Chapter 5: Quantum Electrodynamics

This chapter gives an introduction to **quantum electrodynamics**, the quantum theory of the electromagnetic field and its interactions with electrons and other charged particles. We begin by formulating a quantum Hamiltonian for an electron in a classical electromagnetic field. Then we study how to quantize Maxwell's equations, arriving at a quantum field theory in which the elementary excitations are photons—particles of light. The final step is to formulate a theory in which electrons and photons are treated on the same quantum mechanical footing, as excitations of underlying quantum fields. Along the way, we will see how relativity can be accomodated with quantum theory.

Quantum electrodynamics is an extremely rich and intricate theory, and we will leave out many important topics. Interested readers are referred to are Dyson's 1951 lecture notes on quantum electrodynamics [1], and Zee's textbook *Quantum Field Theory in a Nutshell* [2].

5.1. QUANTIZATION OF THE LORENTZ FORCE LAW

5.1.1. Classical Lagrangian and Hamiltonian

Consider a charged particle in an electromagnetic field. As we are mainly interested in the case where the particle in question is an electron, we will henceforth take the electric charge to be $-e$, where $e = 1.602 \times 10^{-19}\,\text{C}$. For particles with charge q, simply perform the substitution $e \to -q$ in the formulas appearing in this chapter.

Let us formulate the Hamiltonian governing the quantum dynamics of such a particle, subject to some simplifying assumptions: (i) the particle has charge and mass but no other relevant mechanical properties (e.g., we ignore spin); (ii) the electromagnetic field is treated as a classical field, meaning that the electric and magnetic field vectors are classical field variables, not operators; and (iii) the mechanics is non-relativistic. We will later see how to go beyond each of these simplifications.

Classically, the electromagnetic field acts on the particle via the Lorentz force law,

$$\mathbf{F}(\mathbf{r},t) = -e\Big(\mathbf{E}(\mathbf{r},t) + \dot{\mathbf{r}} \times \mathbf{B}(\mathbf{r},t)\Big), \tag{5.1}$$

where $\mathbf{r}$ and $\dot{\mathbf{r}}$ denote the position and velocity of the particle, t is the time, and $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields. With no other forces present, and in the non-relativistic limit, the equation of motion can be derived using Newton's second law:

$$m\ddot{\mathbf{r}} = -e\Big(\mathbf{E}(\mathbf{r},t) + \dot{\mathbf{r}} \times \mathbf{B}(\mathbf{r},t)\Big), \tag{5.2}$$

where m is the particle's mass.

We assert that Eq. (5.2) can be derived from the Lagrangian

$$L(\mathbf{r},\dot{\mathbf{r}},t) = \frac{1}{2}m|\dot{\mathbf{r}}|^2 + e\Big[\Phi(\mathbf{r},t) - \dot{\mathbf{r}}\cdot\mathbf{A}(\mathbf{r},t)\Big], \tag{5.3}$$

where Φ and $\mathbf{A}$ are the scalar and vector potentials, which are related to $\mathbf{E}$ and $\mathbf{B}$ by

$$\mathbf{E}(\mathbf{r},t) = -\nabla\Phi(\mathbf{r},t) - \frac{\partial \mathbf{A}}{\partial t}, \tag{5.4}$$

$$\mathbf{B}(\mathbf{r},t) = \nabla \times \mathbf{A}(\mathbf{r},t). \tag{5.5}$$

Roughly speaking, Eq. (5.3) follows the usual prescription that the Lagrangian is "the kinetic energy minus the potential energy." In this case, the "potential energy" consists of a term contributed by the electric potential, $-e\Phi$, and a term $e\dot{\mathbf{r}} \cdot \mathbf{A}$ that seems to describe a coupling between the electron's velocity and the vector potential.

To show that this is the right Lagrangian, we want to verify that the equation of motion (5.2) is equivalent to the Euler-Lagrange equations

$$\frac{\partial L}{\partial r_i} = \frac{d}{dt}\frac{\partial L}{\partial \dot{r}_i}, \tag{5.6}$$

where r_i denotes the i-th component of $\mathbf{r}$. From Eq. (5.3), the partial derivatives of L are

$$\frac{\partial L}{\partial r_i} = e\Big[\partial_i \Phi - \sum_j \dot{r}_j\, \partial_i A_j\Big], \tag{5.7}$$

$$\frac{\partial L}{\partial \dot{r}_i} = m\dot{r}_i - eA_i, \tag{5.8}$$

where $\partial_i \equiv \partial/\partial r_i$. Next, we want to apply the total time derivative, d/dt, to Eq. (5.8). In doing this, note that the $\mathbf{A}$ field felt by the particle varies with t via $\mathbf{r}(t)$, as well as the t-dependence of the field itself. By the chain rule of total derivatives,

$$\begin{aligned}\frac{d}{dt}\frac{\partial L}{\partial \dot{r}_i} &= m\ddot{r}_i - e\,\frac{d}{dt}A_i(\mathbf{r}(t),t) \\ &= m\ddot{r}_i - e\,\frac{\partial A_i}{\partial t} - e\sum_j \dot{r}_j \partial_j A_i.\end{aligned} \tag{5.9}$$

Plugging Eqs. (5.7) and (5.9) into Eq. (5.6) gives

$$m\ddot{r}_i = -e\left[\left(-\partial_i\Phi - \frac{\partial A_i}{\partial t}\right) + \sum_j \dot{r}_j\Big(\partial_i A_j - \partial_j A_i\Big)\right]. \tag{5.10}$$

We want to compare this to the equation of motion (5.2). The latter is expressed in terms of $\mathbf{E}$ and $\mathbf{B}$, so we first re-express it using Φ and $\mathbf{A}$ via Eqs. (5.4) and (5.5). The $\mathbf{E}$ term then matches the first term in the square brackets in Eq. (5.10). The $\dot{\mathbf{r}} \times \mathbf{B}$ term, which produces the magnetic force, needs a bit more manipulation. Using the Levi-Cevita symbol,

$$(\dot{\mathbf{r}} \times \mathbf{B})_i = \sum_{jk} \varepsilon_{ijk}\dot{r}_j B_k \tag{5.11}$$

$$= \sum_{jk} \varepsilon_{ijk}\dot{r}_j \left(\sum_{pq} \varepsilon_{kpq}\partial_p A_q\right) \tag{5.12}$$

$$= \sum_{jpq} \left(\sum_k \varepsilon_{ijk}\varepsilon_{pqk}\right) \dot{r}_j \partial_p A_q. \tag{5.13}$$

Next, we use the identity

$$\sum_k \varepsilon_{ijk}\varepsilon_{pqk} = \delta_{ip}\delta_{jq} - \delta_{iq}\delta_{jp}. \tag{5.14}$$

This allows us to simplify Eq. (5.13) into

$$(\dot{\mathbf{r}} \times \mathbf{B})_i = \sum_j \left(\dot{r}_j \partial_i A_j - \dot{r}_j \partial_j A_i\right), \tag{5.15}$$

which matches the second term in the square brackets in Eq. (5.10), as desired.

