

221B Lecture Notes

Quantum Field Theory IV (Radiation Field)

1 Quantization of Radiation Field

Early development of quantum mechanics was led by the fact that electromagnetic radiation was quantized: photons. Now that we have gone through quantization of a classical field (Schrödinger field so far), we can proceed to quantize the Maxwell field. The basic idea is pretty much the same, except that there are subtleties associated with the gauge invariance of the vector potential.

1.1 Classical Maxwell Field

The vector potential \vec{A} and the scalar potential ϕ are combined in the four-vector potential

$$A^\mu = (\phi, \vec{A}). \quad (1)$$

Throughout the lecture notes, we use the convention that the metric $g_{\mu\nu} = \text{diag}(+1, -1, -1, -1)$ and hence $A_\mu = g_{\mu\nu}A^\nu = (\phi, -\vec{A})$. The four-vector coordinate is $x^\mu = (ct, \vec{x})$, and correspondingly the four-vector derivative is $\partial_\mu = (\frac{1}{c}\frac{\partial}{\partial t}, \vec{\nabla})$. The field strength is defined as $F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$, and hence $F_{0i} = \partial_0 A_i - \partial_i A_0 = -\dot{\vec{A}}/c - \vec{\nabla}\phi = \vec{E}$, while $F_{ij} = \partial_i A_j - \partial_j A_i = -\vec{\nabla}_i A_j + \vec{\nabla}_j A_i = -\epsilon_{ijk}\vec{B}^k$.

In the unit we have been using where the Coulomb potential is QQ'/r without a factor of $1/4\pi\epsilon_0$, the action for the Maxwell field is

$$S = \int dt d\vec{x} \left[\frac{-1}{8\pi} F^{\mu\nu} F_{\mu\nu} - A_\mu j^\mu \right] = \int dt d\vec{x} \left[\frac{1}{8\pi} (\vec{E}^2 - \vec{B}^2) - A_\mu j^\mu \right]. \quad (2)$$

I included a possible source term for the Maxwell field (electric current density) $j^\mu = (\rho, \vec{j}/c)$. For a point particle of charge e , the charge density is $\rho = e\delta(\vec{x} - \vec{x}_0)$ while the current density is $\vec{j} = e\dot{\vec{x}}\delta(\vec{x} - \vec{x}_0)$. They satisfy the current conservation law

$$\partial_\mu j^\mu = \frac{1}{c} \left(\frac{\partial}{\partial t} \rho + \vec{\nabla} \cdot \vec{j} \right) = 0. \quad (3)$$

The gauge invariance of the Maxwell field is that the vector potential A^μ and $A^\mu + \partial^\mu \omega$ (where ω is an arbitrary function of spacetime) give the same field strength and hence the same action. Using this invariance, one can always choose a particular gauge. For most purposes of non-relativistic systems encountered in atomic, molecular, condensed matter, nuclear and astrophysics, Coulomb gauge is the convenient choice, while for highly relativistic systems such as in high-energy physics. We use Coulomb gauge in this lecture note:

$$\vec{\nabla} \cdot \vec{A} = 0. \quad (4)$$

A word of caution is that this gauge condition is not Lorentz-invariant, *i.e.*, the gauge condition is not frame independent. Therefore, when you go to a different frame of reference, you also need to perform a gauge transformation at the same time to preserve the Coulomb gauge condition. Another point is that, in the Coulomb gauge, the Gauss' law is

$$\vec{\nabla} \cdot \vec{E} = 4\pi j^0, \quad (5)$$

where j^0 is the charge density. Because $\vec{E} = -\dot{\vec{A}} - \vec{\nabla}\phi$ and the Coulomb gauge condition, we find the Poisson equation

$$\Delta\phi = -4\pi\rho, \quad (6)$$

and hence

$$\phi(\vec{x}, t) = \int d\vec{y} \frac{1}{|\vec{x} - \vec{y}|} \rho(\vec{y}, t). \quad (7)$$

Note that the potential is not retarded, but instantaneous (*i.e.*, determined by the charge distribution at the same instance).

Hamiltonian for a particle of electric charge e in the presence of the Maxwell field is

$$H = \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} + e\phi. \quad (8)$$

1.2 Quantization

In order to quantize the Maxwell field, we first determine the “canonically conjugate momentum” for the vector potential \vec{A} . Following the definition $p^i = \partial L / \partial \dot{q}^i$ in particle mechanics, we define the canonically conjugate momentum

$$\pi^i = \frac{\partial \mathcal{L}}{\partial \dot{A}^i} = -\frac{1}{4\pi c} E^i = \frac{1}{4\pi} \left(\frac{1}{c^2} \dot{A}^i + \frac{1}{c} \vec{\nabla}^i \phi \right). \quad (9)$$

In the absence of external sources, the scalar potential identically vanishes in Coulomb gauge (see Eq. (7)). We drop it entirely in this section.¹ Following the normal canonical commutation relation $[q^i, p^j] = i\hbar\delta^{ij}$, we set up the commutation relation

$$[A^i(\vec{x}), \pi^j(\vec{y})] = [A^i(\vec{x}), \frac{1}{4\pi c^2} \dot{A}^j(\vec{y})] = i\hbar\delta^{ij}\delta(\vec{x} - \vec{y}). \quad (10)$$

To satisfy this commutation relation, we introduce the photon creation and annihilation operators

$$[a^i(\vec{p}), a^{j\dagger}(\vec{q})] = \delta^{ij}\delta_{\vec{p},\vec{q}}, \quad (11)$$

and expand the vector potential and its time derivative as

$$A^i(\vec{x}) = \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} \frac{1}{\sqrt{\omega_p}} (a^i(\vec{p})e^{i\vec{p}\cdot\vec{x}/\hbar} + a^{i\dagger}(\vec{p})e^{-i\vec{p}\cdot\vec{x}/\hbar}) \quad (12)$$

$$\dot{A}^i(\vec{x}) = \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} (-i\sqrt{\omega_p}) (a^i(\vec{p})e^{i\vec{p}\cdot\vec{x}/\hbar} - a^{i\dagger}(\vec{p})e^{-i\vec{p}\cdot\vec{x}/\hbar}). \quad (13)$$

Here, $\omega_p = E_p/\hbar = c|\vec{p}|/\hbar$ is the angular frequency for the photon. You can check that this momentum-mode expansion together with the commutation relation Eq. (11) reproduces the canonical commutation relation Eq. (10) as follows.

$$\begin{aligned} & [A^i(\vec{x}), \dot{A}^j(\vec{y})] \\ &= \frac{2\pi\hbar c^2}{L^3} \sum_{\vec{p},\vec{q}} (-i) [a^i(\vec{p})e^{i\vec{p}\cdot\vec{x}/\hbar} + a^{i\dagger}(\vec{p})e^{-i\vec{p}\cdot\vec{x}/\hbar}, a^j(\vec{q})e^{i\vec{q}\cdot\vec{y}/\hbar} - a^{j\dagger}(\vec{q})e^{-i\vec{q}\cdot\vec{y}/\hbar}] \\ &= \frac{2\pi\hbar c^2}{L^3} i \sum_{\vec{p}} \delta^{ij} (e^{i\vec{p}\cdot(\vec{x}-\vec{y})} + e^{-i\vec{p}\cdot(\vec{x}-\vec{y})}) \\ &= 4\pi\hbar c^2 i \delta(\vec{x} - \vec{y}). \end{aligned} \quad (14)$$

At the last step, we used the correspondence in the large volume limit $\sum_{\vec{p}} = L^3 \int d\vec{p}/(2\pi\hbar)^3$.

The problem with what we have done so far is that we have not imposed the Coulomb gauge condition Eq. (4) on the vector potential yet. Acting the divergence on the momentum-mode expansion Eq. (12), we need

$$\vec{p} \cdot \vec{a}(\vec{p}) = 0. \quad (15)$$

¹Even when we have matter particles or fields, their charge density operator commutes with the vector potential, and hence the discussion here goes through unmodified.

The meaning of this equation is obvious: there is no longitudinal photon. There are only two transverse polarizations. To satisfy this constraint while retaining the simple commutation relations among creation and annihilation operators, we introduce the polarization vectors. When $\vec{p} = (0, 0, p)$, the positive helicity (right-handed) circular polarization has the polarization vector $\vec{\epsilon}_+ = (1, i, 0)/\sqrt{2}$, while the negative helicity (left-handed) circular polarization is represented by the polarization vector $\vec{\epsilon}_- = (1, -i, 0)/\sqrt{2}$. In general, for the momentum vector $\vec{p} = p(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$, the circular polarization vectors are given by

$$\vec{\epsilon}_\pm(\vec{p}) = \frac{1}{\sqrt{2}} (\pm \vec{\epsilon}_1 + i \vec{\epsilon}_2), \quad (16)$$

where the linear polarization vectors are given by

$$\vec{\epsilon}_1(\vec{p}) = (\cos \theta \cos \phi, \cos \theta \sin \phi, -\sin \theta), \quad (17)$$

$$\vec{\epsilon}_2(\vec{p}) = (-\sin \phi, \cos \phi, 0). \quad (18)$$

We can check that these two vectors give the complete orthonormal set by checking

$$\vec{\epsilon}_\lambda^*(\vec{p}) \cdot \vec{\epsilon}_{\lambda'}(\vec{p}) = \delta_{\lambda, \lambda'}, \quad (19)$$

$$\sum_\lambda \epsilon_\lambda^i(\vec{p}) \epsilon_\lambda^{*j}(\vec{p}) = \delta^{ij} - \frac{p^i p^j}{\vec{p}^2}. \quad (20)$$

These properties are satisfied for both the basis with linear polarizations $i, j = 1, 2$ and the helicity basis $i, j = \pm$. The last expression is a projection on the transverse direction, consistent with the Coulomb gauge condition we have imposed.

Given the polarization vectors, we re-expand the vector potential in terms of the creation/annihilation operators

$$A^i(\vec{x}) = \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} \frac{1}{\sqrt{\omega_p}} \sum_{\pm} (\epsilon_\pm^i(\vec{p}) a_\pm(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} + \epsilon_\pm^i(\vec{p})^* a_\pm^\dagger(\vec{p}) e^{-i\vec{p}\cdot\vec{x}/\hbar}) \quad (21)$$

$$\dot{A}^i(\vec{x}) = \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} (-i\sqrt{\omega_p}) \sum_{\pm} (\epsilon_\pm^i(\vec{p}) a_\pm(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} - \epsilon_\pm^i(\vec{p})^* a_\pm^\dagger(\vec{p}) e^{-i\vec{p}\cdot\vec{x}/\hbar}). \quad (22)$$

With this expansion, the Coulomb gauge condition is automatically satisfied, while the creation/annihilation operators obey the commutation relations

$$[a_\lambda(\vec{p}), a_{\lambda'}^\dagger(\vec{q})] = \delta_{\lambda,\lambda'} \delta_{\vec{p},\vec{q}} \quad (23)$$

for $\lambda, \lambda' = \pm$. We could also have used the linearly polarized photons

$$\begin{aligned} A^i(\vec{x}) &= \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} \frac{1}{\sqrt{\omega_p}} \sum_{\lambda=1}^2 (\epsilon_\lambda^i(\vec{p}) a_\lambda(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} + \epsilon_\lambda^i(\vec{p}) a_\lambda^\dagger(\vec{p}) e^{-i\vec{p}\cdot\vec{x}/\hbar}) \quad (24) \\ \dot{A}^i(\vec{x}) &= \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{p}} (-i\sqrt{\omega_p}) \sum_{\lambda=1}^2 (\epsilon_\lambda^i(\vec{p}) a_\lambda(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} - \epsilon_\lambda^i(\vec{p}) a_\lambda^\dagger(\vec{p}) e^{-i\vec{p}\cdot\vec{x}/\hbar}). \end{aligned} \quad (25)$$

with

$$[a_\lambda(\vec{p}), a_{\lambda'}^\dagger(\vec{q})] = \delta_{\lambda,\lambda'} \delta_{\vec{p},\vec{q}} \quad (26)$$

for $\lambda, \lambda' = 1, 2$. Clearly, two sets of operators are related by

$$a_1 = \frac{1}{\sqrt{2}}(a_+ + a_-), \quad a_2 = \frac{i}{\sqrt{2}}(a_+ - a_-). \quad (27)$$

Once we have the mode expansion for the vector potential, one can work out the Hamiltonian

$$H = \int d\vec{x} \frac{1}{8\pi} (\vec{E}^2 + \vec{B}^2) = \sum_{\vec{p}} \sum_{\pm} \hbar\omega_p \left(a_\pm^\dagger(\vec{p}) a_\pm(\vec{p}) + \frac{1}{2} \right). \quad (28)$$

Because $\hbar\omega_p = c|\vec{p}|$, the dispersion relation for the photon is the familiar one $E = c|\vec{p}|$ for a massless relativistic particle.

2 Classical Electromagnetic Field

Now that we found photons (particles) from the quantized radiation field, what is a classic electromagnetic field?

