value simply means $\langle A \rangle = \text{tr} \, \rho A$. Recall also from Lecture 2 that for a time-translation invariant unperturbed Hamiltonian, $\chi(t, t') = \chi(t - t')$. Similarly for a space-translation invariant Hamiltonian, $\chi(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r} - \mathbf{r}')$. We will assume time-translation invariance but not space-translation invariance. For a time-translation invariant system, what is more useful than the time-dependent susceptibility is its Fourier transform $\chi^{A,A}(\mathbf{r}, \mathbf{r}', \omega)$. If we take the Kubo formula (for the ground state, i.e., at zero temperature), expand the commutator, and insert a complete set of states in between the two **A**s, then the frequency-domain susceptibility is simply

$$\chi^{A,A}(\mathbf{r},\mathbf{r}',\omega) = -\frac{1}{\hbar}\sum_n \left(\frac{A_i^{0n}(\mathbf{r})A_j^{n0}(\mathbf{r}')}{\omega-\omega_{n0}+i\eta} - \frac{A_j^{0n}(\mathbf{r}')A_i^{n0}(\mathbf{r})}{\omega+\omega_{n0}+i\eta} \right), \tag{6.0.5}$$

For a system at finite temperature, taking the trace of the thermal density matrix and the commutator immediately yields

$$\chi^{A,A}(\mathbf{r},\mathbf{r}',\omega) = -\frac{1}{\hbar Z}\sum_{m,n} e^{-\beta\hbar\omega_m} \left(\frac{A_i^{mn}(\mathbf{r})A_j^{nm}(\mathbf{r}')}{\omega-\omega_{nm}+i\eta} - \frac{A_j^{mn}(\mathbf{r}')A_i^{nm}(\mathbf{r})}{\omega+\omega_{nm}+i\eta} \right). \tag{6.0.6}$$

While evaluation of the trace necessary to arrive at this result is straightforward, it is illuminating to realize that this formula for the finite-temperature susceptibility is simply the result of noting that: (1) at finite temperature, all quantum states m are occupied with probability $p_m = e^{-\beta\hbar\omega_m}/Z$, (2) Equation (278) generalizes to an initial eigenstate $|m\rangle$ by $0 \to m$, and (3) Equation (278) is simply a weighted average over such generalizations to different eigenstates, with thermal probability p_m.

As we discussed in the general discussion of linear response functions of Lecture 2, the imaginary part of this response function tells us about energy dissipation. In particular, Im $\chi^{A,A}(\mathbf{r},\mathbf{r}',\omega)$ is a measure of how much the energy of the field **X** at frequency ω changes due to interaction with the quantum system. If the imaginary part is positive, then energy is absorbed and transferred to the quantum system. If negative, then energy is (stimulatedly) emitted and transferred to the field. As can be seen from Equation (279), the imaginary part of the response is given simply by

$$\mathrm{Im}\,\chi_{ij}^{A,A}(\mathbf{r},\mathbf{r}',\omega) = \frac{\pi}{\hbar Z}\sum_{m,n} e^{-\beta\hbar\omega_m} \Big(A_i^{mn}(\mathbf{r})A_j^{nm}(\mathbf{r}')\delta(\omega-\omega_{nm}) - A_j^{mn}(\mathbf{r}')A_i^{nm}(\mathbf{r})\delta(\omega+\omega_{nm}) \Big). \tag{6.0.7}$$

This may be further cleaned up by taking $m \leftrightarrow n$ in the second term, which yields

$$\mathrm{Im}\,\chi_{ij}^{A,A}(\mathbf{r},\mathbf{r}',\omega) = \frac{\pi}{\hbar Z}\sum_{m,n} (e^{-\beta\hbar\omega_m} - e^{-\beta\hbar\omega_n}) A_i^{mn}(\mathbf{r})A_j^{nm}(\mathbf{r}')\delta(\omega-\omega_{nm}). \tag{6.0.8}$$

This will be our final form for the dissipation. Let us now relate this dissipation to fluctuations (thermal and quantum) of the observable **A**. To this end, let us define the correlation function

$$S^{AA}(\mathbf{r},\mathbf{r}',t,t') \equiv \langle \mathbf{A}(\mathbf{r},t)\mathbf{A}(\mathbf{r}',t')\rangle = \mathrm{tr}\,\rho\mathbf{A}(\mathbf{r},t)\mathbf{A}(\mathbf{r}',t'). \tag{6.0.9}$$