We now proceed to Hamiltonian mechanics. Following the usual procedure, we first defining the canonical momentum, $p_i = \partial L/\partial \dot{r}_i$. Using the Lagrangian (5.3), we obtain

$$m\dot{\mathbf{r}} = \mathbf{p} + e\mathbf{A}(\mathbf{r}, t). \tag{5.16}$$

The Hamiltonian is then defined as

$$H(\mathbf{r}, \mathbf{p}) = \mathbf{p} \cdot \dot{\mathbf{r}} - L. \tag{5.17}$$

We plug Eqs. (5.3) and (5.16) into Eq. (5.17), to express H in terms of $\mathbf{r}$ and $\mathbf{p}$, without $\dot{\mathbf{r}}$:

$$H = \mathbf{p} \cdot \left(\frac{\mathbf{p} + e\mathbf{A}}{m}\right) - \left(\frac{|\mathbf{p} + e\mathbf{A}|^2}{2m} + e\Phi - \frac{e}{m}(\mathbf{p} + e\mathbf{A}) \cdot \mathbf{A}\right) \tag{5.18}$$

$$= \frac{|\mathbf{p} + e\mathbf{A}(\mathbf{r}, t)|^2}{2m} - e\Phi(\mathbf{r}, t). \tag{5.19}$$

Let us compare the result (5.19) to the Hamiltonian for a non-relativistic particle in a scalar potential,

$$H = \frac{|\mathbf{p}|^2}{2m} + V(\mathbf{r}, t).$$

The $-e\Phi$ term acts like a potential energy, which is no surprise. More interestingly, the vector potential enters into the kinetic energy term, through the substitution

$$\mathbf{p} \to \mathbf{p} + e\mathbf{A}(\mathbf{r}, t). \tag{5.20}$$

Why does the vector potential manifest as some kind of momentum shift? This can be traced back to Eq. (5.16), which says that in the presence of a vector potential, the quantity $m\dot{\mathbf{r}}$—which we normally think of as the "kinetic momentum" giving rise to the particle's kinetic energy—differs from the canonical momentum $\mathbf{p}$ by a shift of $e\mathbf{A}$. Recall that the concept of canonical momentum is tied to Noether's theorem, which states that any symmetry of a system is associated with a conservation law. For translational symmetry, the conserved quantity is the canonical momentum. Hamilton's equation,

$$\frac{dp_i}{dt} = \frac{\partial H}{\partial r_i},$$

implies that if H is $\mathbf{r}$-independent, $d\mathbf{p}/dt = 0$. However, for a particle in a vector potential, even if $\mathbf{A}$ is $\mathbf{r}$-independent (i.e., translationally symmetric), $m\dot{\mathbf{r}}$ is *not* necessarily conserved! For example, consider the $\mathbf{r}$-independent potentials

$$\Phi(\mathbf{r}, t) = 0, \quad \mathbf{A}(\mathbf{r}, t) = Ct\hat{z}, \tag{5.21}$$

where C is some constant. Thanks to the t-dependence in the $\mathbf{A}$ potential, plugging these potentials into Eqs. (5.4)–(5.5) gives a non-vanishing electric field:

$$\mathbf{E}(\mathbf{r},t) = -C\hat{z}, \quad \mathbf{B}(\mathbf{r},t) = 0. \tag{5.22}$$

Therefore, $m\dot{\mathbf{r}}$ is not conserved:

$$\frac{d}{dt}(m\dot{\mathbf{r}}) = eC\hat{z}. \tag{5.23}$$

On the other hand, the canonical momentum defined in Eq. (5.16) is conserved:

$$\frac{d\mathbf{p}}{dt} = \frac{d}{dt}(m\dot{\mathbf{r}} - e\mathbf{A}) = eC\hat{z} - eC\hat{z} = 0. \tag{5.24}$$

5.1.2. Quantum Hamiltonian

From the classical Hamiltonian (5.19), we can formulate the Hamiltonian operator for a nonrelativistic quantum particle in an electromagnetic field. As usual, the quantization procedure merely involves replacing the $\mathbf{r}$ and $\mathbf{p}$ variables with $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ operators:

$$\hat{H} = \frac{|\hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}},t)|^2}{2m} - e\Phi(\hat{\mathbf{r}},t). \tag{5.25}$$

Both the scalar and vector potential terms are functions of the position operator $\hat{\mathbf{r}}$, so if we want to expand the square in the first term of Eq. (5.25), it is important to note that $\hat{\mathbf{p}}$ and $\mathbf{A}(\hat{\mathbf{r}},t)$ need not commute:

$$\left|\hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}},t)\right|^2 = \sum_j \left[\hat{p}_j + eA_j(\hat{\mathbf{r}},t)\right]\left[\hat{p}_j + eA_j(\hat{\mathbf{r}},t)\right] \tag{5.26}$$

$$= \sum_j \left(\hat{p}_j^2 + e\left[\hat{p}_j A_j(\hat{\mathbf{r}},t) + A_j(\hat{\mathbf{r}},t)p_j\right] + e^2 A_j^2(\hat{\mathbf{r}},t)^2\right). \tag{5.27}$$

For example, if we are working in the position representation (i.e., using wavefunctions), then $\hat{\mathbf{p}} = -i\hbar\nabla$. When dealing with $\hat{p}_j A_j(\mathbf{r},t)$, the gradient in the momentum operator applies to everything on its right, i.e., both A_j and the wavefunction. By the product rule,

$$\hat{p}_j A_j(\mathbf{r},t)\psi(\mathbf{r},t) = -i\hbar\left[\frac{\partial A_j}{\partial r_j} + A_j\frac{\partial}{\partial r_j}\right]\psi(\mathbf{r},t). \tag{5.28}$$

Thus, in the position representation, Eq. (5.27) can also be written as

$$\left|\hat{\mathbf{p}} + e\mathbf{A}\right|^2 = -\frac{\hbar^2}{2m}\nabla^2 - 2i\hbar e\mathbf{A}\cdot\nabla - i\hbar e\left(\nabla\cdot\mathbf{A}\right) + e^2|\mathbf{A}|^2. \tag{5.29}$$