To answer this question, we study the quantum-mechanical Hamiltonian for the photons in the presence of a source. Starting from the action Eq. (2), we find the Hamiltonian

$$H = \int d\vec{x} \left[\frac{1}{8\pi} (\vec{E}^2 + \vec{B}^2) - \frac{1}{c} \vec{A} \cdot \vec{j} \right]$$

$$\begin{aligned}
&= \sum_{\vec{p}, \lambda} \left(\hbar \omega_p a_\lambda^\dagger(\vec{p}) a_\lambda(\vec{p}) \right. \\
&\quad \left. - \frac{1}{c} \sqrt{\frac{2\pi\hbar c^2}{L^3}} \frac{1}{\sqrt{\omega_p}} (\vec{\epsilon}_\lambda(\vec{p}) \cdot \vec{j}(\vec{p}) a_\lambda(\vec{p}) + \vec{\epsilon}_\lambda^*(\vec{p}) \cdot \vec{j}^*(\vec{p}) a_\lambda^\dagger(\vec{p})) \right). \quad (29)
\end{aligned}$$

Here, we omitted the zero-point energy because it is not relevant for the discussions below, and the Fourier modes of the source is defined by

$$\vec{j}(\vec{p}) \equiv \int d\vec{x} \vec{j}(\vec{x}) e^{i\vec{p}\cdot\vec{x}/\hbar}, \quad (30)$$

and $\vec{j}^*(\vec{p}) = \vec{j}(-\vec{p})$. The interesting point is that for each momentum \vec{p} and polarization state λ , the Hamiltonian Eq. (29) is of the type

$$\hbar\omega(a^\dagger a - f^* a - a^\dagger f), \quad (31)$$

whose ground state is

$$\hbar\omega(a^\dagger a - f^* a - a^\dagger f)|f\rangle = -\hbar\omega f^* f|f\rangle. \quad (32)$$

In other words, the ground state of the Hamiltonian for photons in the presence of a source term is a coherent state $|f\rangle \equiv \prod_{\vec{p}, \lambda} |f_\lambda(\vec{p})\rangle$, with

$$f_\lambda(\vec{p}) = \sqrt{\frac{2\pi\hbar}{L^3}} \frac{1}{\hbar\omega_p^{3/2}} \vec{\epsilon}_\lambda^* \cdot \vec{j}^*(\vec{p}). \quad (33)$$

The vector potential has an expectation value in the coherent state, given by

$$\begin{aligned}
&\langle f|A^i(\vec{x})|f\rangle \\
&= \sum_{\vec{p}, \lambda} \sqrt{\frac{2\pi\hbar c^2}{L^3}} \frac{1}{\hbar\omega_p^2} (\vec{\epsilon}_\lambda^i(\vec{p}) f_\lambda(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} + \vec{\epsilon}_\lambda^{i*}(\vec{p}) f_\lambda^*(\vec{p}) e^{-i\vec{p}\cdot\vec{x}/\hbar}) \\
&= \frac{2\pi\hbar}{L^3} \sum_{\vec{p}} \frac{c}{\hbar\omega_p^2} \left(j^{k*}(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} \sum_{\lambda} \epsilon_\lambda^i(\vec{p}) \epsilon_\lambda^{k*}(\vec{p}) + c.c. \right). \quad (34)
\end{aligned}$$

Even though the expression is somewhat complicated, one can check that this expectation value satisfies

$$\vec{\nabla} \times \langle f|\vec{B}|f\rangle = -\Delta \langle f|\vec{A}|f\rangle = \frac{4\pi}{c} \vec{j}, \quad (35)$$

using the identity Eq. (20) together with the Coulomb gauge condition $\vec{\nabla} \cdot \vec{A} = 0$. Actually, the term proportional to \vec{p}^i is a gradient $-i\hbar\nabla^i$ and hence gauge-dependent. Ignoring the gauge-dependent term, we find a simpler expression

$$\begin{aligned} \langle f|A^k(\vec{x})|f\rangle &= \frac{2\pi}{L^3} \sum_{\vec{p}} \frac{c}{\hbar\omega_p^2} \left(j^{k*}(\vec{p}) e^{i\vec{p}\cdot\vec{x}/\hbar} + c.c. \right) \\ &= \frac{4\pi}{c} \frac{1}{L^3} \sum_{\vec{p}} \left(\frac{1}{\vec{k}^2} j^{k*}(\vec{p}) e^{i\vec{k}\cdot\vec{x}} + c.c. \right), \end{aligned} \quad (36)$$

which shows manifestly that it is a solution to the Poisson equation in the wave vector space $\Delta = -\vec{k}^2$.

What we have learnt here is that the ground state for the photon Hamiltonian in the presence of a source is given by a coherent state, which has an expectation value for the vector potential. This expectation value is nothing but what we normally obtain by solving Maxwell's equations for the classical Maxwell's field.

The solution we obtained, however, is not a “radiation” because it does not propagate. We can produce a radiation by turning off the current instantaneously at $t = 0$. Classically, it corresponds to a non-static source which can radiate electromagnetic wave. Quantum mechanically, we can use the “sudden” approximation that the same state given above now starts evolving according to the free photon Hamiltonian without the source term from $t = 0$ and on.

The time evolution of a coherent state is very simple. For the free Hamiltonian $H = \hbar\omega a^\dagger a$, the time evolution is

$$\begin{aligned} |f, t\rangle &= e^{-iHt} e^{-f^* f/2} e^{fa^\dagger} |0\rangle \\ &= e^{-f^* f/2} e^{-i\omega a^\dagger t} \sum_{n=0}^{\infty} \frac{f^n}{n!} (a^\dagger)^n e^{i\omega a^\dagger t} e^{-i\omega a^\dagger t} |0\rangle \\ &= e^{-f^* f/2} \sum_{n=0}^{\infty} \frac{f^n}{n!} \left(e^{-i\omega a^\dagger t} a^\dagger e^{i\omega a^\dagger t} \right)^n |0\rangle \\ &= e^{-f^* f/2} \sum_{n=0}^{\infty} \frac{f^n}{n!} (a^\dagger e^{-i\omega t})^n |0\rangle \\ &= e^{-f^* f/2} e^{f e^{-i\omega t} a^\dagger} |0\rangle \\ &= |f e^{-i\omega t}\rangle. \end{aligned} \quad (37)$$

In other words, the time evolution keeps a coherent state still a coherent state, but with a different eigenvalue for the annihilation operator $f e^{-i\omega t}$.

Then the expectation value for the vector potential can also be written down right away:

$$\langle f, t | A^k(\vec{x}) | f, t \rangle = \frac{4\pi}{c} \frac{1}{L^3} \sum_{\vec{p}} \left(\frac{1}{\vec{k}^2} j^{k*}(\vec{p}) e^{i\vec{k}\cdot\vec{x} - i\omega_p t} + c.c. \right). \quad (38)$$

One can see that this vector potential describes a propagating electromagnetic wave in the vacuum because of the factor $e^{i\vec{p}\cdot\vec{x}/\hbar} e^{-i\omega_p t} = e^{i(\vec{k}\cdot\vec{x} - c|\vec{k}|t)}$ with $\vec{k} = \vec{p}/\hbar$ and $\omega_p = c|\vec{k}|$. The quantum mechanical state is still a coherent state with time-dependent eigenvalues for the annihilation operators.

The analogy to Bose–Einstein condensate is intriguing. In the case of Bose–Einstein condensate, we have a collection of particles which can be described either in terms of particle Hamiltonian or quantized Schrödinger field. After the condensate develops, it cannot be described by the particle Hamiltonian anymore, but rather by a “unquantized” version of Schrödinger field. The system exhibits macroscopic coherence. For the case of an electromagnetic wave, it is normally described by a classical Maxwell field. But one can talk about photons which appear in quantized radiation field. Then the “unquantized” version of the Maxwell field exhibits the macroscopic coherence.

Therefore, as long as the amplitude for the Maxwell field is “large,” the number–phase uncertainty relation can easily be satisfied while manifesting coherence, and the quantum state is well described by a classical field, namely the Maxwell field.

As an example, laser is described in terms of a coherent state of photons. The stimulated emission builds up photons in such a way that it becomes a coherent state.

3 Interaction With Matter

Now that we know how we get photons, we would like to discuss how photons are emitted or absorbed by matter.

When I was taking quantum mechanics courses myself, I was very frustrated. You hear about motivations why you need to study quantum mechanics, and most (if not all) of the examples involve photons: Planck’s law, photoelectric effect, Compton scattering, emission spectrum from atoms, etc. But the standard quantum mechanics is incapable of dealing with creation and annihilation of particles, as we had discussed already. Now that we

have creation and annihilation operators for photons, we are in the position to discuss emission and absorption of photons due to their interaction with matter.

3.1 Hamiltonian

In this section, we deal with matter with conventional quantum mechanics, while with photons with quantized radiation field. This formulation is appropriate for decays of excited states of atoms, for instance. To be concrete, let us consider a hydrogen-like atom and its interaction with photons. We start with the Hamiltonian

$$H = \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r}. \quad (39)$$

Obviously, this Hamiltonian does not contain photons nor their interaction with the electron. The correct Hamiltonian for us is

$$H = \frac{(\vec{p} - \frac{e}{c}\vec{A})^2}{2m} - \frac{Ze^2}{r} + \sum_{\vec{p},\lambda} \hbar\omega_p a_\lambda^\dagger(\vec{p}) a_\lambda(\vec{p}). \quad (40)$$

The first term describes the interaction of the electron with the vector potential $\vec{A}(\vec{x})$. For instance, the motion of electron in the constant magnetic field is described by this Hamiltonian with $A_x = -By/2$, $A_y = Bx/2$. For our purpose, however, the vector potential is not a function of \vec{x} alone, which is an operator for the position of electron, but also contains creation and annihilation operators for photons. We rewrite the Hamiltonian Eq. (40 in two pieces

$$H = H_0 + V = H_e + H_\gamma + V, \quad (41)$$

$$H_e = \frac{\vec{p}^2}{2m} - \frac{Ze^2}{r}, \quad (42)$$

$$H_\gamma = \sum_{\vec{p},\lambda} \hbar\omega_p a_\lambda^\dagger(\vec{p}) a_\lambda(\vec{p}) \quad (43)$$

$$V = -\frac{e}{c} \frac{\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}}{2m} + \frac{e^2}{c^2} \frac{\vec{A} \cdot \vec{A}}{2m}. \quad (44)$$

We regard H_0 as the unperturbed Hamiltonian, and V as a perturbation. It is useful to know that $\vec{p} \cdot \vec{A} = \vec{A} \cdot \vec{p}$ in the Coulomb gauge because the difference is $\vec{p} \cdot \vec{A} - \vec{A} \cdot \vec{p} = -i\hbar \vec{\nabla} \cdot \vec{A} = 0$.

3.2 Free Hamiltonian

In perturbation theory, we have to solve the unperturbed system exactly so that we can perturb around it. What are the eigenstates and energy eigenvalues of the unperturbed Hamiltonian H_0 in our case? The point here is that there is no communication between the electron in H_e and photons in H_γ . Therefore, all we need to know is the eigenstates and eigenvalues of two separate Hamiltonians. The full eigenstates are product of two eigenstates, and the eigenvalues sum of two eigenvalues. For instance, we can consider states such as

$$\begin{aligned} & |1s\rangle|0\rangle, \\ & |3d\rangle a_{\lambda_1}^\dagger(\vec{p}_1) a_{\lambda_2}^\dagger(\vec{p}_2) a_{\lambda_3}^\dagger(\vec{p}_3) a_{\lambda_4}^\dagger(\vec{p}_4) |0\rangle, \\ & |k, l, m\rangle a_\lambda(\vec{p}) |0\rangle, \end{aligned}$$

and so on. The first state with the ground state of the system, with electron in the $1s$ state and no photons. The second state has the electron in an excited $3d$ state, with four photons. The last state has the electron in the continuum state with the momentum $\hbar k$ and angular momentum l, m together with a photon. Their eigenvalues are simply the sum of the electron energy and photon energy (energies).

Therefore, we have solved the unperturbed Hamiltonian H_0 exactly.

3.3 Dipole Transition Rates

The next step is to deal with the interaction Hamiltonian V . What we use is the Fermi's golden rule for transition rates

$$W_{fi} = \frac{1}{\hbar} |\langle f|V|i\rangle|^2 2\pi\delta(E_f - E_i) \quad (45)$$

to the lowest order in perturbation theory.