Taking as our density matrix the thermal density matrix, and inserting a complete set of states, it is immediately clear that for a time-translation invariant system

$$S_{ij}^{AA}(\mathbf{r},\mathbf{r}',t,t') = S_{ij}^{AA}(\mathbf{r},\mathbf{r}',t-t') = \frac{1}{Z}\sum_{m,n} e^{i\omega_{mn}(t-t')-\beta\hbar\omega_m} A_i^{mn}(\mathbf{r})A_j^{nm}(\mathbf{r}'). \tag{6.0.10}$$

This leads immediately to the Fourier transform

$$S_{ij}^{AA}(\mathbf{r},\mathbf{r}',\omega) = \frac{2\pi}{Z}\sum_{m,n} e^{-\beta\hbar\omega_m} A_i^{mn}(\mathbf{r})A_j^{nm}(\mathbf{r}')\delta(\omega-\omega_{nm}). \tag{6.0.11}$$

Already one sees a close relation between these fluctuations and the dissipation. In fact, they are proportional. Take equation (281) and factor out $e^{-\beta\hbar\omega_m}$ to obtain

$$\mathrm{Im}\,\chi_{ij}^{A,A}(\mathbf{r},\mathbf{r}',\omega) = \frac{\pi}{\hbar Z}(1-e^{-\beta\hbar\omega})\sum_{m,n} e^{-\beta\hbar\omega_m} A_i^{mn}(\mathbf{r})A_j^{nm}(\mathbf{r}')\delta(\omega-\omega_{nm}), \tag{6.0.12}$$

where we have made use of the delta function constraint. This immediately leads to the *fluctuation-dissipation theorem*

$$\mathrm{Im}\,\chi_{ij}^{A,A}(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{2\hbar}(1-e^{-\beta\hbar\omega})S_{ij}^{AA}(\mathbf{r},\mathbf{r}',\omega). \tag{6.0.13}$$

We note briefly that we have considered an *unsymmetrized* correlation function. It is also sometimes relevant to consider symmetrized correlation functions of the form

$$S_{ij}^{AA,\mathrm{sym}}(\mathbf{r},\mathbf{r}',t,t') \equiv \langle A_i(\mathbf{r},t)A_j(\mathbf{r}',t') + A_j(\mathbf{r}',t')A_i(\mathbf{r},t)\rangle. \tag{6.0.14}$$

A similar set of manipulations as before immediately yields

$$\mathrm{Im}\,\chi_{ij}^{A,A}(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{2\hbar}\tanh\left(\frac{1}{2}\beta\hbar\omega\right)S_{ij}^{AA,\mathrm{sym}}(\mathbf{r},\mathbf{r}',\omega). \tag{6.0.15}$$

This is one of those cases where a set of mundane and simple manipulations leads to a result of *deep* and *extreme* physical importance. Let us take a breath and reflect on what we've done. The theorems of Equations 286 and 288 connect non-equilibrium energy-transfer to equilibrium fluctuations in the system. This theorem leads to a lot of surprising connections between seemingly disparate physical phenomena.

6.0.4 Electromagnetic field operator in an absorbing medium

We may now use what we have developed to quantize the electromagnetic field in a dissipative medium. In particular, the dissipation in the material, by the fluctuation dissipation theorem, is related to fluctuations of the underlying currents in the material. In particular, fluctuations in the polarization density are related by the polarization-polarization susceptibility by

$$\mathrm{Im}\,\chi_{ij}^{P,P}(\mathbf{r},\mathbf{r}',\omega) = \frac{1}{2\hbar}\tanh\left(\frac{1}{2}\beta\hbar\omega\right)S_{ij}^{PP,\mathrm{sym}}(\mathbf{r},\mathbf{r}',\omega). \tag{6.0.16}$$