5.1.3. Gauge symmetry

It is interesting that the Hamiltonian (5.25) is expressed in terms of the scalar and vector potentials, Φ and $\mathbf{A}$. In classical electromagnetism, it is known that Φ and $\mathbf{A}$ do not uniquely define the $\mathbf{E}$ and $\mathbf{B}$ fields. Suppose we perform a **gauge transformation** on the potentials,

$$\Phi(\mathbf{r},t) \to \Phi(\mathbf{r},t) - \dot{\Lambda}(\mathbf{r},t) \tag{5.30}$$
$$\mathbf{A}(\mathbf{r},t) \to \mathbf{A}(\mathbf{r},t) + \nabla\Lambda(\mathbf{r},t), \tag{5.31}$$

where $\Lambda(\mathbf{r},t)$ is an arbitrary scalar field. Plugging these into Eqs. (5.4) and (5.5), we find that the $\mathbf{E}$ and $\mathbf{B}$ fields are unchanged; thus, the gauge transformation has no effect on the dynamics of any charged particle interacting with the electromagnetic field.

In the quantum theory, this feature manifests as a subtle symmetry of the Hamiltonian, called **gauge symmetry**. Let us insert the gauge transformed potentials (5.30)–(5.31) into the Hamiltonian (5.25). This results in the transformed Hamiltonian

$$\hat{H}_\Lambda = \frac{|\hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}},t) + e\nabla\Lambda(\hat{\mathbf{r}},t)|^2}{2m} - e\Phi(\hat{\mathbf{r}},t) + e\dot{\Lambda}(\hat{\mathbf{r}},t). \tag{5.32}$$

We will work in the position representation. Suppose the wavefunction $\psi(\mathbf{r},t)$ is a solution to the Schrödinger wave equation under the original Hamiltonian,

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi(\mathbf{r},t). \tag{5.33}$$

Then we assert that there is a corresponding solution for the gauge transformed Hamiltonian:

$$i\hbar\frac{\partial\psi_\Lambda}{\partial t} = \hat{H}_\Lambda\psi_\Lambda(\mathbf{r},t), \tag{5.34}$$
$$\psi_\Lambda(\mathbf{r},t) = \psi(\mathbf{r},t)\,\exp\left(-\frac{ie\Lambda(\mathbf{r},t)}{\hbar}\right). \tag{5.35}$$

To prove this, observe how time and space derivatives act on ψ_Λ:

$$\begin{aligned}\frac{\partial}{\partial t}\left[\psi\,\exp\left(-\frac{ie\Lambda}{\hbar}\right)\right] &= \left[\frac{\partial\psi}{\partial t} - \frac{ie}{\hbar}\dot{\Lambda}\,\psi\right]\exp\left(\frac{ie\Lambda}{\hbar}\right)\\ \nabla\left[\psi\,\exp\left(-\frac{ie\Lambda}{\hbar}\right)\right] &= \left[\nabla\psi - \frac{ie}{\hbar}\nabla\Lambda\,\psi\right]\exp\left(\frac{ie\Lambda}{\hbar}\right).\end{aligned} \tag{5.36}$$

When the extra terms generated by the $\exp(ie\Lambda/\hbar)$ factor are slotted into the Schrödinger equation, they cancel the gauge terms in the scalar and vector potentials. For example,

$$\left(-i\hbar\nabla + e\mathbf{A} + e\nabla\Lambda\right)\left[\psi\,\exp\left(-\frac{ie\Lambda}{\hbar}\right)\right] = \left[\left(-i\hbar\nabla + e\mathbf{A}\right)\psi\right]\,\exp\left(-\frac{ie\Lambda}{\hbar}\right) \tag{5.37}$$

If we apply $(-i\hbar\nabla + e\mathbf{A} + e\nabla\Lambda)$ another time, it has a similar effect, but with the quantity in square brackets on the right-hand side of Eq. (5.37) taking the place of ψ. Hence,

$$\left|-i\hbar\nabla + e\mathbf{A} + e\nabla\Lambda\right|^2\left[\psi\,\exp\left(-\frac{ie\Lambda}{\hbar}\right)\right] = \left[\left|-i\hbar\nabla + e\mathbf{A}\right|^2\psi\right]\,\exp\left(-\frac{ie\Lambda}{\hbar}\right). \tag{5.38}$$

By applying this observation to the left and right sides of Eq. (5.34), we find that it reduces to the original Schrödinger equation (5.33).

The above result can be stated in a simpler form if the potential fields are static. In this case, the time-independent electromagnetic Hamiltonian is

$$\hat{H} = \frac{|\hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}})|^2}{2m} - e\Phi(\hat{\mathbf{r}}). \tag{5.39}$$

By a time-independent gauge transformation, we can define

$$\hat{H}_\Lambda = \frac{|\hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}}) + e\nabla\Lambda(\mathbf{r})|^2}{2m} - e\Phi(\hat{\mathbf{r}}) \tag{5.40}$$

Then the gauge symmetry states that

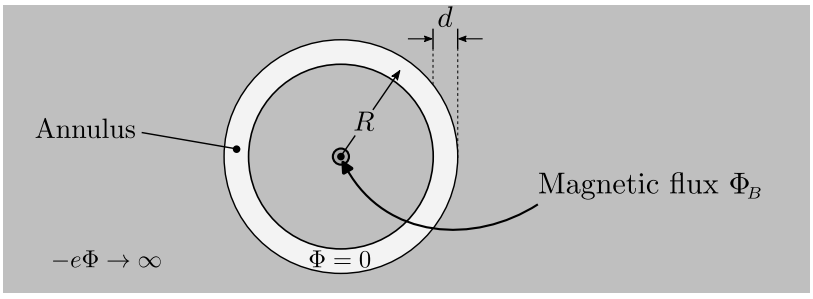
$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad \Leftrightarrow \quad \begin{cases} \hat{H}_\Lambda\psi_\Lambda(\mathbf{r}) = E\psi_\Lambda(\mathbf{r}), \\ \psi_\Lambda(\mathbf{r}) = \psi(\mathbf{r})\exp\left(-\dfrac{ie\Lambda(\mathbf{r})}{\hbar}\right). \end{cases} \tag{5.41}$$

In other words, the gauge transformed Hamiltonian has the same energy spectrum, and its eigenfunctions are the original eigenfunctions modified by a phase factor involving $\Lambda(\mathbf{r})$.