To be specific, let us consider the decay of $2p$ state to $1s$ by emission of a photon. In other words,

$$|i\rangle = |2p\rangle|0\rangle \quad (46)$$

$$|f\rangle = |1s\rangle|\vec{q}, \lambda\rangle, \quad (47)$$

where the one-photon state is defined by

$$|\vec{q}, \lambda\rangle = a_\lambda^\dagger(\vec{q})|0\rangle. \quad (48)$$

Because the initial and final states differ by one in the number of photons, and the vector potential \vec{A} changes the number of photons by one, \vec{A}^2 term in V cannot contribute. Therefore,

$$\langle f|V|i\rangle = -\frac{e}{c} \frac{1}{m} \langle f|\vec{p} \cdot \vec{A}(\vec{x})|i\rangle, \quad (49)$$

where we used the Coulomb gauge $\vec{p} \cdot \vec{A} = \vec{A} \cdot \vec{p}$. Now we can expand the vector potential in the momentum modes Eq. (21)

$$A^i(\vec{x}) = \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{q}', \lambda'} \frac{1}{\sqrt{\omega_{q'}}} (\epsilon_{\lambda'}^i(\vec{q}') a_{\lambda'}(\vec{q}') e^{i\vec{q}' \cdot \vec{x}/\hbar} + \epsilon_{\lambda'}^i(\vec{q}')^* a_{\lambda'}^\dagger(\vec{q}') e^{-i\vec{q}' \cdot \vec{x}/\hbar}) \quad (50)$$

with a word of caution. \vec{x} is an *operator* describing the position of the electron, while \vec{q}' is a dummy *c*-number variable you sum over (so is the helicity λ'). \vec{p} in Eq. (49), on the other hand, is also an *operator* describing the momentum of the electron. Because the final state has a photon while the initial state doesn't, only the piece with creation operator contributes to the amplitude Eq. (49). Therefore,

$$\langle f|V|i\rangle = -\frac{e}{c} \frac{1}{m} \langle \vec{q}, \lambda | \sqrt{\frac{2\pi\hbar c^2}{L^3}} \sum_{\vec{q}', \lambda'} \frac{1}{\sqrt{\omega_{q'}}} \vec{\epsilon}_{\lambda'}^*(\vec{q}') a_{\lambda'}^\dagger(\vec{q}') |0\rangle \cdot \langle 1s|\vec{p} e^{-i\vec{q} \cdot \vec{x}/\hbar} |2p\rangle. \quad (51)$$

The photon part of the matrix element is easy:

$$\langle \vec{q}, \lambda | a_{\lambda'}^\dagger(\vec{q}') |0\rangle = \delta_{\vec{q}, \vec{q}'} \delta_{\lambda, \lambda'} \quad (52)$$

and the summation over \vec{q}' , λ' goes away. (Note that we can also easily deal with stimulated emission by having N photons in the initial state and $N+1$ photons in the final state, and the stimulated emission factor of \sqrt{N} in the amplitude comes out automatically.) Now the amplitude Eq. (51) reduces to

$$\langle f|V|i\rangle = -\frac{e}{c} \frac{1}{m} \sqrt{\frac{2\pi\hbar c^2}{L^3}} \frac{1}{\sqrt{\omega_q}} \vec{\epsilon}_{\lambda}^*(\vec{q}) \cdot \langle 1s|\vec{p} e^{-i\vec{q} \cdot \vec{x}/\hbar} |2p\rangle. \quad (53)$$

Next, we point out that the exponential factor can be dropped as a good approximation. A higher order term in $\vec{q} \cdot \vec{x}/\hbar$ is of order of magnitude of the size of the electron wave function $a_0 = \hbar^2/Zme^2 = \hbar c/\alpha mc^2$ times the

energy of the photon $E_\gamma = E_{2p} - E_{1s} = \frac{1}{2}Z^2\alpha^2mc^2(1 - \frac{1}{2^2})$ divided by c , $|\vec{q}| = E_\gamma/c$, and is hence suppressed by a factor of $Z\alpha$. This factor is small for a typical hydrogen-like atom. Finally, we use the identity

$$[H_e, \vec{x}] = -i\hbar \frac{\vec{p}}{m}, \quad (54)$$

and hence

$$\langle 1s|\vec{p}|2p\rangle = i\frac{m}{\hbar}\langle 1s|[H_e, \vec{x}]|2p\rangle = i\frac{m}{\hbar}(E_{1s} - E_{2p})\langle 1s|\vec{x}|2p\rangle = -i\frac{m}{\hbar}E_\gamma\langle 1s|\vec{x}|2p\rangle. \quad (55)$$

It is customary to write the last factor in terms of the electric dipole operator

$$\vec{D} = e\vec{x}, \quad (56)$$

and hence the transition amplitude Eq. (53) is

$$\langle f|V|i\rangle = \frac{i}{\hbar}|\vec{q}|\sqrt{\frac{2\pi\hbar c^2}{L^3}}\frac{1}{\sqrt{\omega_q}}\vec{\epsilon}_\lambda^*(\vec{q}) \cdot \langle 1s|\vec{D}|2p\rangle. \quad (57)$$

Because the transition amplitude is given in terms of the matrix element of the electric dipole operator, it is called the dipole transition.

Back to Fermi's golden rule Eq. (45), we now find

$$W_{fi} = \frac{1}{\hbar}\frac{1}{\hbar^2}\vec{q}^2\frac{2\pi\hbar c^2}{L^3}\frac{1}{\omega_q}|\vec{\epsilon}_\lambda^*(\vec{q}) \cdot \langle 1s|\vec{D}|2p\rangle|^2 2\pi\delta(E_f - E_i). \quad (58)$$

When one is interested in the total decay rate of the $2p$ state, we sum over all possible final states, namely the polarization and momentum of the photon. The decay rate of the $2p$ state is then

$$\begin{aligned} W_i &= \sum_{\vec{q}, \lambda} \frac{|\vec{q}|}{\hbar^2 c} \frac{2\pi\hbar c^2}{L^3} |\vec{\epsilon}_\lambda^*(\vec{q}) \cdot \langle 1s|\vec{D}|2p\rangle|^2 2\pi\delta(E_f - E_i) \\ &= \int \frac{d\vec{q}}{(2\pi\hbar)^3} \frac{2\pi c|\vec{q}|}{\hbar} \sum_\lambda |\vec{\epsilon}_\lambda^*(\vec{q}) \cdot \langle 1s|\vec{D}|2p\rangle|^2 2\pi\delta(E_f - E_i). \end{aligned} \quad (59)$$

Here we used the large volume limit $\sum_{\vec{q}} = L^3 \int d\vec{q}/(2\pi\hbar)^3$.

The transition matrix element of the electric dipole operator can be obtained easily. For example, for $m = 0$ state, only the z -component of the

dipole operator is non-vanishing because of the axial symmetry around the z -axis, and

$$\langle 1s | \vec{D} | 2p, m = 0 \rangle = e \int_0^\infty r^2 dr d\Omega \frac{1}{a^3} 2e^{-r/a} Y_0^0 \frac{\sqrt{16}}{12} \frac{r}{a} e^{-r/2a} Y_1^0 r \cos \theta = e \frac{1}{\sqrt{2}} \frac{256}{243} a, \quad (60)$$

with $a = a_0/Z$. By taking the sum over the polarization states using the two linear polarization states Eq. (17), only the first one contributes. Note also that $2\pi\delta(E_f - E_i) = 2\pi\delta(|\vec{q}| - (E_{2p} - E_{1s})/c)/c$ and hence

$$\begin{aligned} W_i &= \int \frac{d\Omega_q}{(2\pi\hbar)^3} |\vec{q}|^2 \frac{(2\pi)^2 |\vec{q}|}{\hbar} \left| \epsilon_{z,1}(\vec{q}) e \frac{1}{\sqrt{2}} \frac{256}{243} a \right|^2 \\ &= \int \frac{d\Omega_q}{2\pi\hbar^4} |\vec{q}|^3 \left(e \frac{1}{\sqrt{2}} \frac{256}{243} a \right)^2 \sin^2 \theta \\ &= \frac{2}{3} \left(\frac{256}{243} \right)^2 e^2 \frac{q^3 a^2}{\hbar^4} \\ &= \frac{256}{6561} Z^4 \alpha^5 \frac{mc^2}{\hbar} \\ &= 6.27 \times 10^8 \text{sec}^{-1} Z^4. \end{aligned} \quad (61)$$

This result agrees well with the observed value of $6.2648 \times 10^8 \text{sec}^{-1}$. In other words, the lifetime of the $2p$ state of hydrogen atom is $W_i^{-1} = 1.60 \times 10^{-9} \text{sec}$.

It is interesting to think about $\sin \theta$ behavior of the amplitude. The reason behind it is fairly simple. Because we took $m = 0$ state as the initial state, there is no spin along the z -axis. On the other hand, in the final state, the atom does not carry spin (s -state) and the only carrier of spin is the photon. And the spin of the photon is always along the direction of its motion, either parallel (helicity $+1$) or anti-parallel (helicity -1). If the photon was emitted along the z -axis, there is net spin along the positive z -axis in the final state, ± 1 for the helicity ± 1 of the photon. To conserve angular momentum, such an amplitude should vanish identically, which is done precisely by $\sin \theta = 0$ at $\theta = 0$. Photon emission along the negative z -axis must be likewise forbidden, by $\sin \theta = 0$ at $\theta = \pi$. The $m = 0$ state has its angular momentum $l = 1$ oriented in the x - y plane, which matches the helicity of the photon when emitted at $\theta = \pi/2$, causing the maximum amplitude in $\sin \theta = 1$. Because the algebra is somewhat lengthy, albeit straightforward, it always helps to have a simple understanding of the result based on intuitive arguments.

3.4 Photon Scattering on an Atom

The next process we will study is the scattering of a photon by an atom. We start with the initial state of the atom A with a photon of momentum \vec{q}_i and polarization λ_i (linear or circular). The final state is the atom in state B with a photon of momentum \vec{q}_f and polarization λ_f . When $A = B$, it is an elastic scattering, while when $A \neq B$, it is an inelastic scattering.

Because the initial and the final states have the same number of photons (one), the Fermi's golden rule at the first-order in perturbation theory used in the decay of $2p$ state discussed in the previous section cannot cause this process. We have to go to the second order in perturbation theory. Therefore, we first develop the second-order formula of Fermi's golden rule first, and then apply it to the photon-atom scattering.

3.4.1 Second-order Fermi's Golden Rule

We first recall the derivation of Fermi's golden rule at the first order in perturbation theory. We use a derivation slightly different from that in the class, but the result is the same. In class, we "turned on" the perturbation V at $t = 0$, and discussed the time evolution to t . In the end we obtained the result for $t \rightarrow \infty$ limit. Here, we try to calculate the transition for an infinite time interval from the beginning.

The time-dependent perturbation theory uses the interaction picture, where operators evolve according to the unperturbed Hamiltonian H_0 :

$$O_I(t) = e^{iH_0t/\hbar} O e^{-iH_0t/\hbar}, \quad (62)$$

while the states evolve according to the time-evolution operator

$$U_I(t_f, t_i) = T e^{-\frac{i}{\hbar} \int_{t_i}^{t_f} V_I(t) dt} \quad (63)$$

from the infinite past. Here, V is the interaction Hamiltonian and $V_I(t) = e^{iH_0t/\hbar} V e^{-iH_0t/\hbar}$. T stands for the time-ordered product of operators that follow it.

The initial and final states are eigenstates of the unperturbed Hamiltonian, $H_0|i\rangle = E_i|i\rangle$, $H_0|f\rangle = E_f|f\rangle$. The amplitude we need is

$$\lim_{\substack{t_f \rightarrow \infty \\ t_i \rightarrow -\infty}} \langle f | U_I(t_f, t_i) | i \rangle. \quad (64)$$

Up to the first order, Taylor expansion of $U_I(t_f, t_i)$ gives

$$\langle f|U_I(t_f, t_i)|i\rangle = \langle f|1 - \frac{i}{\hbar} \int_{t_i}^{t_f} V_I(t)dt|i\rangle + O(V^2). \quad (65)$$

Rewriting $V_I(t') = e^{iH_0t'/\hbar}V e^{-iH_0t'/\hbar}$, and using the eigenvalues of H_0 on the initial and final states,

$$\langle f|U_I(t_f, t_i)|i\rangle = \delta_{fi} - \frac{i}{\hbar} \int_{t_i}^{t_f} e^{iE_f t/\hbar} \langle f|V|i\rangle e^{-iE_i t/\hbar} dt + O(V^2). \quad (66)$$

When $t_i \rightarrow -\infty$ and $t_f \rightarrow \infty$, the t integration gives simply

$$\begin{aligned} \lim_{\substack{t_f \rightarrow \infty \\ t_i \rightarrow -\infty}} \langle f|U_I(t_f, t_i)|i\rangle &= \delta_{fi} - \frac{i}{\hbar} 2\pi\hbar\delta(E_f - E_i) \langle f|V|i\rangle + O(V^2) \\ &= \delta_{fi} - i2\pi\delta(E_f - E_i) \langle f|V|i\rangle + O(V^2) \end{aligned} \quad (67)$$

The probability of the transition over the infinite time interval is then (assuming $f \neq i$),

$$|\langle f|U_I(t)|i\rangle|^2 = |\langle f|V|i\rangle|^2 (2\pi\delta(E_f - E_i))^2. \quad (68)$$

The square of the delta function is of course singular. To see what it is, we rewrite the square as

$$(2\pi\delta(E_f - E_i))^2 = 2\pi\delta(E_f - E_i) \frac{1}{\hbar} \lim_{\substack{t_f \rightarrow \infty \\ t_i \rightarrow -\infty}} \int_{-t_f}^{t_i} e^{i(E_f - E_i)t/\hbar} dt. \quad (69)$$

Because the first delta function forces $E_f = E_i$ in the integrand, the integral gives the (infinite) time interval $T = t_f - t_i$,

$$(2\pi\delta(E_f - E_i))^2 = 2\pi\delta(E_f - E_i) \frac{1}{\hbar} T. \quad (70)$$

Using this expression,

$$|\langle f|U_I(t)|i\rangle|^2 = |\langle f|V|i\rangle|^2 2\pi\delta(E_f - E_i) \frac{T}{\hbar}. \quad (71)$$

The probability of the transition per unit time, namely the transition rate, is therefore obtained from the above expression divided by the time interval T ,

$$W_{fi} = \frac{1}{\hbar} |\langle f|V|i\rangle|^2 2\pi\delta(E_f - E_i). \quad (72)$$

This is Fermi's golden rule we had used at the first order in perturbation theory.