From the kind of reasoning we used in Lecture 2, we note that the imaginary part of the polarization-polarization susceptibility is simply $\epsilon_0\mathrm{Im}\,\epsilon(\mathbf{r},\mathbf{r}',\omega)$ with ϵ the dielectric permittivity. For our next discussion involving Green's functions, it will be useful to connect polarization-polarization correlators to current-current correlators. That can be done using the relation $\mathbf{j} = \partial_t\mathbf{P}$. It is clear then that the current-current correlator can be written as

$$\langle j_i(\mathbf{r},\omega)j_j(\mathbf{r}',\omega) + j_j(\mathbf{r}',\omega)j_i(\mathbf{r},\omega)\rangle = 2\epsilon_0\hbar\omega^2\coth\left(\frac{1}{2}\beta\hbar\omega\right)\mathrm{Im}\,\epsilon_{ij}(\mathbf{r},\mathbf{r}',\omega). \tag{6.0.17}$$

Note that the dielectric function, which connects the electric field to the electric displacement, is in general nonlocal, in that the displacement field at a point is influenced by the electric field in a neighborhood around that point. However, in almost all cases of interest, as we probe materials with electromagnetic fields which are long compared to the atomic scale, these nonlocalities still look local on the scale of the wavelength, and we may then make a local approximation for the permittivity:

$$\epsilon_{ij}(\mathbf{r},\mathbf{r}',\omega) = \epsilon_{ij}(\mathbf{r},\omega)\delta(\mathbf{r}-\mathbf{r}'). \tag{6.0.18}$$

We will assume this. In such a situation,

$$\langle j_i(\mathbf{r},\omega)j_j(\mathbf{r}',\omega) + j_j(\mathbf{r}',\omega)j_i(\mathbf{r},\omega)\rangle = 2\epsilon_0\hbar\omega^2 \coth\left(\frac{1}{2}\beta\hbar\omega\right) \operatorname{Im}\epsilon_{ij}(\mathbf{r},\omega)\delta(\mathbf{r}-\mathbf{r}'). \tag{6.0.19}$$

We will also further simplify matters here by assuming that ϵ is diagonal, which is simply to say that we are working in a coordinate system whose axes correspond with the material's principal axes. We are now ready to quantize the electromagnetic field in absorbing media.

As discussed initially, the approach is to quantize the currents. Therefore, we would like a current operator. Once the current operator is quantized, we may simply plug it into Equation (274) in order to arrive at a quantized electromagnetic field operator. To do the quantization, as we did in the lossless case, we need to identify the independent degrees of freedom, and then somehow impose canonical commutation relations on ladder operators which create and annihilate quanta of the field that we are quantizing. We noted in Equation (274) that the field is essentially spanned by time-harmonic point-dipoles, which are specified by their position, their frequency, and their Cartesian direction. Therefore, we can write the positive-frequency current operator as

$$\mathbf{j}^{(+)}(\mathbf{r},t) = \int \frac{d\omega}{2\pi} \sum_k N_k(\mathbf{r},\omega)\hat{f}_k(\mathbf{r},\omega)e^{-i\omega t}, \tag{6.0.20}$$

where $\hat{f}_k(\mathbf{r},\omega)$ is an annihilation operator that annihilates a point-dipole excitation at position $\mathbf{r}$, ω, and direction k. Now, in writing an annihilation operator, we must specify the quantum statistics of the currents. In particular, they will obey bosonic statistics, in order to for the corresponding electromagnetic field to obey bosonic statistics. Thus, we must have

$$[\hat{f}_k(\mathbf{r},\omega), \hat{f}^\dagger_{k'}(\mathbf{r}',\omega')] = \delta_{kk'}\delta(\mathbf{r}-\mathbf{r}')\delta(\omega-\omega'). \tag{6.0.21}$$