5.1.4. The Aharonov-Bohm effect

The Hamiltonian's gauge symmetry might tempt us to speculate that even though $\hat{H}$ is expressed using Φ and $\mathbf{A}$, maybe only $\mathbf{E}$ and $\mathbf{B}$ actually govern physical behavior, as is the case in classical electrodynamics. But this turns out to be false: quantum electrodynamics depends on the potentials, not just $\mathbf{E}$ and $\mathbf{B}$. In particular, a charged particle can experience $\mathbf{B} = 0$ and yet be affected by the $\mathbf{A}$ field, a phenomenon called the **Aharonov-Bohm effect**.

A setup for realizing the Aharonov-Bohm effect is depicted below. We place a particle on a ring, or "annulus," of radius R and width $d \ll R$. Outside the annulus, in the regions shaded in gray, the scalar potential is $\Phi \to -\infty$; this means the potential energy is $-e\Phi \to \infty$, forcing the wavefunction to vanish. The wavefunction is thus confined to the annulus, where we set the scalar potential to be $\Phi = 0$.



We assume all fields and wavefunctions to be independent of z (the out-of-plane direction). The in-plane position can be expressed using polar coordinates (r, ϕ), such that the annulus is centered at the coordinate origin.

Suppose we use an infinitesimally thin solenoid to thread a magnetic flux Φ_B through the origin. This can be described by the vector potential

$$\mathbf{A}(r,\phi) = \frac{\Phi_B}{2\pi r}\,\mathbf{e}_\phi, \tag{5.42}$$

where $\mathbf{e}_\phi$ is the unit vector pointing in the azimuthal direction. With this choice of $\mathbf{A}$ field, the magnetic flux through a loop of radius r around the origin is

$$\oint \mathbf{A}\cdot d\mathbf{r} = \left(\frac{\Phi_B}{2\pi r}\right)\cdot(2\pi r) = \Phi_B, \tag{5.43}$$

independent of r. Thus, the magnetic flux density is entirely concentrated at the origin. Away from the origin, we have $\mathbf{A} \neq 0$ and $\mathbf{B} = 0$.

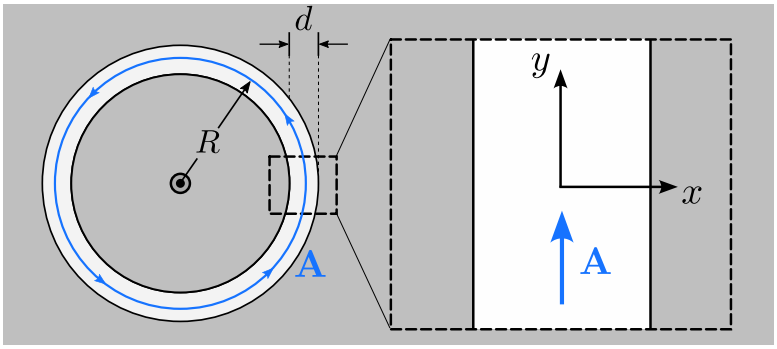
Plugging this $\mathbf{A}$ field into the Hamiltonian (5.39), we arrive at the time-independent Schrödinger wave equation

$$\frac{1}{2m}\left|-i\hbar\nabla + \frac{e\Phi_B}{2\pi r}\,\mathbf{e}_\phi\right|^2 \psi(r,\phi) = E\psi(r,\phi). \tag{5.44}$$

Due to rotational symmetry, the eigenfunctions should have the form

$$\psi(r,\phi) = \psi_0\, A(r)\, e^{in\phi}, \quad n \in \mathbb{Z}. \tag{5.45}$$

Since the annulus is very thin ($d \ll R$), let us zoom in on a representative local segment at $\phi = 0$, as shown below:



Locally, the annulus looks like a straight waveguide. Let us adopt local Cartesian coordinates $x = r - R$ and $y = R\phi$. Now $\mathbf{A}$ points in the y direction, so Eq. (5.44) reduces to

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial y} + \frac{e\Phi_B}{2\pi R}\right)^2\right]\psi(x,y) \approx E\psi(x,y). \tag{5.46}$$

Meanwhile, the ansatz (5.45) reduces to

$$\psi(x,y) = A(x)e^{iny/R}, \tag{5.47}$$

which is a waveguide mode with transverse profile $A(x)$ and wavenumber $k_y = n/R$. This allows us to substitute $\partial/\partial y \to in/R$ in Eq. (5.46), giving

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2m}\left(\frac{n\hbar}{R} + \frac{e\Phi_B}{2\pi R}\right)^2\right]A(x) = EA(x). \tag{5.48}$$

Since the wavefunction vanishes on the inner and outer walls of the annulus, the transverse profile must satisfy

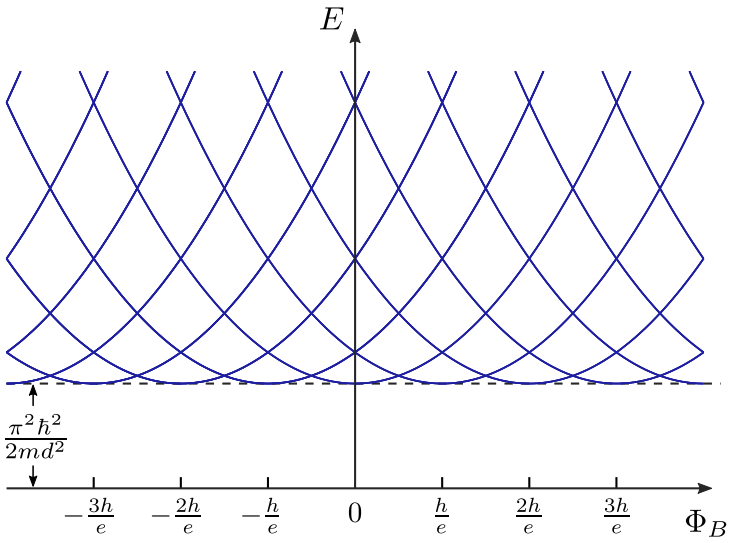
$$A(\pm d/2) = 0. \tag{5.49}$$

We pick the solution $A(x) = \cos(\pi x/d)$, which corresponds to the fundamental waveguide mode. Applying this to Eq. (5.48) yields

$$E = \frac{1}{2m}\left[\left(\frac{n\hbar}{R} + \frac{e\Phi_B}{2\pi R}\right)^2 + \left(\frac{\pi\hbar}{d}\right)^2\right] \tag{5.50}$$

$$= \frac{e^2}{8\pi^2 m R^2}\left(\Phi_B + \frac{nh}{e}\right)^2 + \frac{\pi^2\hbar^2}{2md^2}. \tag{5.51}$$

There is an infinite set of solutions, indexed by $n \in \mathbb{Z}$. For each n, the energy varies quadratically with the magnetic flux Φ_B, with an n-dependent Φ_B offset and a constant energy offset. The spectrum is plotted against Φ_B below:



Evidently, varying Φ_B affects the energy eigenvalues, in spite of the fact that the electron resides in the annulus where $\mathbf{B} = 0$. This is the Aharonov-Bohm effect.