Now we extend the discussion to the second order. The second-order piece in $\langle f|U_I(t)|i\rangle$ is

$$\frac{1}{2!} \left(\frac{-i}{\hbar}\right)^2 \langle f|T(V_I(t')V_I(t''))|i\rangle = -\frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \langle f|V_I(t')V_I(t'')|i\rangle. \quad (73)$$

In the second expression, I used the explicit definition of time-ordering together with the fact that two possible orderings give identical contributions cancelling the prefactor $1/2!$. Using the definition of V_I , and inserting the complete set of intermediate states $1 = \sum_m |m\rangle\langle m|$, it becomes

$$\begin{aligned} &= -\frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \langle f|V_I(t')V_I(t'')|i\rangle \\ &= -\frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \sum_m e^{iE_f t'/\hbar} \langle f|V|m\rangle e^{-iE_m t'/\hbar} e^{iE_m t''/\hbar} \langle m|V|i\rangle e^{-iE_i t''/\hbar} \\ &= -\frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' e^{i(E_f - E_m)t'/\hbar} e^{i(E_m - E_i)t''/\hbar} \sum_m \langle f|V|m\rangle \langle m|V|i\rangle. \quad (74) \end{aligned}$$

To integrate over t'' from $-\infty$, we have to worry about the convergence. One way to ensure the convergence is to add a small damping factor in the exponent $e^{\epsilon t''}$ that damps in $t \rightarrow -\infty$, and the t'' integral gives

$$= -\frac{1}{\hbar^2} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' e^{i(E_f - E_m)t'/\hbar} \frac{\hbar e^{i(E_m - E_i)t'/\hbar}}{i(E_m - E_i) + \epsilon} \sum_m \langle f|V|m\rangle \langle m|V|i\rangle. \quad (75)$$

Then the remaining t' integral gives the delta function,

$$\begin{aligned} &= -\frac{1}{\hbar^2} 2\pi\hbar\delta(E_f - E_i) \frac{\hbar}{i(E_m - E_i) + \epsilon} \sum_m \langle f|V|m\rangle \langle m|V|i\rangle \\ &= -i \sum_m \frac{\langle f|V|m\rangle \langle m|V|i\rangle}{E_i - E_m + i\epsilon} 2\pi\delta(E_f - E_i). \quad (76) \end{aligned}$$

The ϵ appears in the same way as in the energy denominator in the Lippman–Schwinger equation. Putting together with the first-order piece, we find the amplitude

$$\langle f|U_I(t)|i\rangle = \delta_{fi} - i2\pi\delta(E_f - E_i) \left(\langle f|V|i\rangle + \sum_m \frac{\langle f|V|m\rangle \langle m|V|i\rangle}{E_i - E_m + i\epsilon} \right) + O(V^3). \quad (77)$$

3.4.2 Cross Section

The interaction Hamiltonian is the same as before,

$$V = -\frac{e}{c} \frac{\vec{p} \cdot \vec{A}(\vec{x})}{m} + \frac{e^2}{c^2} \frac{\vec{A}(\vec{x}) \cdot \vec{A}(\vec{x})}{2m}. \quad (78)$$

Here, Coulomb gauge is already used to simplify the first term. For the transition amplitude

$$\langle B; \vec{q}_f, \lambda_f | U_I(t_f, t_i) | A; \vec{q}_i, \lambda_i \rangle, \quad (79)$$

we have to keep the number of photons (from one to one). This can be done by using the $\vec{A} \cdot \vec{A}$ operator in V at the first order, while using the $\vec{p} \cdot \vec{A}$ operator in V twice would also do the job. In terms of coupling factors, both of these contributions appear at $O(e^2)$. Therefore,

$$\begin{aligned} & \langle B; \vec{q}_f, \lambda_f | U_I(t_f, t_i) | A; \vec{q}_i, \lambda_i \rangle \\ &= -i2\pi\delta(E_f - E_i) \left(\langle B; \vec{q}_f, \lambda_f | \frac{e^2}{c^2} \frac{\vec{A}(\vec{x}) \cdot \vec{A}(\vec{x})}{2m} | A; \vec{q}_i, \lambda_i \rangle \right. \\ & \quad \left. + \sum_m \frac{\langle B; \vec{q}_f, \lambda_f | -\frac{e}{c} \frac{\vec{p} \cdot \vec{A}(\vec{x})}{m} | m \rangle \langle m | -\frac{e}{c} \frac{\vec{p} \cdot \vec{A}(\vec{x})}{m} | i \rangle}{E_i - E_m + i\epsilon} \right) \end{aligned} \quad (80)$$

up to the second order in e^2 .

Let us start from the first term in the parentheses. Here, one factor of the vector potential should annihilate the photon in the initial state, while the other should create the photon in the final state. That is done by taking the square of Eq. (21) and taking the cross term (with a factor of two of course), and picking the creation/annihilation operators of relevant momenta and polarizations. We find

$$\begin{aligned} & \langle B; \vec{q}_f, \lambda_f | \frac{e^2}{c^2} \frac{\vec{A}(\vec{x}) \cdot \vec{A}(\vec{x})}{2m} | A; \vec{q}_i, \lambda_i \rangle \\ &= \frac{e^2}{c^2} \frac{1}{m} \frac{2\pi\hbar c^2}{L^3} \frac{1}{\sqrt{\omega_i \omega_f}} \langle B; \vec{q}_f, \lambda_f | \vec{\epsilon}_i \cdot \vec{\epsilon}_f^* a_{\lambda_f}^\dagger(\vec{q}_f) e^{-i\vec{q}_f \cdot \vec{x}/\hbar} a_{\lambda_i}(\vec{q}_i) e^{i\vec{q}_i \cdot \vec{x}/\hbar} | A; \vec{q}_i, \lambda_i \rangle \\ &= \frac{e^2}{mc^2} \frac{2\pi\hbar c^2}{L^3} \frac{1}{\sqrt{\omega_i \omega_f}} \vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \langle B | e^{-i\vec{q}_f \cdot \vec{x}/\hbar} e^{i\vec{q}_i \cdot \vec{x}/\hbar} | A \rangle. \end{aligned} \quad (81)$$

Here and below, we use the short-hand notation $\vec{\epsilon}_i = \epsilon_{\lambda_i}(\vec{q}_i)$, and $\vec{\epsilon}_f = \epsilon_{\lambda_f}(\vec{q}_f)$. Within the same spirit of approximation as in the dipole decay rate, we can ignore $\vec{q} \cdot \vec{x} \ll \hbar$ for photon energies comparable to atomic levels, and we find

$$\langle B; \vec{q}_f, \lambda_f | \frac{e^2}{c^2} \frac{\vec{A}(\vec{x}) \cdot \vec{A}(\vec{x})}{2m} | A; \vec{q}_i, \lambda_i \rangle = \frac{e^2}{mc^2} \frac{2\pi\hbar c^2}{L^3} \frac{1}{\sqrt{\omega_i \omega_f}} \vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \delta_{B,A}. \quad (82)$$

Now let us see what kind of intermediate states m contribute to the sum in Eq. (80). One possibility is that m is an atomic state I with no photon.² Then we pick the relevant creation operator in the first matrix element and the relevant annihilation operator in the second matrix element, and

$$\begin{aligned} & \sum_I \frac{\langle B; \vec{q}_f, \lambda_f | -\frac{e}{c} \frac{\vec{p} \cdot \vec{A}(\vec{x})}{m} | I \rangle \langle I | -\frac{e}{c} \frac{\vec{p} \cdot \vec{A}(\vec{x})}{m} | A; \vec{q}_i, \lambda_i \rangle}{E_i - E_m + i\epsilon} \\ &= \frac{e^2}{c^2} \frac{1}{m^2} \frac{2\pi\hbar c^2}{L^3} \frac{1}{\sqrt{\omega_i \omega_f}} \\ & \quad \sum_I \frac{\langle B; \vec{q}_f, \lambda_f | \vec{p} \cdot \epsilon_f^* a_{\lambda_f}^\dagger(\vec{q}_f) e^{-i\vec{q}_f \cdot \vec{x}/\hbar} | I \rangle \langle I | \vec{p} \cdot \epsilon_i a_{\lambda_i}(\vec{q}_i) e^{i\vec{q}_i \cdot \vec{x}/\hbar} | A; \vec{q}_i, \lambda_i \rangle}{E_i - E_m + i\epsilon} \\ &= \frac{e^2}{c^2} \frac{1}{m^2} \frac{2\pi\hbar c^2}{L^3} \frac{1}{\sqrt{\omega_i \omega_f}} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_f^* e^{-i\vec{q}_f \cdot \vec{x}/\hbar} | I \rangle \langle I | \vec{p} \cdot \epsilon_i e^{i\vec{q}_i \cdot \vec{x}/\hbar} | A \rangle}{E_i - E_m + i\epsilon}. \end{aligned} \quad (83)$$

Again for $\vec{q} \cdot \vec{x} \ll \hbar$, it becomes

$$= \frac{e^2}{c^2} \frac{1}{m^2} \frac{2\pi\hbar c^2}{L^3} \frac{1}{\sqrt{\omega_i \omega_f}} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{E_A + \hbar\omega_i - E_I + i\epsilon}. \quad (84)$$

We used $E_i = E_A + \hbar\omega_i$ and $E_m = E_I$.

The other possibility for the intermediate states in Eq. (80) is that m is an atomic state together with two photons $|m\rangle = |I; \vec{q}_f, \lambda_f; \vec{q}_i, \lambda_i\rangle$. In this case, we pick annihilation operator in the first matrix element and creation operator in the second matrix element, and similar calculation as the previous case gives

$$\begin{aligned} & \sum_I \frac{\langle B; \vec{q}_f, \lambda_f | -\frac{e}{c} \frac{\vec{p} \cdot \vec{A}(\vec{x})}{m} | I; \vec{q}_f, \lambda_f; \vec{q}_i, \lambda_i \rangle \langle I; \vec{q}_f, \lambda_f; \vec{q}_i, \lambda_i | -\frac{e}{c} \frac{\vec{p} \cdot \vec{A}(\vec{x})}{m} | A; \vec{q}_i, \lambda_i \rangle}{E_i - E_m + i\epsilon} \\ &= \frac{e^2}{c^2} \frac{1}{m^2} \frac{2\pi\hbar c^2}{L^3} \frac{1}{\sqrt{\omega_i \omega_f}} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{E_A - \hbar\omega_f - E_I + i\epsilon}. \end{aligned} \quad (85)$$

²The state I may be either one of the bound atomic states or a continuum state.

We used $E_m = E_I + \hbar\omega_f + \hbar\omega_i$.

Putting all of them together,

$$\begin{aligned} & \langle B; \vec{q}_f, \lambda_f | U_I(t_f, t_i) | A; \vec{q}_i, \lambda_i \rangle \\ &= -i2\pi\delta(E_f - E_i) \frac{2\pi\hbar c^2}{L^3} \frac{e^2}{mc^2} \frac{1}{\sqrt{\omega_i\omega_f}} \left(\vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \delta_{B,A} \right. \\ & \quad \left. + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{E_A + \hbar\omega_i - E_I + i\epsilon} + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{E_A - \hbar\omega_f - E_I + i\epsilon} \right) \end{aligned} \quad (86)$$

The combination $r_0 \equiv e^2/mc^2$ is called the classical radius of electron,³ and is numerically $r_0 = 2.82 \times 10^{-13}$ cm.