Note that in order for this to true, we must have that the permittivity is local and also diagonal, so that as per the fluctuation-dissipation theorem, currents at different points and in different directions are really independent of each other and thus represent independent degrees of freedom. We have expressed the current operator up to a normalization $N_k(\mathbf{r},\omega)$. We can use the fluctuation-dissipation theorem to constrain it. In particular, let us calculate the fluctuations of the current operator. Namely, let us calculate

$$\langle j_i(\mathbf{r},t)j_j(\mathbf{r}',t')\rangle = \int \frac{d\omega}{2\pi}\frac{d\omega'}{2\pi} \left\langle \left(N_i(\mathbf{r},\omega)\hat{f}_i(\mathbf{r},\omega)e^{-i\omega t} + \text{h.c.}\right) \left(N_j(\mathbf{r}',\omega')\hat{f}_j(\mathbf{r}',\omega')e^{-i\omega' t} + \text{h.c.}\right)\right\rangle, \tag{6.0.22}$$

where we have simply noted that $\mathbf{j}(\mathbf{r},t) = \mathbf{j}^{(+)}(\mathbf{r},t) + \mathbf{j}^{(-)}(\mathbf{r},t)$. The expectation value can be taken at any temperature, and the end result for the normalization will be the same, thus we do the calculation for zero temperature, meaning that the expectation value is simply against the ground state of the bosonic system. It immediately follows that

$$\langle j_i(\mathbf{r},t) j_j(\mathbf{r}',t')\rangle = \int \frac{d\omega}{(2\pi)^2} e^{-i\omega(t-t')} N_i(\mathbf{r},\omega) N_i(\mathbf{r},\omega)\delta_{ij}\delta(\mathbf{r}-\mathbf{r}'). \tag{6.0.23}$$

Thus, the Fourier transform of the correlations being equal to the value specified by the fluctuation-dissipation theorem requires that

$$N_i(\mathbf{r},\omega) = \sqrt{4\pi\epsilon_0\hbar\omega^2 \text{Im } \epsilon_{ii}(\mathbf{r},\omega)}. \tag{6.0.24}$$

To write down the expression for the Heisenberg operator for the electric field, we note from Equation (274) that

$$\mathbf{E}(\mathbf{r},t) = i\mu_0 \int\limits_0^\infty \frac{d\omega}{2\pi} \int d^3r' \; \omega \left(\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)\mathbf{j}(\mathbf{r}',\omega)e^{-i\omega t} - \mathbf{G}^*(\mathbf{r},\mathbf{r}',\omega)\mathbf{j}^*(\mathbf{r}',\omega)e^{i\omega t}\right). \tag{6.0.25}$$

Plugging in the current operator, with its normalization, and using the correspondence $j \to f$ and $j^* \to f^\dagger$ yields our final result

$$\mathbf{E}(\mathbf{r},t) = i\sqrt{\frac{\hbar}{\pi\epsilon_0}} \int\limits_0^\infty d\omega \; \frac{\omega^2}{c^2} \int d^3r' \; \sqrt{\text{Im } \epsilon(\mathbf{r}',\omega)} (\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)\mathbf{f}(\mathbf{r}',\omega)e^{-i\omega t} - \mathbf{G}^*(\mathbf{r},\mathbf{r}',\omega)\mathbf{f}^\dagger(\mathbf{r}',\omega)e^{i\omega t}). \tag{6.0.26}$$

This is our final result for the quantized field operator in an absorbing medium. We will now revisit examples of QED calculations using this framework. It is worth mentioning that the electric field operator essentially replaces the mode expansion result which we have used in the Hamiltonian. The "field Hamiltonian" is essentially just

$$H_{em} = \int d^3r d\omega \sum_k f_k^\dagger(\mathbf{r},\omega) f_k(\mathbf{r},\omega), \tag{6.0.27}$$

a sum of harmonic oscillator Hamiltonians for each degree of freedom, as expected. Thus, the only change to calculations we have done in the past is to replace the mode-expansion field operators with these field operators which are valid in absorbing media.

It is worthwhile mentioning, especially for the next section that the vector potential (the part that satisfies the generalized Coulomb gauge condition) is given by

$$\mathbf{A}(\mathbf{r},t) = \sqrt{\frac{\hbar}{\pi\epsilon_0}} \int\limits_0^\infty d\omega \; \frac{\omega}{c^2} \int d^3r' \; \sqrt{\text{Im } \epsilon(\mathbf{r}',\omega)} (\mathbf{G}(\mathbf{r},\mathbf{r}',\omega)\mathbf{f}(\mathbf{r}',\omega)e^{-i\omega t} + \mathbf{G}^*(\mathbf{r},\mathbf{r}',\omega)\mathbf{f}^\dagger(\mathbf{r}',\omega)e^{i\omega t}). \tag{6.0.28}$$