A further noteworthy feature of this spectrum is that if Φ_B changes by a multiple of the constant h/e (called the **magnetic flux quantum**), the spectrum is left unchanged. This invariance property turns out to be tied to gauge symmetry. Eq. (5.42) says that if an extra flux nh/e (where $n \in \mathbb{Z}$) is threaded through the annulus, the vector potential changes by $\Delta\mathbf{A} = (n\hbar/er)\mathbf{e}_\phi$. But we can undo this via the following gauge transformation:

$$\Lambda(r,\phi) = -\frac{n\hbar}{e}\,\phi \quad \Rightarrow \begin{cases} \nabla\Lambda & = -(n\hbar/er)\,\mathbf{e}_\phi \\ e^{-ie\Lambda/\hbar} & = e^{in\phi}. \end{cases} \tag{5.52}$$

Note that Λ is not single-valued, but that's not a problem, as both $\nabla\Lambda$ and $\exp(-ie\Lambda/\hbar)$, which enter into the gauge symmetry relations (5.32)–(5.35), are single-valued.

Remarkably, this gauge argument does not require the electron to live on an annulus; we can consider a confinement region of any shape, so long as it encircles the magnetic flux. In

general, the energy spectrum need not be given by Eq. (5.51), but the gauge argument says that it must be invariant under a flux change of $\Delta\Phi_B = nh/e$.

This invariance property is also closely related to a famous argument by Dirac, showing that if there exists a magnetic monopole—a hypothetical particle that produces a magnetic field $\mathbf{B} = (\mu/4\pi r^2)\,\mathbf{e}_r$—then its magnetic charge μ must be a multiple of h/e. Conversely, if there exists a single magnetic monopole of charge μ anywhere in the universe, electric charges must come in multiples of h/μ, which could be regarded as an explanation for the quantization of electric charge [3].

5.2. DIRAC'S THEORY OF THE ELECTRON

5.2.1. The Dirac Hamiltonian

So far, we have been using $p^2/2m$-type Hamiltonians, which are limited to describing non-relativistic particles. In 1928, Paul Dirac formulated a Hamiltonian that can describe electrons moving close to the speed of light, thus successfully combining quantum theory with special relativity. Another triumph of Dirac's theory is that it accurately predicts the magnetic moment of the electron.

Dirac's theory begins from the time-dependent Schrödinger wave equation,

$$i\hbar\,\partial_t\,\psi(\mathbf{r},t) = \hat{H}\psi(\mathbf{r},t). \tag{5.53}$$

Note that the left side has a first-order time derivative. On the right, the Hamiltonian $\hat{H}$ contains spatial derivatives in the form of momentum operators. We know that time and space derivatives of the wavefunction are related to energy and momentum, respectively:

$$i\hbar\,\partial_t \;\leftrightarrow\; E, \qquad -i\hbar\,\partial_j \;\leftrightarrow\; p_j. \tag{5.54}$$

We also know that the energy and momentum of a relativistic particle are related by

$$E^2 = m^2c^4 + \sum_{j=1}^{3} p_j^2 c^2, \tag{5.55}$$

where m is the rest mass and c is the speed of light. (Following the usual practice in relativity theory, we use Roman indices $j \in \{1,2,3\}$ for the spatial coordinates $\{x,y,z\}$.)

Since the left side of Eq. (5.53) has a first-order time derivative, we guess that the Hamiltonian on the right should involve first-order spatial derivatives. Let us take

$$\hat{H} = \alpha_0 mc^2 + \sum_{j=1}^{3} \alpha_j \hat{p}_j c, \tag{5.56}$$

where $\hat{p}_j \equiv -i\hbar\partial_j$. The mc^2 and c factors are placed for later convenience. To determine the dimensionless "coefficients" α_0, α_1, α_2, and α_3, consider a wavefunction with definite energy E and momentum $\mathbf{p}$:

$$\begin{cases} \hat{H}\psi = E\psi \\ \hat{p}_i\psi = p_i\psi \end{cases} \quad\Rightarrow\quad \left(\alpha_0 mc^2 + \sum_{j=1}^{3} \alpha_j p_j c\right)\psi = E\,\psi. \tag{5.57}$$

If ψ is a scalar, this would imply that

$$\alpha_0 mc^2 + \sum_j \alpha_j p_j c = E$$

for certain scalar coefficients $\{\alpha_0, \ldots, \alpha_3\}$, which does not match Eq. (5.55) at all!

But we can get things to work if $\psi(\mathbf{r}, t)$ is a multi-component wavefunction, rather than a scalar wavefunction, and the α's are matrices acting on those components via the matrix-vector product operation. In that case,

$$\hat{H} = \hat{\alpha}_0 mc^2 + \sum_{j=1}^{3} \hat{\alpha}_j \hat{p}_j c, \quad \text{where} \quad \hat{p}_j \equiv -i\hbar\,\partial_j, \tag{5.58}$$

where the hats on $\{\hat{\alpha}_0, \ldots, \hat{\alpha}_3\}$ indicate that they are matrix-valued. Applying the Hamiltonian twice gives

$$\left(\hat{\alpha}_0 mc^2 + \sum_j \hat{\alpha}_j p_j c\right)^2 \psi = E^2\,\psi. \tag{5.59}$$

This can be satisfied if

$$\left(\hat{\alpha}_0 mc^2 + \sum_j \hat{\alpha}_j p_j c\right)^2 = E^2\,\hat{I}, \tag{5.60}$$

where $\hat{I}$ is the identity matrix. Expanding the square (and taking care of the fact that the $\hat{\alpha}_\mu$ matrices need not commute) yields

$$\hat{\alpha}_0^2 m^2 c^4 + \sum_j \left(\hat{\alpha}_0\hat{\alpha}_j + \hat{\alpha}_j\hat{\alpha}_0\right) mc^3 p_j + \sum_{jj'} \hat{\alpha}_j\hat{\alpha}_{j'}\, p_j p_{j'}\, c^2 = E^2\hat{I}. \tag{5.61}$$