Finally, we obtain the expression for the scattering cross section. We square the transition amplitude above to obtain the transition probability. We use Eq. (70) to deal with the square of the delta function, and divide the result by the time interval T to obtain the transition rate:

$$\begin{aligned} W_{fi} &= 2\pi\delta(E_f - E_i) \left(\frac{2\pi\hbar c^2}{L^3} \right)^2 r_0^2 \frac{1}{\omega_i\omega_f} \left| \vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \delta_{B,A} \right. \\ & \quad \left. + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{E_A + \hbar\omega_i - E_I + i\epsilon} + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{E_A - \hbar\omega_f - E_I + i\epsilon} \right|^2. \end{aligned} \quad (87)$$

Total cross section is obtained by dividing the transition rate by the flux of photons and summing over all possible final states. In our case, there is one photon in the initial state in the volume L^3 moving with speed of light. Therefore, the photon meets the atom with a flux of one per area L^2 per time L/c , and hence the flux is c/L^3 . The summation over final states is done by summing over final photon momentum \vec{q}_f and polarization λ_f . Using the large volume limit, we replace the sum over possible final momenta $\sum_{\vec{q}_f}$ by an integral $L^3 \int d\vec{q}_f / (2\pi\hbar)^3$. Therefore,

$$\begin{aligned} \sigma &= \frac{L^3}{c} \int \frac{L^3 d\vec{q}_f}{(2\pi\hbar)^3} \sum_{\lambda_f} W_{fi} \\ &= r_0^2 \frac{c^3}{\hbar^2} \frac{1}{\omega_i\omega_f} \int d\vec{q}_f \delta(E_f - E_i) \left| \vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \delta_{B,A} \right. \end{aligned}$$

³Lorentz tried to understand electron basically as a spherical ball spinning around. The electrostatic energy of a charged ball is approximately $E \sim e^2/r$, which he equated to the rest energy of the electron mc^2 . That way, you can see the meaning of the ‘‘classical radius of electron.’’

$$\begin{aligned}
& + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{E_A + \hbar\omega_i - E_I + i\epsilon} + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{E_A - \hbar\omega_f - E_I + i\epsilon} \Big|^2 \\
= & r_0^2 \frac{\omega_f}{\omega_i} \int d\Omega_f \left| \vec{\epsilon}_i \cdot \vec{\epsilon}_f^* \delta_{B,A} \right. \\
& \left. + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{E_A + \hbar\omega_i - E_I + i\epsilon} + \frac{1}{m} \sum_I \frac{\langle B | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{E_A - \hbar\omega_f - E_I + i\epsilon} \right|^2 \quad (88)
\end{aligned}$$

The dependence on the size of the box disappeared as desired, and we did the integration over $|\vec{q}_f|$ using the delta function $\delta(E_f - E_i) = \delta(c|\vec{q}_f| + E_B - c|\vec{q}_i| - E_A)$.

3.4.3 Rayleigh Scattering

Rayleigh scattering is the photon-atom scattering in the regime where the photon energy is much less than the excitation energy ΔE of the atom. In this case, the energy denominator is large and the cross section is suppressed as $(\hbar\omega/\Delta E)^4$. We will see this explicitly in the following calculation. The steep dependence on the cross section on the frequency (or wave length) of the photon is why the sky is blue and the sunset is red.

When $\hbar\omega \ll \Delta E$, there are many cancellations in the amplitude. To see this, we need to make each contribution to the amplitude look similar to each other. Therefore, we rewrite the simple term $\vec{\epsilon}_i \cdot \vec{\epsilon}_f^*$ in a form as ugly as the rest. Then we can see the cancellations explicitly and obtain a form that shows the suppression factor. We will assume $A = B$ because the photon does not have enough energy to excite the atom in the final state. It also means $\omega_i = \omega_f = \omega$.

The trick is the simple point

$$[\vec{\epsilon}_i \cdot \vec{x}, \vec{\epsilon}_f^* \cdot \vec{p}] = i\hbar \vec{\epsilon}_i \cdot \vec{\epsilon}_f^*. \quad (89)$$

Then the first term in the absolute square in Eq. (88) can be rewritten as

$$\vec{\epsilon}_i \cdot \vec{\epsilon}_f^* = \frac{1}{i\hbar} \langle A | [\vec{\epsilon}_i \cdot \vec{x}, \vec{\epsilon}_f^* \cdot \vec{p}] | A \rangle. \quad (90)$$

Then we insert a complete set of states $1 = \sum_I |I\rangle \langle I|$,

$$\vec{\epsilon}_i \cdot \vec{\epsilon}_f^* = \frac{1}{i\hbar} \sum_I \left(\langle A | \vec{\epsilon}_i \cdot \vec{x} | I \rangle \langle I | \vec{\epsilon}_f^* \cdot \vec{p} | A \rangle - \langle A | \vec{\epsilon}_f^* \cdot \vec{p} | I \rangle \langle I | \vec{\epsilon}_i \cdot \vec{x} | A \rangle \right). \quad (91)$$

Then we further use the same trick we used in dipole transitions backwards,

$$\langle A|\vec{\epsilon}_i \cdot \vec{x}|I\rangle = \frac{1}{E_A - E_I} \langle A|[H_0, \vec{\epsilon}_i \cdot \vec{x}]|I\rangle = \frac{-i\hbar}{m} \frac{1}{E_A - E_I} \langle A|\vec{\epsilon}_i \cdot \vec{p}|I\rangle. \quad (92)$$

Therefore,

$$\vec{\epsilon}_i \cdot \vec{\epsilon}_f^* = -\frac{1}{m} \sum_I \left(\frac{\langle A|\vec{\epsilon}_i \cdot \vec{p}|I\rangle \langle I|\vec{\epsilon}_f^* \cdot \vec{p}|A\rangle}{E_A - E_I} - \frac{\langle A|\vec{\epsilon}_f^* \cdot \vec{p}|I\rangle \langle I|\vec{\epsilon}_i \cdot \vec{p}|A\rangle}{E_I - E_A} \right). \quad (93)$$

This expression looks similar enough to the rest of the terms in Eq. (88). The cross section can then be written as

$$\begin{aligned} \sigma &= r_0^2 \int d\Omega_f \left| -\frac{1}{m} \sum_I \left(\frac{\langle A|\vec{\epsilon}_i \cdot \vec{p}|I\rangle \langle I|\vec{\epsilon}_f^* \cdot \vec{p}|A\rangle}{E_A - E_I} - \frac{\langle A|\vec{\epsilon}_f^* \cdot \vec{p}|I\rangle \langle I|\vec{\epsilon}_i \cdot \vec{p}|A\rangle}{E_I - E_A} \right) \right. \\ &\quad \left. + \frac{1}{m} \sum_I \frac{\langle A|\vec{p} \cdot \epsilon_f^*|I\rangle \langle I|\vec{p} \cdot \epsilon_i|A\rangle}{E_A + \hbar\omega - E_I + i\epsilon} + \frac{1}{m} \sum_I \frac{\langle A|\vec{p} \cdot \epsilon_i|I\rangle \langle I|\vec{p} \cdot \epsilon_f^*|A\rangle}{E_A - \hbar\omega - E_I + i\epsilon} \right|^2 \\ &= r_0^2 \frac{1}{m^2} \int d\Omega_f \left| -\sum_I \frac{\hbar\omega \langle A|\vec{p} \cdot \epsilon_f^*|I\rangle \langle I|\vec{p} \cdot \epsilon_i|A\rangle}{(E_A + \hbar\omega - E_I + i\epsilon)(E_A - E_I)} \right. \\ &\quad \left. + \sum_I \frac{\hbar\omega \langle A|\vec{p} \cdot \epsilon_i|I\rangle \langle I|\vec{p} \cdot \epsilon_f^*|A\rangle}{(E_A - \hbar\omega - E_I + i\epsilon)(E_A - E_I)} \right|^2. \end{aligned} \quad (94)$$

The terms in the absolute square are suppressed by $\hbar\omega$.

It turns out, however, that there is even further cancellation between two terms. That is because

$$\begin{aligned} & -\sum_I \frac{\langle A|\vec{p} \cdot \epsilon_f^*|I\rangle \langle I|\vec{p} \cdot \epsilon_i|A\rangle}{(E_A - E_I)^2} + \sum_I \frac{\langle A|\vec{p} \cdot \epsilon_i|I\rangle \langle I|\vec{p} \cdot \epsilon_f^*|A\rangle}{(E_A - E_I)^2} \\ &= \frac{m}{i\hbar} \sum_I \left(-\frac{\langle A|[\vec{x} \cdot \epsilon_f^*, H_0]|I\rangle \langle I|[\vec{x} \cdot \epsilon_i, H_0]|A\rangle}{(E_A - E_I)^2} + \frac{\langle A|[\vec{x} \cdot \epsilon_i, H_0]|I\rangle \langle I|[\vec{x} \cdot \epsilon_f^*, H_0]|A\rangle}{(E_A - E_I)^2} \right) \\ &= \frac{m}{i\hbar} \sum_I \left(\langle A|\vec{x} \cdot \epsilon_f^*|I\rangle \langle I|\vec{x} \cdot \epsilon_i|A\rangle - \langle A|\vec{x} \cdot \epsilon_i|I\rangle \langle I|\vec{x} \cdot \epsilon_f^*|A\rangle \right) \\ &= \frac{m}{i\hbar} \langle A|[\vec{x} \cdot \epsilon_f^*, \vec{x} \cdot \epsilon_i]|A\rangle = 0. \end{aligned} \quad (95)$$

In the second last step, we used the completeness $\sum_I |I\rangle \langle I| = 1$. Therefore, we can subtract this vanishing expression inside the absolute square in

Eq. (94) and find

$$\begin{aligned}
\sigma &= r_0^2 \frac{1}{m^2} \int d\Omega_f \\
&\left| -\sum_I \left(\frac{\hbar\omega \langle A | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{(E_A + \hbar\omega - E_I + i\epsilon)(E_A - E_I)} - \frac{\hbar\omega \langle A | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{(E_A - E_I)^2} \right) \right. \\
&\quad \left. + \sum_I \left(\frac{\hbar\omega \langle A | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{(E_A - \hbar\omega - E_I + i\epsilon)(E_A - E_I)} - \frac{\hbar\omega \langle A | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{(E_A - E_I)^2} \right) \right|^2 \\
&= r_0^2 \frac{1}{m^2} \int d\Omega_f \left| \sum_I \frac{(\hbar\omega)^2 \langle A | \vec{p} \cdot \epsilon_f^* | I \rangle \langle I | \vec{p} \cdot \epsilon_i | A \rangle}{(E_A + \hbar\omega - E_I + i\epsilon)(E_A - E_I)^2} \right. \\
&\quad \left. + \sum_I \frac{(\hbar\omega)^2 \langle A | \vec{p} \cdot \epsilon_i | I \rangle \langle I | \vec{p} \cdot \epsilon_f^* | A \rangle}{(E_A - \hbar\omega - E_I + i\epsilon)(E_A - E_I)^2} \right|^2. \tag{96}
\end{aligned}$$

This expression no longer has big cancellations, and shows that the cross section is suppressed by $(\hbar\omega)^4$.

In order to make an order-of-magnitude estimate of the cross section, it is useful to rewrite the matrix element further using the same trick $[\vec{x}, H_0] = i\hbar\vec{p}/m$. We find

$$\begin{aligned}
\sigma &= r_0^2 m^2 \omega^4 \int d\Omega_f \left| \sum_I \frac{\langle A | \vec{x} \cdot \epsilon_f^* | I \rangle \langle I | \vec{x} \cdot \epsilon_i | A \rangle}{E_A + \hbar\omega - E_I + i\epsilon} \right. \\
&\quad \left. + \sum_I \frac{\langle A | \vec{x} \cdot \epsilon_i | I \rangle \langle I | \vec{x} \cdot \epsilon_f^* | A \rangle}{E_A - \hbar\omega - E_I + i\epsilon} \right|^2. \tag{97}
\end{aligned}$$

From this expression, the size of the matrix elements are of the order of the Bohr radius $a = \hbar^2/Zme^2$, the energy denominator is of the order of $E_{2p} - E_{1s} = 3Z^2e^4m/8\hbar^2$, and the classical radius of electron is $r_0 = e^2/mc^2 = 2.82 \times 10^{-13}$ cm. Ignoring coefficients of order unity, we find

$$\sigma \sim r_0^2 m^2 \omega^4 \left(\frac{(\hbar^2/Zme^2)^2}{Z^2e^4m/\hbar^2} \right)^2 = r_0^2 \left(\frac{\hbar\omega}{Z^2e^4m/\hbar^2} \right)^4. \tag{98}$$

Numerically, for $Z \sim 1$ and $\lambda \sim 7000\text{\AA}$ (red), we have $\hbar\omega \sim 0.28$ eV, and $\sigma \sim 9.0 \times 10^{-3}$ cm². This is a very small cross section. For $\lambda \sim 4000\text{\AA}$ (blue), however, the cross section is $(7/4)^4 = 9.4$ times larger. In a gas at STP, the mean free paths are 4×10^8 km and 4×10^7 km, respectively. These are long enough distances that Sun does not appear blurred by the atmosphere.

However, the scattered light by the atmosphere is 10 times stronger in blue than in red, explaining why the sky is blue. Similarly, blue light is scattered away 10 times more in blue than in red when the Sun is setting and the light traverses a long distance in the atmosphere.

Note that it makes sense intuitively why the cross section vanishes for $\omega \rightarrow 0$ or $\lambda \rightarrow \infty$. For a photon with a long wavelength, it is hard to see any structure at scales less than λ . Therefore, the neutral atoms appear point-like neutral objects, and by definition, photon does not “see” them; it couples only to electric charges. Only for a sufficiently short wavelength, photon can see that the neutral atoms actually consist of electrically charged objects, and can scatter off them. Therefore, the cross section should vanish with some power of $1/\lambda$. With an actual calculation, we found that it goes with the fourth power, a very steep dependence.

3.4.4 Resonant Scattering

In Eq. (88), it appears troublesome when $E_A + \hbar\omega \rightarrow E_I$. The energy denominator vanishes and the cross section blows up. What is wrong?

When you consider the scattering of a photon with hydrogen atom in the $1s$ state, and when the photon energy is close to $E_{2p} - E_{1s}$, we can excite the atom to the $2p$ state, which decays later down to $1s$ state again. This causes a big enhancement in the photon-atom scattering cross section. We had studied this phenomenon in the context of potential scattering before, and had identified such an enhancement as a consequence of a resonance. We had also learned back then that the energy of a resonance is slightly shifted downward on the complex plane, namely the energy has a negative imaginary part. How do we see that for the $2p$ state here?

The answer is quite simple. When you calculate a shift in the energy eigenvalue at the second order in perturbation theory, the formula is

$$\Delta E = \sum_f \frac{\langle i|V|f\rangle\langle f|V|i\rangle}{E_i - E_f}. \quad (99)$$

Here, i is the state of your interest ($|2p\rangle$ in our case) and f runs over all possible intermediate states ($|1s\rangle|\vec{q}, \lambda\rangle$ in our case). However, when the intermediate state is a continuum, E_i and E_f can in general be exactly the same. That would cause a singularity. To avoid it, we take the same prescription as we took in Lippmann–Schwinger equation to insert a factor of

$i\epsilon$:

$$\Delta E = \sum_f \frac{\langle i|V|f\rangle\langle f|V|i\rangle}{E_i - E_f + i\epsilon}. \quad (100)$$

Having done that, we now write the denominator factor in the standard way as

$$\frac{1}{E_i - E_f + i\epsilon} = \mathcal{P} \frac{1}{E_i - E_f} - i\pi\delta(E_i - E_f). \quad (101)$$

Therefore the energy shift now has an imaginary part! We find

$$\Im\Delta E = -\pi \sum_f \langle i|V|f\rangle\langle f|V|i\rangle\delta(E_i - E_f). \quad (102)$$

You can see that it is related to Fermi's golden rule by

$$-\frac{\Gamma_i}{2} \equiv \Im\Delta E = -\frac{1}{2}\hbar \sum_f W_{fi} = -\frac{1}{2}\hbar W_i, \quad (103)$$

and hence the imaginary part of the energy is related to the decay rate of the unstable state (resonance) precisely in the way we discussed in the scattering theory.

In general, around $\hbar\omega_i \sim E_I - E_A$, the cross section Eq. (88) is dominated by one term,

$$\sigma = r_0^2 \frac{\omega_f}{\omega_i} \int d\Omega_f \left| \frac{\langle B|\vec{p} \cdot \epsilon_f^*|I\rangle\langle I|\vec{p} \cdot \epsilon_i|A\rangle}{E_A + \hbar\omega_i - E_I + i\Gamma_I/2} \right|^2, \quad (104)$$

where Γ_I is the width of the state I . The matrix elements vary slowly with ω_i , while the energy denominator produces a strong peak at $\hbar\omega_i = E_I - E_A$. The dependence is approximately that of Breit–Wigner function as we saw in the scattering theory. Γ_I is the HWFM of the Breit–Wigner resonance shape as a function of the energy, while $\tau_I \equiv 1/W_I = \hbar/\Gamma_I$ is the lifetime of the resonance.

4 Multi-Pole Expansion

In many applications, it is useful to consider photons in angular-momentum eigenstates. This is equivalent to the multi-pole expansion of electromagnetic field.

4.1 Spinless Schrödinger Field

First of all, the multi-pole expansion of the Schrödinger field $\psi(\vec{x})$ without spin is given by the Laplace equation

$$(\Delta + k^2)\psi(\vec{x}) = \left(\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} + k^2 \right) \psi(\vec{x}) = 0. \quad (105)$$

The solutions regular at the origin are

$$u_{klm}(\vec{x}) = 2j_l(kr)Y_l^m(\theta, \phi). \quad (106)$$

It is normalized as

$$\int d\vec{x} u_{klm} u_{k'l'm'}^* = \delta_{ll'} \delta_{mm'} \frac{2\pi}{k^2} \delta(k - k'). \quad (107)$$

Expanding a field in terms of angular momentum eigenmodes is the multi-pole expansion:

$$\psi(\vec{x}) = \sum_{lm} \int \frac{dk}{2\pi} k^2 a_{klm} u_{klm}(\vec{x}). \quad (108)$$

The canonical commutation relation $[\psi(\vec{x}), \psi^\dagger(\vec{y})] = \delta(\vec{x} - \vec{y})$ implies the commutation relation

$$[a_{klm}, a_{k'l'm'}^\dagger] = \delta_{ll'} \delta_{mm'} \frac{2\pi}{k^2} \delta(k - k'). \quad (109)$$

This set of creation and annihilation operators obey delta-function normalization because we have not put the system in a box. Correspondingly, a state created by the creation operator also satisfies the delta-function normalization

$$\langle k'l'm' | klm \rangle = \langle 0 | a_{k'l'm'}^\dagger a_{klm} | 0 \rangle = \delta_{ll'} \delta_{mm'} \frac{2\pi}{k^2} \delta(k - k'). \quad (110)$$

4.2 Vector Potential

How do we expand a vector potential? We certainly need to find vectors out of u_{klm} . We do so by acting certain differential operators. Define

$$\vec{u}_{kjm}^L = \frac{1}{k} \vec{\nabla} u_{kjm} \quad (111)$$

$$\vec{u}_{kjm}^M = \frac{1}{\sqrt{l(l+1)}} (\vec{x} \times \vec{\nabla}) u_{kjm} \quad (112)$$

$$\vec{u}_{kjm}^E = \frac{1}{k\sqrt{l(l+1)}} \vec{\nabla} \times (\vec{x} \times \vec{\nabla}) u_{kjm}. \quad (113)$$

Due to the reason we will see below, they are longitudinal, magnetic, and electric multipoles, respectively. They all satisfy the Laplace equation Eq. (105) because the differential operators acting on u_{kjm} all commute with the Laplacian. They also satisfy the normalization

$$\int d\vec{x} \vec{u}_{kjm}^A \cdot \vec{u}_{k'j'm'}^{B*} = \delta_{AB} \delta_{ll'} \delta_{mm'} \frac{2\pi}{k^2} 2\pi \delta(k - k'), \quad (114)$$

for $A, B = L, E, M$. Given this orthonormal set, we expand the vector potential as

$$\vec{A} = \sum_{lm} \sum_A \int \frac{dk}{2\pi} k^2 \sqrt{\frac{2\pi\hbar c^2}{\omega}} (a_{kjm}^A \vec{u}_{kjm}^A + a_{kjm}^{A\dagger} \vec{u}_{kjm}^{A*}), \quad (115)$$

and correspondingly,

$$\dot{\vec{A}} = \sum_{lm} \sum_A \int \frac{dk}{2\pi} k^2 (-i) \sqrt{2\pi\hbar c^2 \omega} (a_{kjm}^A \vec{u}_{kjm}^A - a_{kjm}^{A\dagger} \vec{u}_{kjm}^{A*}), \quad (116)$$

The creation and annihilation operators satisfy the commutation relation

$$[a_{kjm}^A, a_{k'j'm'}^{A\dagger}] = \delta_{AB} \delta_{ll'} \delta_{mm'} \frac{2\pi}{k^2} \delta(k - k'). \quad (117)$$

You can check the commutation relation Eq. (10) with this multipole expansion.

In the Coulomb gauge, we simply drop $A = L$ from the summation because

$$\vec{\nabla} \cdot \vec{u}_{kjm}^L = \frac{1}{k} \Delta u_{kjm} = -k u_{kjm} \neq 0, \quad (118)$$

and hence does not satisfy the gauge condition. Electric and magnetic multipoles satisfy the Coulomb gauge condition.

The reason behind the names is very simple. Electric (magnetic) multipoles have non-vanishing radial component of electric (magnetic) field, while magnetic (electric) multipoles don't. Both $u_{kjm}^{\vec{M}, E}$ describes a mode with total angular momentum j , with parity $(-1)^{j+1}$ for magnetic and $(-1)^j$ for electric multipoles (we will see this in the next section). An important point is that both multipoles vanish identically when $j = 0$, and hence *a photon carries always angular momentum $j = 1$ or more*. This is easy to see. The magnetic multipoles have basically the angular momentum operator acting

on the spinless case $u_{klm}^M = (\vec{x} \times \vec{\nabla})u_{klm} = \frac{i}{\hbar}\vec{L}u_{klm}$. Therefore it is non-vanishing only when $l \neq 0$. The electric multipoles are curl of the magnetic ones, and again only non-vanishing ones are $l \neq 0$.

It may be confusing that I'm switching back and forth between j and l . Let us check what $\vec{J} = \vec{L} + \vec{S}$ actually does on these modes. $\vec{L} = -i\hbar(\vec{x} \times \vec{\nabla})$ is the usual one acting on the modes. (Note that we use \vec{L} or \vec{p} and their commutation relations in this discussion, but we only use them as short-hand notation for differential operators. They are not operators acting on the photon Fock space, but differential operators acting on the c -number mode functions \vec{u}_{klm}^A with which we are expanding the operator vector potential.) The spin matrices are obviously those for spin one case, and are given by

$$S_x = -i\hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, \quad S_y = -i\hbar \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad S_z = -i\hbar \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (119)$$

Note that $\vec{u}_{kjm}^M = \frac{i}{\hbar}\vec{L}u_{klm}$. Acting $\vec{J}^2 = \vec{L}^2 + 2\vec{L} \cdot \vec{S} + \vec{S}^2$ on \vec{u}_{kjm}^M , we can see that $\vec{L}^2 = l(l+1)\hbar^2$, and $\vec{S}^2 = 2\hbar^2$ because \vec{L} commutes with both of them. The action of $\vec{L} \cdot \vec{S}$ needs to be worked out:

$$\begin{aligned} \vec{L} \cdot \vec{S} \vec{u}_{kjm}^M &= -i\hbar \begin{pmatrix} 0 & L_z & -L_y \\ -L_z & 0 & L_x \\ L_y & -L_x & 0 \end{pmatrix} \frac{i}{\hbar} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} u_{klm} \\ &= \begin{pmatrix} [L_z, L_y] \\ [L_x, L_z] \\ [L_y, L_x] \end{pmatrix} u_{klm} \\ &= -\hbar^2 \vec{u}_{kjm}^M. \end{aligned} \quad (120)$$

Therefore $\vec{L} \cdot \vec{S} = -\hbar^2$, and hence $\vec{J}^2 = \vec{L}^2 + 2\vec{L} \cdot \vec{S} + \vec{S}^2 = l(l+1)\hbar^2 - 2\hbar^2 + 2\hbar^2 = l(l+1)\hbar^2$. That is why u_{klm} gives the total angular momentum $j = l$, and we've used them interchangeably. It is also an eigenstate of the $J_z = m\hbar$, because

$$\begin{aligned} J_z \vec{u}_{kjm}^M &= (L_z + S_z) \frac{i}{\hbar} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} u_{klm} \\ &= \frac{i}{\hbar} \begin{pmatrix} L_z L_x - i\hbar L_y \\ L_z L_y + i\hbar L_x \\ L_z L_z \end{pmatrix} u_{klm} \end{aligned}$$

$$\begin{aligned}
&= \frac{i}{\hbar} \begin{pmatrix} L_x L_z \\ L_y L_z \\ L_z L_z \end{pmatrix} u_{klm} \\
&= m\hbar \vec{u}_{kjm}^M.
\end{aligned} \tag{121}$$

It is not in a helicity eigenstate, however. The helicity is the spin along the direction of the momentum $h = (\vec{S} \cdot \vec{p})/|\vec{p}|$. If you act $\vec{S} \cdot \vec{p}$ on \vec{u}_{klm}^M , you find

$$\begin{aligned}
(\vec{S} \cdot \vec{p})\vec{u}_{kjm}^M &= -i\hbar \begin{pmatrix} 0 & p_z & -p_y \\ -p_z & 0 & p_x \\ p_y & -p_x & 0 \end{pmatrix} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} u_{klm} \\
&= \hbar^2 \vec{\nabla} \times \vec{u}_{klm}^M \\
&= \hbar^2 k \vec{u}_{klm}^E.
\end{aligned} \tag{122}$$

The electric multipoles \vec{u}_{kjm}^E also have the eigenvalues $\vec{J}^2 = l(l+1)\hbar^2$, $J_z = m\hbar$. That can be shown by the fact that $\vec{u}_{klm}^E = (\vec{S} \cdot \vec{p})\vec{u}_{kjm}^M/\hbar^2 k$, and that $(\vec{S} \cdot \vec{p})$ commutes with \vec{J} . Acting $(\vec{S} \cdot \vec{p})$ on \vec{u}_{kjm}^M brings back \vec{u}_{kjm}^M .

4.3 Parity

Parity is the reflection of space: $\vec{x} \rightarrow -\vec{x}$. Another advantage of the multipole expansion is that the photon is not only in the angular momentum eigenstate but also in the parity eigenstate. The combination of them leads to useful selection rules in the transition amplitudes.