This reduces to Eq. (5.55) if the $\hat{\alpha}_\mu$ matrices satisfy

$$\begin{aligned} \hat{\alpha}_\mu^2 &= \hat{I} \quad \text{for} \quad \mu = 0, 1, 2, 3, \quad \text{and} \\ \hat{\alpha}_\mu\hat{\alpha}_\nu + \hat{\alpha}_\nu\hat{\alpha}_\mu &= 0 \quad \text{for} \quad \mu \neq \nu. \end{aligned} \tag{5.62}$$

(We use Greek symbols for indices ranging over the four spacetime coordinates $\{0, 1, 2, 3\}$.) The above can be written more concisely using the anticommutator:

$$\{\hat{\alpha}_\mu, \hat{\alpha}_\nu\} = 2\delta_{\mu\nu}, \quad \text{for} \quad \mu, \nu = 0, 1, 2, 3. \tag{5.63}$$

Also, we need the $\hat{\alpha}_\mu$ matrices to be Hermitian, so that $\hat{H}$ is Hermitian.

It turns out that the smallest possible Hermitian matrices that can satisfy Eq. (5.63) are 4×4 matrices. The choice of matrices (or "representation") is not uniquely determined. One particularly useful choice is called the **Dirac representation**:

$$\begin{aligned} \hat{\alpha}_0 &= \begin{bmatrix} \hat{I} & \hat{0} \\ \hat{0} & -\hat{I} \end{bmatrix}, \quad \hat{\alpha}_1 = \begin{bmatrix} \hat{0} & \hat{\sigma}_1 \\ \hat{\sigma}_1 & \hat{0} \end{bmatrix} \\ \hat{\alpha}_2 &= \begin{bmatrix} \hat{0} & \hat{\sigma}_2 \\ \hat{\sigma}_2 & \hat{0} \end{bmatrix}, \quad \hat{\alpha}_3 = \begin{bmatrix} \hat{0} & \hat{\sigma}_3 \\ \hat{\sigma}_3 & \hat{0} \end{bmatrix}, \end{aligned} \tag{5.64}$$

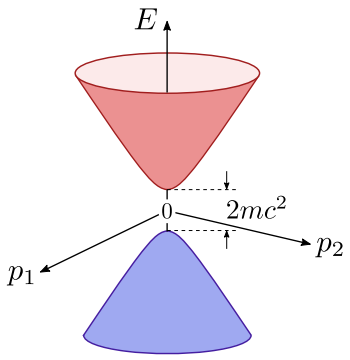
where $\{\hat{\sigma}_1, \hat{\sigma}_2, \hat{\sigma}_3\}$ denote the usual Pauli matrices. Since the $\hat{\alpha}_\mu$'s are 4×4 matrices, the field $\psi(\mathbf{r})$, at each point $\mathbf{r}$, is a four-component object, called a **spinor** (it's not a vector since its behaves differently under coordinate transformations; we won't get into the details).

5.2.2. Eigenstates of the Dirac Hamiltonian

According to Eq. (5.55), the energy eigenvalues of the Dirac Hamiltonian are

$$E = \pm\sqrt{m^2c^4 + \sum_j p_j^2 c^2}. \tag{5.65}$$

This is plotted below:



The energy spectrum forms two hyperbolas. The upper hyperbola matches the standard dispersion relation for a massive relativistic particle. But what about the negative-energy hyperbola? Nobody ordered that, and we might be tempted to simply ignore the negative-energy states, focusing only on the positive-energy states. However, this becomes untenable once we couple the electron to additional systems like the electromagnetic field: even if the electron starts with $E > 0$, it can hop to the negative-energy hyperbola by shedding energy into the external system. This seems like a glaring problem, but let us wait till Section 5.2.4 to discuss how to resolve it.

Notice also that for each $\mathbf{p}$, the Dirac Hamiltonian reduces to a 4×4 matrix, so there are four orthogonal eigenstates. Hence, both energy hyperbolas are two-fold degenerate. The four degrees of freedom (two from the choice of positive/negative E, two from the degeneracy) are related to the four spinor components in a somewhat subtle way. To help understand this, let us adopt the Dirac representation (5.64), and divide the spinor as follows:

$$\psi(\mathbf{r}, t) = \begin{bmatrix} \psi_A(\mathbf{r}, t) \\ \psi_B(\mathbf{r}, t) \end{bmatrix}, \tag{5.66}$$

where ψ_A and ψ_B have two components each. Using the Dirac Hamiltonian (5.58), we derive

$$\psi_A = \frac{1}{E - mc^2} \sum_j \hat{\sigma}_j p_j \psi_B, \tag{5.67}$$

$$\psi_B = \frac{1}{E + mc^2} \sum_j \hat{\sigma}_j p_j \psi_A. \tag{5.68}$$

For $|\mathbf{p}| \to 0$, E approaches either mc^2 or $-mc^2$. On the upper hyperbola ($E \sim mc^2$), the vanishing of the denominator in Eq. (5.67) implies that ψ_A dominates the wavefunction, with $\psi_B \sim 0$. On the lower hyperbola ($E \sim -mc^2$), ψ_B dominates, with $\psi_A \sim 0$. In the

next section, we will develop this further and show that the two-fold degree of freedom of each sub-spinor, ψ_A and ψ_B, corresponds to the electron's spin.

However, this association only holds in the non-relativistic limit! In the relativistic regime, $|\mathbf{p}| \sim |E| \gg mc^2$, Eqs. (5.67) and (5.68) imply that $|\psi_A| \sim |\psi_B|$ for both positive-energy and negative-energy eigenstates. (There does exist a way to make the upper/lower spinor components correspond rigorously to positive/negative E, but this requires adopting a more complicated matrix representation [4].)

5.2.3. Dirac electron in an electromagnetic field

Let us next look at how Dirac's electron interacts with an electromagnetic field. To introduce the electromagnetic field into the theory, we follow the same procedure as in the non-relativistic theory (Section 5.1.1): add $-e\Phi(\mathbf{r}, t)$ as a scalar potential function, and add the vector potential via the substitution

$$\hat{\mathbf{p}} \to \hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}}, t). \tag{5.69}$$

Applying this recipe to the Dirac Hamiltonian (5.58) yields

$$i\hbar\,\partial_t\psi = \left\{\hat{\alpha}_0 mc^2 - e\Phi(\mathbf{r}, t) + \sum_j \hat{\alpha}_j\Big[-i\hbar\,\partial_j + eA_j(\mathbf{r}, t)\Big]c\right\}\psi(\mathbf{r}, t). \tag{5.70}$$

You can check that this has the same gauge symmetry properties as the non-relativistic theory discussed in Section 5.1.3.