In quantum mechanics, parity P is a unitary and hermitean operator. Like any other symmetry operators such as translation, rotation, time evolution, etc, it has to be unitary $PP^\dagger = 1$ to preserve the probabilities. But doing parity twice is the same as doing nothing, $PP = 1$. Then we find $P = P^\dagger$ and hence it is hermitean. Therefore, states can be classified according to the eigenvalues of the parity operator. If the Hamiltonian is parity-invariant, $PHP = H$, it also means $[P, H] = 0$ (use $P^2 = 1$) and hence the parity is conserved. In other words, if the initial state is an eigenstate of the parity, and final state also should have the same parity eigenvalue. For instance, a particle in a central potential is described by the Hamiltonian

$$H = \frac{\vec{p}^2}{2m} + V(r), \tag{123}$$

which is parity invariant. To see this, we use the definition $P\vec{x}P = -\vec{x}$, and note that the canonical commutation relation $[x^i, p^j] = i\hbar\delta^{ij}$ requires the momentum to also flip its sign $P\vec{p}P = -\vec{p}$. The radius $r = |\vec{x}|$ of course doesn't change under parity. For convenience, I call the parity on the charged particle (say, electron) P_e instead of just P . This is because I need a separate parity acting on the vector potential below.

The parity on the vector potential is

$$P_\gamma\vec{A}(\vec{x})P_\gamma = -\vec{A}(-\vec{x}). \quad (124)$$

Under this transformation, the electric and magnetic fields transform as

$$P_\gamma\vec{E}(\vec{x})P_\gamma = -\vec{E}(-\vec{x}), \quad P_\gamma\vec{B}(\vec{x})P_\gamma = \vec{B}(-\vec{x}). \quad (125)$$

It is easy to check that the Hamiltonian of the radiation field is invariant under parity.

Finally, we look at the interaction Hamiltonian

$$\frac{(\vec{p} - \frac{e}{c}\vec{A}(\vec{x}))^2}{2m}. \quad (126)$$

Acting P_e makes it to

$$P_e\frac{(\vec{p} - \frac{e}{c}\vec{A}(\vec{x}))^2}{2m}P_e = \frac{(-\vec{p} - \frac{e}{c}\vec{A}(-\vec{x}))^2}{2m}, \quad (127)$$

which is not the same. But further acting P_γ makes it to

$$P_\gamma P_e\frac{(\vec{p} - \frac{e}{c}\vec{A}(\vec{x}))^2}{2m}P_e P_\gamma = P_\gamma\frac{(-\vec{p} - \frac{e}{c}\vec{A}(-\vec{x}))^2}{2m}P_\gamma = \frac{(-\vec{p} + \frac{e}{c}\vec{A}(\vec{x}))^2}{2m} = \frac{(\vec{p} - \frac{e}{c}\vec{A}(\vec{x}))^2}{2m} \quad (128)$$

and hence the Hamiltonian is invariant under the product $P \equiv P_\gamma P_e$. Therefore the parity eigenvalue that is conserved is the *product* of parity eigenvalues of electrons and photons.

Now we try to identify the parity of a photon in a multipole. The starting point is the property of the spherical harmonics

$$Y_l^m(\pi - \theta, \phi + \pi) = (-1)^l Y_l^m(\theta, \phi). \quad (129)$$

The argument $(\pi - \theta, \phi + \pi)$ corresponds to the reflected position vector $-\vec{x}$. Based on this property, it is usually said that the state with orbital

angular momentum l is an eigenstate of parity with the eigenvalue $(-1)^l$. The magnetic multipole mode function is defined by acting $\vec{x} \times \vec{\nabla}$, which is even under parity. Therefore,

$$\vec{u}_{kjm}^M(-\vec{x}) = (-1)^j \vec{u}_{kjm}^M(\vec{x}). \quad (130)$$

The electric multiple mode functions are obtained by taking curl of the magnetic ones, and therefore there is an additional sign under parity, and hence

$$\vec{u}_{kjm}^E(-\vec{x}) = (-1)^{j+1} \vec{u}_{kjm}^E(\vec{x}). \quad (131)$$

Now the right-hand side of Eq. (124) is

$$\begin{aligned} -\vec{A}(-\vec{x}) &= -\sum_{jm} \int \frac{dk}{2\pi} k^2 (a_{jkm}^E \vec{u}_{jkm}^E(-\vec{x}) + a_{jkm}^M \vec{u}_{jkm}^M(-\vec{x}) + \text{h.c.}) \\ &= \sum_{jm} \int \frac{dk}{2\pi} k^2 ((-1)^j a_{jkm}^E \vec{u}_{jkm}^E(\vec{x}) + (-1)^{j+1} a_{jkm}^M \vec{u}_{jkm}^M(\vec{x}) + \text{h.c.}), \end{aligned} \quad (132)$$

where h.c. stands for hermitean conjugate. On the other hand, the only operator in the multipole expansion of the vector potential is the creation and annihilation operators, and only they are affected by P_γ . The l.h.s of eq. (124) is then

$$P_\gamma \vec{A}(\vec{x}) P_\gamma = \sum_{jm} \int \frac{dk}{2\pi} k^2 (P_\gamma a_{jkm}^E P_\gamma \vec{u}_{jkm}^E(\vec{x}) + P_\gamma a_{jkm}^M P_\gamma \vec{u}_{jkm}^M(\vec{x}) + \text{h.c.}). \quad (133)$$

Comparing Eqs. (133,132), we find

$$P_\gamma a_{jkm}^E P_\gamma = (-1)^j a_{jkm}^E, \quad P_\gamma a_{jkm}^M P_\gamma = (-1)^{j+1} a_{jkm}^M. \quad (134)$$

The parity eigenvalues of photon states in a given multipole are

$$P_\gamma |jkm, E\rangle = P_\gamma a_{jkm}^{E\dagger} |0\rangle = (-1)^j a_{jkm}^{E\dagger} |0\rangle = (-1)^j |jkm, E\rangle, \quad (135)$$

where I used $P_\gamma |0\rangle = |0\rangle$. Therefore the parity eigenvalue of a photon in electric multipoles is given by $P_\gamma = (-1)^j$. Similarly, they are $P_\gamma = (-1)^{j+1}$ for photons in magnetic multipoles.

Conservation of parity provides powerful selection rules in many systems, especially atomic, molecular and nuclear transitions by emission or absorption of photons. This is because electromagnetism conserves parity. Until

1957, all forces in Nature were believed to conserve parity. The space looks symmetric between right and left, right? Of course! But in 1957, T.D. Lee and C.N. Yang pointed out that parity may be violated in weak interactions. Their study started with what was called τ - θ puzzle. These particles were discovered in cosmic rays, later produced artificially in accelerators, and studied (mostly) in bubble chambers. τ^+ particle was identified by its decay into π^+ and π^0 (remember Yukawa's pions responsible for binding protons and neutrons in nuclei), while θ^+ into $\pi^+\pi^+\pi^-$. Because pions have odd intrinsic parity, and the decay is dominated by S -wave, τ^+ has even parity and θ^+ odd. The puzzle was that they appeared to have exactly the same mass and lifetime. It was too much of a coincidence that Nature provides two particles with identical mass and lifetime. Given this puzzle, Lee and Yang pointed out that maybe τ^+ and θ^+ are not separate particles which happen to have the same masses and lifetimes, but are a single particle with different decay modes. For this to be true, a particle must be decaying into final states with opposite parities, and hence the parity must be broken (i.e., not conserved). Then they asked the question how well parity conservation has been tested experimentally, and to surprise of many people, found that the parity conservation has been tested only in electromagnetic and strong interactions, to some extent in gravity, but never in weak interactions which are responsible for nuclear β -decay and decay of τ and θ particles. They proposed various ways to test (or see violation of) parity in weak interactions. One of them was to study a possible correlation between the spin of nucleus and the momentum of the β -electron. Under parity, spin remains the same while the momentum flips. Therefore, if there is any correlation between the spin and the momentum, it means parity is broken. This experiment was done soon after Lee-Yang's paper by C.S. Wu. She studied the β decay of ^{60}Co . She was clever to use the then-novel discovery that one can polarize nuclei in a magnetic field even when the temperature is not so low. Recall that the nuclear magneton is 2000 times smaller than the Bohr magneton, and it appears it would require an extremely large magnetic field and low temperature to polarize nuclei. However, a magnetic field polarizes unpaired electrons in the atom, which in turn polarizes nuclei due to hyperfine interactions. This turned out to be a much more effective way to polarize nuclei. She still needed a cryostat of course. (I didn't look up the parameters.) She could demonstrate that the β -electrons are emitted preferentially parallel to the spin of the nucleus, while the preference slowly disappeared once she turned off the cryostat. Since then, we know that there is a fundamental

distinction between left and right. The division in Congress has a deep root, indeed!

4.4 Multipole Transitions

Emission of photons in $\vec{u}_{kjm}^{E,M}$ is called Ej or Mj transitions. For instance, the electric dipole transition produces a photon in the state \vec{u}_{k1m}^E , and is called E1 transition. The coupling of a magnetic moment to magnetic field in the Hamiltonian can cause the emission of a photon by a M1 transition. Because $j_l(kr) = (kr)^l/(2l+1)!!$ at small r , higher multipole transitions are suppressed by powers of kr , similarly to the reason why we could omit higher powers in $\vec{q} \cdot \vec{x}/\hbar$ in the $2p \rightarrow 1s$ E1 transition discussed above.

As an example, we recalculate the $2p$ to $1s$ transition using the multipole expansion. In this case, the angular momentum of the atom changes by one unit, which needs to be carried away by the photon. Therefore, only possibilities are E1 and M1 transitions. This way, you can see that the dipole transitions are the only possibilities even before doing any calculations; this is a big advantage in the multipole expansion. To proceed, we need the mode functions $u^{M,E}$ for $j=1$. We take $|2p, m=0\rangle$ again as the initial state, and hence the only mode functions we need are $\vec{u}_{k10}^{M,E}$. First,

$$\begin{aligned}
\vec{u}_{k10}^M &= \frac{i}{\hbar} \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} 2j_1(kr)Y_1^0 \frac{1}{\sqrt{1(1+1)}} \\
&= \frac{i}{\hbar} \begin{pmatrix} (L_+ + L_-)/2 \\ (L_+ - L_-)/2i \\ L_z \end{pmatrix} 2j_1(kr)Y_1^0 \frac{1}{\sqrt{2}} \\
&= i \begin{pmatrix} (Y_1^1 + Y_1^{-1})/2 \\ (Y_1^1 - Y_1^{-1})/2i \\ 0 \end{pmatrix} 2j_1(kr) \frac{1}{\sqrt{2}} \\
&= \sqrt{\frac{3}{2\pi}} \begin{pmatrix} \sin\theta \sin\phi \\ -\sin\theta \cos\phi \\ 0 \end{pmatrix} j_1(kr). \tag{136}
\end{aligned}$$

Using the behavior for small kr , $j_1(kr) \simeq kr/3$, we find

$$\vec{u}_{k10}^M \simeq \frac{k}{\sqrt{6\pi}} \begin{pmatrix} y \\ -x \\ 0 \end{pmatrix}. \tag{137}$$

On the other hand, the electric dipole mode is

$$\vec{u}_{k10}^E = \frac{1}{k} \vec{\nabla} \times \vec{u}_{k10}^M \simeq -\sqrt{\frac{2}{3\pi}} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (138)$$

Note that there is no suppression due to kr in the electric dipole mode and hence is dominant over the magnetic dipole transition. (Another reason why the magnetic dipole transition is not important is because it is forbidden for $2p \rightarrow 1s$ transition due to parity conservation. We actually know that before working out the mode function.) In general, magnetic multipole transitions are suppressed relative to the electric ones for the same multipole in non-relativistic systems.

The only important piece in the multipole expansion of the vector potential is then

$$\vec{A}(\vec{x}) \ni \int_0^\infty \frac{dk}{2\pi} k^2 \sqrt{\frac{2\pi\hbar c^2}{\omega_k}} a_{k10}^\dagger \left(-\sqrt{\frac{2}{3\pi}} \right) \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (139)$$

(I'm using a sloppy notation that \ni means the r.h.s. is only the important part of the l.h.s.) Then the interaction Hamiltonian is

$$V = -\frac{e}{c} \frac{1}{m} p_z A_z \ni \frac{e}{mc} \sqrt{\frac{2}{3\pi}} p_z \int_0^\infty \frac{dk}{2\pi} k^2 \sqrt{\frac{2\pi\hbar c^2}{\omega_k}} a_{k10}^\dagger. \quad (140)$$

The matrix element is (see Eq. (60))

$$\begin{aligned} & \langle 1s | \langle k10 | V | 0 \rangle | 2p, m=0 \rangle \\ &= \frac{e}{mc} \sqrt{\frac{2}{3\pi}} \int_0^\infty \frac{dk'}{2\pi} k'^2 \sqrt{\frac{2\pi\hbar c^2}{\omega_{k'}}} \langle k10 | a_{k'10}^\dagger | 0 \rangle \langle 1s | p_z | 2p, m=0 \rangle \\ &= \frac{e}{mc} \sqrt{\frac{2}{3\pi}} \sqrt{\frac{2\pi\hbar c^2}{\omega_k}} \frac{1}{\sqrt{2}} \frac{256}{243} \frac{m}{\hbar} E_\gamma. \end{aligned} \quad (141)$$

(Recall $q = \hbar k = E_\gamma/c = \hbar\omega_k/c$.)