We now take the Dirac representation (5.64). Moreover, following Eq. (5.66), let ψ_A and ψ_B denote the the Dirac wavefunction's upper and lower components (each having two components). Then Eq. (5.70) reduces to

$$i\hbar\,\partial_t\,\psi_A = \big(+mc^2 - e\Phi\big)\,\psi_A \,+\, \sum_j \hat{\sigma}_j\big(-i\hbar\partial_j + eA_j\big)\,c\,\psi_B \tag{5.71}$$

$$i\hbar\,\partial_t\,\psi_B = \big(-mc^2 - e\Phi\big)\,\psi_B \,+\, \sum_j \hat{\sigma}_j\big(-i\hbar\partial_j + eA_j\big)\,c\,\psi_A, \tag{5.72}$$

In the non-relativistic limit, we can seek solutions of the form

$$\psi_{A/B}(\mathbf{r}, t) = \Psi_{A/B}(\mathbf{r}, t)\,\exp\left[-i\left(\frac{mc^2}{\hbar}\right)t\right]. \tag{5.73}$$

The phase factor on the right side comes from the rest energy mc^2. This is assumed to be by far the largest energy scale in the problem, corresponding to a fast oscillation. (By using mc^2 rather than $-mc^2$, we are focusing on the positive-energy states.) The functions Ψ_A and Ψ_B are "slowly-varying envelopes", which have t-dependences much slower than the phase factor. When $\mathbf{p} = 0$ and $\Phi = \mathbf{A} = 0$, they reduce to constants.

Plugging this ansatz into Eqs. (5.71)–(5.72) gives

$$i\hbar\,\partial_t\,\Psi_A = -e\Phi\;\Psi_A \,+\, \sum_j \hat{\sigma}_j\big(-i\hbar\partial_j + eA_j\big)c\,\Psi_B \tag{5.74}$$

$$\big(i\hbar\,\partial_t \,+ 2mc^2 + e\Phi\big)\Psi_B = \sum_j \hat{\sigma}_j\big(-i\hbar\partial_j + eA_j\big)c\,\Psi_A. \tag{5.75}$$

On the left side of Eq. (5.75), the $2mc^2$ term dominates over the other two, so

$$\Psi_B \approx \frac{1}{2mc} \sum_j \hat{\sigma}_j \big(-i\hbar\partial_j + eA_j \big) \Psi_A. \tag{5.76}$$

Plugging this into Eq. (5.74) yields

$$i\hbar\,\partial_t \Psi_A = \left\{ -e\Phi + \frac{1}{2m} \sum_{jk} \hat{\sigma}_j \hat{\sigma}_k \big(-i\hbar\partial_j + eA_j \big) \big(-i\hbar\partial_k + eA_k \big) \right\} \Psi_A. \tag{5.77}$$

Using the identity $\hat{\sigma}_j\hat{\sigma}_k = \delta_{jk}\hat{I} + i\sum_i \varepsilon_{ijk}\sigma_i$:

$$\begin{aligned} i\hbar\,\partial_t \Psi_A = \Bigg\{ & -e\Phi + \frac{1}{2m} \big| -i\hbar\nabla + e\mathbf{A} \big|^2 \\ & + \frac{i}{2m} \sum_{ijk} \varepsilon_{ijk} \hat{\sigma}_i \big(-i\hbar\partial_j + eA_j \big) \big(-i\hbar\partial_k + eA_k \big) \Bigg\} \Psi_A. \end{aligned} \tag{5.78}$$

Look carefully at the last term in the curly brackets. Expanding the square yields

$$\frac{i}{2m} \sum_{ijk} \varepsilon_{ijk} \hat{\sigma}_i \Big(-\partial_j\partial_k - i\hbar e \partial_j A_k - i\hbar e \big[A_k\partial_j + A_j\partial_k \big] + e^2 A_j A_k \Big).$$

Due to the antisymmetry of ε_{ijk}, all terms inside the parentheses that are symmetric under j and k cancel out when summed over. The only survivor is the second term, which gives

$$\frac{\hbar e}{2m} \sum_{ijk} \varepsilon_{ijk} \hat{\sigma}_i \partial_j A_k = \frac{\hbar e}{2m} \hat{\boldsymbol{\sigma}} \cdot \mathbf{B}(\mathbf{r}, t), \tag{5.79}$$

where $\mathbf{B} = \nabla \times \mathbf{A}$ is the magnetic field. Hence,

$$i\hbar\,\partial_t \Psi_A = \left\{ -e\Phi + \frac{1}{2m} \big| -i\hbar\nabla + e\mathbf{A} \big|^2 - \left(-\frac{\hbar e}{2m}\,\hat{\boldsymbol{\sigma}} \right) \cdot \mathbf{B} \right\} \Psi_A. \tag{5.80}$$

On the right side, we see the Hamiltonian for a non-relativistic electron in an electromagnetic field, Eq. (5.25), but with an additional term of the form $-\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{B}}$. This new term matches the potential energy of a magnetic dipole of moment $\boldsymbol{\mu}$ in a magnetic field $\mathbf{B}$. Therefore, the theory predicts that the electron has a magnetic dipole moment of

$$|\boldsymbol{\mu}| = \frac{\hbar e}{2m}. \tag{5.81}$$

Remarkably, this matches the experimentally-observed magnetic dipole moment to about one part in 10^3. The residual mismatch between Eq. (5.81) and the actual magnetic dipole moment of the electron is understood to arise from quantum fluctuations of the electronic and electromagnetic quantum fields. Using the full theory of quantum electrodynamics, that "anomalous magnetic moment" can also be calculated and matches experiment to around one part in 10^9, making it one of the most precise theoretical predictions in physics [2]!

It is noteworthy that we did not set out to include spin in the theory, yet it arose, seemingly unavoidably, as a by-product of formulating a relativistic theory of the electron. This is a manifestation of the principle that relativistic quantum theory is more constrained than non-relativistic quantum theory [1]. To satisfy the relativistic symmetries, spin cannot be an optional part of the theory—it must be built-in at a fundamental level.