The decay rate is again given by the Fermi's golden rule Eq. (45). The only non-trivial difference is that the summation over the final state is given by

$$\sum_f = \sum_{jm} \int \frac{dk}{2\pi} k^2, \quad (142)$$

while only $j = 1$, $m = 0$ contributes in our case. Therefore,

$$\begin{aligned} W_i &= \frac{1}{\hbar} \int \frac{dk}{2\pi} k^2 \frac{e^2}{m^2 c^2} \frac{2}{3\pi} \frac{2\pi \hbar^2 c}{q} \left(\frac{1}{\sqrt{2}} \frac{256}{243} a \right)^2 \frac{m^2}{\hbar^2} (cq)^2 2\pi \delta(E_f - E_i) \\ &= \frac{e^2}{\hbar^4} q^3 a^2 \frac{2}{3} \left(\frac{256}{243} \right)^2, \end{aligned} \quad (143)$$

which precisely agrees with Eq. (61).

As we have seen in this example, the advantage of the multipole expansion is that the selection rule is manifest. For a given initial and final state with fixed angular momenta and parities, one can immediately tell that multipole would dominate in the transition.

There is an example in nuclear γ decay from a 2^+ state to a 5^+ state. From the angular momentum consideration, the photon must be in the multipoles of $j = 3, 4, 5, 6$, or 7 . From the parity consideration, it has to have even parity. Therefore, allowed multipole transitions are M3, E4, M5, E6, M7. Higher multipoles have higher powers in kr and hence are suppressed. However, as we saw above, the electric multipoles have one less power in kr compared to the corresponding magnetic ones. Therefore, M3 and E4 transitions appear with the same power in kr (third power) and they both contribute in this transition and they interfere.

5 Casimir Effect

So far, we had not cared much about the zero-point energy of the photons in Eq. (28). It is often said that the zero-point energy just amounts to the baseline energy and all other energies are measured relative to it. In other words, pretending it doesn't exist is enough. But the zero-point energy plays a role if a change in the system affects the zero-point energy itself. (See Milonni, P. W., and Shih, M. L., 1992, *Contemp. Phys.* **33**, 313. for a review.)

To be concrete, put two conducting plates parallel to each other. The distance between the plates is d (at $z = 0$ and $z = d$), and the plates are very large of area L^2 where we take $L \rightarrow \infty$. To simplify the discussions, we also place thin plates at $x = 0$, $x = L$ and $y = 0$, $y = L$ to form a box. A conducting plate imposes boundary conditions on the radiation field $E_{\parallel} = 0$ and $B_{\perp} = 0$. Given these boundary conditions, the vector potential

is expanded in modes as

$$\vec{A}(\vec{x}) \sim \vec{\epsilon} \sin(n_x, n_y, n_z) \left(\frac{\pi n_x}{L} x + \frac{\pi n_y}{L} y + \frac{\pi n_z}{d} z \right), \quad (144)$$

for n_x, n_y , and n_z non-negative integers. For each wave vector $\vec{k} = (\pi n_x/L, \pi n_y/L, \pi n_z/d)$, the polarization vector is transverse: $\vec{k} \cdot \vec{\epsilon} = 0$. If one of the n 's vanishes, however, say $\vec{k} = (0, \pi n_y/L, \pi n_z/d)$, the polarization vector $\vec{\epsilon} = (1, 0, 0)$ is not allowed because that would give $A_x \neq 0$ for any x (and generic y, z) and violates the boundary condition $E_{\parallel} = 0$. Therefore, we have only one polarization whenever one of n 's vanishes.

The sum of zero point energies in this set up is therefore given by

$$U(d) = \sum' \frac{1}{2} \hbar \omega \times 2 = \sum'_{n_x, n_y, n_z} \hbar c \left[\left(\frac{\pi n_x}{L} \right)^2 + \left(\frac{\pi n_y}{L} \right)^2 + \left(\frac{\pi n_z}{d} \right)^2 \right]^{1/2}. \quad (145)$$

The summation \sum' means that whenever one of n 's vanishes, we drop the multiplicity 2 for possible transverse polarizations. Because we regard the size of the plate to be large $L \rightarrow \infty$, we can replace the sum over n_x, n_y in terms of integrals over $k_{x,y} = \pi n_{x,y}/L$,

$$U(d) = \left(\frac{L}{\pi} \right)^2 \sum'_{n_z} \int_0^{\infty} dk_x \int_0^{\infty} dk_y \hbar c \left[k_x^2 + k_y^2 + \left(\frac{\pi n_z}{d} \right)^2 \right]^{1/2}. \quad (146)$$

Recall that we are interested in the *difference* in the zero-point energy when d is varied. Therefore, it is useful to compare it to the case when the plates don't exist. We can compute the zero-point energy density in the infinite volume as usual, and then calculate the energy $U_0(d)$ multiplied by the volume $L^2 d$:

$$\begin{aligned} U_0(d) &= Ld^2 \int \frac{d\vec{k}}{(2\pi)^3} \hbar c [k_x^2 + k_y^2 + k_z^2]^{1/2} \\ &= Ld^2 \int_0^{\infty} \frac{dk_x}{\pi} \int_0^{\infty} \frac{dk_y}{\pi} \int_0^{\infty} \frac{dk_z}{\pi} \hbar c [k_x^2 + k_y^2 + k_z^2]^{1/2}. \end{aligned} \quad (147)$$

What is observable is the difference

$$\begin{aligned} &U(d) - U_0(d) \\ &= \frac{L^2}{\pi^2} \hbar c \int_0^{\infty} dk_x dk_y \left\{ \sum'_{n_z} \left[k_x^2 + k_y^2 + \left(\frac{\pi n_z}{d} \right)^2 \right]^{1/2} - \frac{d}{\pi} \int_0^{\infty} dk_z [k_x^2 + k_y^2 + k_z^2]^{1/2} \right\}. \end{aligned} \quad (148)$$

Switching to the circular coordinates,

$$\int_0^\infty dk_x dk_y = \int_0^\infty k_\perp dk_\perp \int_0^{\pi/2} d\phi = \frac{\pi}{4} \int_0^\infty dk_\perp^2,$$

we find

$$\begin{aligned} U(d) - U_0(d) &= \frac{L^2}{\pi^2} \hbar c \frac{\pi}{4} \int_0^\infty dk_\perp^2 \left\{ \sum'_{n_z} \left[k_\perp^2 + \left(\frac{\pi n_z}{d} \right)^2 \right]^{1/2} - \frac{d}{\pi} \int_0^\infty dk_z [k_\perp^2 + k_z^2]^{1/2} \right\}. \end{aligned} \quad (149)$$

This expression appears problematic because it looks badly divergent. The divergence appears when the wave vector is large, which corresponds to high frequency photons. The point is that the conducting plates are transparent to, say, gamma rays, or in general for photons whose wavelengths are shorter than interatomic separation a . Therefore, there is naturally a damping factor $f(\omega) = f(c(k_\perp^2 + k_z^2)^{1/2})$ with $f(0) = 1$ which smoothly cuts off the integral for $\omega \gtrsim c/a$. In particular, $f(\infty) = 0$. Then the expression is safe and allows us to use standard mathematical tricks. Changing to dimensionless variables $u = (k_\perp d/\pi)^2$ and $n_z = k_z d/\pi$,

$$U(d) - U_0(d) = \frac{\pi^2 L^2 \hbar c}{4d^3} \int_0^\infty du \left\{ \sum'_{n_z} \sqrt{u + n_z^2} - \int_0^\infty dn_z \sqrt{u + n_z^2} \right\} f(\omega). \quad (150)$$

Interchanging the sum and integral, we define the integral

$$F(n) = \int_0^\infty du \sqrt{u + n^2} f(\omega) = \int_{n^2}^\infty du \sqrt{u} f(\omega) \quad (151)$$

with $\omega = \pi c \sqrt{u}/d$ in the last expression. Using this definition, we can write

$$U(d) - U_0(d) = \frac{\pi^2 L^2 \hbar c}{4d^3} \left\{ \frac{1}{2} F(0) + \sum_{n=1}^\infty F(n) - \int_0^\infty dn F(n) \right\}. \quad (152)$$

Here we can use the Euler–McLaurin formula

$$\frac{1}{2} F(0) + \sum_{n=1}^\infty F(n) - \int_0^\infty F(n) = -\frac{1}{2!} B_2 F'(0) - \frac{1}{4!} B_4 F'''(0) - \dots \quad (153)$$

The coefficientss B_k are Bernoulli numbers defined by the Taylor expansion

$$\frac{x}{e^x - 1} = \sum_{k=0}^{\infty} B_k \frac{x^k}{k!}, \quad (154)$$

and $B_0 = 1$, $B_1 = -1/2$, $B_2 = 1/6$, $B_4 = -1/30$, and all odd ones B_{2n-1} vanish except B_1 .

Here is a physicist's proof of the Euler–McLaurin formula. Using the Taylor expansion that defines the Bernoulli numbers, we replace x to a derivative operator ∂_x

$$\frac{\partial_x}{e^{\partial_x} - 1} = \sum_{k=0}^{\infty} B_k \frac{\partial_x^k}{k!}. \quad (155)$$

We act this operator on a function $F(x)$ and integrate it over x from 0 to ∞ ,

$$\int_0^{\infty} dx \frac{\partial_x}{e^{\partial_x} - 1} F(x) = \int_0^{\infty} dx \sum_{k=0}^{\infty} B_k \frac{\partial_x^k}{k!} F(x). \quad (156)$$

The l.h.s. of Eq. (156) is then

$$\begin{aligned} \int_0^{\infty} \sum_{k=0}^{\infty} B_k \frac{\partial_x^k}{k!} F(x) &= \int_0^{\infty} F(x) dx + \sum_{k=1}^{\infty} B_k \left[\frac{\partial_x^{k-1}}{k!} F(x) \right]_0^{\infty} \\ &= \int_0^{\infty} F(x) dx - \sum_{k=0}^{\infty} B_k \frac{1}{k!} F^{(k-1)}(0) \\ &= \int_0^{\infty} F(x) dx + \frac{1}{2} F(0) - \sum_{k=1}^{\infty} B_{2k} \frac{1}{(2k)!} F^{(2k-1)}(0). \end{aligned} \quad (157)$$

On the other hand, the r.h.s. of Eq. (156) is

$$\int_0^{\infty} dx \frac{\partial_x}{e^{\partial_x} - 1} F(x). \quad (158)$$

By Taylor expanding the denominator,

$$\frac{\partial_x}{e^{\partial_x} - 1} F(x) = - \sum_{n=0}^{\infty} \partial_x e^{n\partial_x} F(x). \quad (159)$$

Note that $e^{a\partial_x} F(x) = \sum_{m=0}^{\infty} \frac{1}{m!} a^m F^{(m)}(x) = F(x+a)$ and hence the r.h.s. is

$$\int_0^{\infty} dx \frac{\partial_x}{e^{\partial_x} - 1} F(x) = - \int_0^{\infty} dx \partial_x \sum_{n=0}^{\infty} F(x+n) = \sum_{n=0}^{\infty} F(n). \quad (160)$$

By comparing both sides of Eq. (156), we now find

$$\sum_{n=0}^{\infty} F(n) = \int_0^{\infty} F(x) dx + \frac{1}{2} F(0) - \sum_{k=1}^{\infty} B_{2k} \frac{1}{(2k)!} F^{(2k-1)}(0). \quad (161)$$

Moving first two terms in the r.h.s. to the l.h.s, we obtain the Euler–McLaurin formula

$$\frac{1}{2}F(0) + \sum_{n=1}^{\infty} F(n) - \int_0^{\infty} F(x)dx = - \sum_{k=1}^{\infty} B_{2k} \frac{1}{(2k)!} F^{(2k-1)}(0). \quad (162)$$

Wondering why all odd B_k vanish except for B_1 ? It is easy to check that

$$\frac{x}{e^x - 1} + \frac{1}{2}x = \frac{x(2 + e^x - 1)}{2(e^x - 1)} = \frac{x}{2} \coth \frac{x}{2} \quad (163)$$

which is manifestly an even function of x .

Going back to the definition of our function $F(n)$ Eq. (151), we find

$$F'(n) = -2n^2 f(\pi cn/d). \quad (164)$$

As we will see below, we have d of order micron in our mind. This distance is far larger than the interatomic spacing, and hence $f(\pi cn/d)$ is constant $f = 1$ in the region of our interest. Therefore, we can ignore derivatives $f^{(n)}(0)$, and hence the only important term in the Euler–McLaurin formula Eq. (153) is $F'''(0) = -4$. We obtain

$$U(d) - U_0(d) = -\frac{\pi^2 L^2 \hbar c}{4d^3} F'''(0) \frac{1}{4!} B_4 = -\frac{\pi^2 L^2 \hbar c}{720d^3}. \quad (165)$$

In other words, there is an *attractive* force between two conducting plates

$$F = [U(d) - U_0(d)]' = \frac{\pi^2 L^2 \hbar c}{240d^4} \quad (166)$$

which is numerically

$$\frac{0.013 \text{dyn/cm}^2}{(d/\mu\text{m})^3} \quad (167)$$

per unit area. This is indeed a tiny force, but Sparnay has observed it for the first time in 1958. He placed chromium steel and aluminum plates at distances between $0.3\text{--}2\mu\text{m}$, attached to a spring. The plates are also connected to a capacitor. By measuring the capacitance, he could determine the distance, while the known spring constant can convert it to the force.