5.2.4. Positrons and the Dirac Field

As noted in Section 5.2.2, the Dirac Hamiltonian has both positive-energy and negative-energy eigenstates, and the presence of the negative-energy states threatens to destabilize the positive-energy states. To get around this, Dirac suggested that the "vacuum" might actually be a multi-particle state, called the **Dirac sea**, in which all negative-energy states are occupied. Since electrons are fermions, the Pauli exclusion principle forbids decay into the negative-energy states, thus stabilizing the positive-energy solutions.

At first blush, the idea seems ridiculous; how can the vacuum contain an infinite number of particles? However, we shall see that the idea becomes more plausible if Dirac's single-particle Hamiltonian is reinterpreted using quantum field theory. After all, the Dirac sea idea is an inherently multi-particle concept, and we know from Chapter 4 that quantum field theory is the natural framework for working with such ideas.

For the single-particle Dirac Hamiltonian, let $|\mathbf{k}, +, \sigma\rangle$ denote a positive-energy state of momentum $\hbar\mathbf{k}$, where $\sigma = 1, 2$ indexes the spin degree of freedom (i.e., the two-fold degeneracy of each hyperbola). On the other hand, let $|\mathbf{k}, -, \sigma\rangle$ denote a negative-energy state of momentum $-\hbar\mathbf{k}$ (not $\hbar\mathbf{k}$; we will justify this convention later). Hence,

$$\hat{H}|\mathbf{k}, \pm, \sigma\rangle = \pm E_{\mathbf{k}} |\mathbf{k}, \pm, \sigma\rangle, \tag{5.82}$$

where $E_{\mathbf{k}} = E_{-\mathbf{k}} > 0$ comes from the relativistic energy-mass-momentum relation (5.55).

Following the second quantization procedure from Chapter 4, we introduce a fermionic Fock space $\mathscr{H}_-^F$, and a set of creation/annihilation operators. We will use different labels for the positive- and negative-energy states:

$$\begin{aligned} \hat{b}^\dagger_{\mathbf{k}\sigma} \text{ and } \hat{b}_{\mathbf{k}\sigma} &\text{ create/annihilate } |\mathbf{k}, +, \sigma\rangle \\ \hat{d}^\dagger_{\mathbf{k}\sigma} \text{ and } \hat{d}_{\mathbf{k}\sigma} &\text{ create/annihilate } |\mathbf{k}, -, \sigma\rangle. \end{aligned}$$

These obey the fermionic anticommutation relations

$$\begin{aligned} &\{\hat{b}_{\mathbf{k}\sigma}, \hat{b}^\dagger_{\mathbf{k}'\sigma'}\} = \delta^3(\mathbf{k} - \mathbf{k}')\,\delta_{\sigma\sigma'}, \quad \{\hat{d}_{\mathbf{k}\sigma}, \hat{d}^\dagger_{\mathbf{k}'\sigma'}\} = \delta^3(\mathbf{k} - \mathbf{k}')\,\delta_{\sigma\sigma'} \\ &\{\hat{b}_{\mathbf{k}\sigma}, \hat{b}_{\mathbf{k}'\sigma'}\} = \{\hat{b}_{\mathbf{k}\sigma}, \hat{d}_{\mathbf{k}'\sigma'}\} = \{\hat{d}_{\mathbf{k}\sigma}, \hat{d}_{\mathbf{k}'\sigma'}\} = 0, \quad \text{etc.} \end{aligned} \tag{5.83}$$

We can then define the multi-particle Hamiltonian

$$\hat{H} = \int d^3k \sum_\sigma E_{\mathbf{k}} \left(\hat{b}^\dagger_{\mathbf{k}\sigma} \hat{b}_{\mathbf{k}\sigma} - \hat{d}^\dagger_{\mathbf{k}\sigma} \hat{d}_{\mathbf{k}\sigma} \right), \tag{5.84}$$

where the negative sign inside the integrand accounts for the negative energy of the d-type electrons. We also have the vacuum state $|\varnothing\rangle$, which satisfies

$$\hat{b}_{\mathbf{k}\sigma}|\varnothing\rangle = \hat{d}_{\mathbf{k}\sigma}|\varnothing\rangle = 0. \tag{5.85}$$

Next, let us define

$$\begin{aligned} \hat{c}_{\mathbf{k}\sigma} &= \hat{d}^\dagger_{\mathbf{k}\sigma} \\ \hat{c}^\dagger_{\mathbf{k}\sigma} &= \hat{d}_{\mathbf{k}\sigma}. \end{aligned} \tag{5.86}$$

Using these, we can rewrite the anticommutation relations (5.83) as

$$\begin{aligned}&\{\hat{b}_{\mathbf{k}\sigma}, \hat{b}^\dagger_{\mathbf{k}'\sigma'}\} = \delta^3(\mathbf{k}-\mathbf{k}')\,\delta_{\sigma\sigma'}, \quad \{\hat{c}_{\mathbf{k}\sigma}, \hat{c}^\dagger_{\mathbf{k}'\sigma'}\} = \delta^3(\mathbf{k}-\mathbf{k}')\,\delta_{\sigma\sigma'}\\ &\{\hat{b}_{\mathbf{k}\sigma}, \hat{b}_{\mathbf{k}'\sigma'}\} = \{\hat{b}_{\mathbf{k}\sigma}, \hat{c}_{\mathbf{k}'\sigma'}\} = \{\hat{c}_{\mathbf{k}\sigma}, \hat{c}_{\mathbf{k}'\sigma'}\} = 0, \quad \text{etc.}\end{aligned} \tag{5.87}$$

This implies that we can treat $\hat{c}^\dagger_{\mathbf{k}\sigma}$ and $\hat{c}_{\mathbf{k}\sigma}$ as creation and annihilation operators in their own right, taking over from $\hat{d}_{\mathbf{k}\sigma}$ and $\hat{d}^\dagger_{\mathbf{k}\sigma}$. The particle created by $\hat{c}^\dagger_{\mathbf{k}\sigma}$ is called a **positron**. By definition, the *presence* of a positron is equivalent to the *absence* of a negative-energy electron; hence, the positron has *positive* energy. Indeed, by converting the d's to c's in Eq. (5.84), we can rewrite the Hamiltonian as

$$\hat{H} = \int d^3k \sum_\sigma E_{\mathbf{k}} \left(\hat{b}^\dagger_{\mathbf{k}\sigma}\hat{b}_{\mathbf{k}\sigma} - \hat{c}_{\mathbf{k}\sigma}\hat{c}^\dagger_{\mathbf{k}\sigma}\right) \tag{5.88}$$

$$= \int d^3k \sum_\sigma E_{\mathbf{k}} \left(\hat{b}^\dagger_{\mathbf{k}\sigma}\hat{b}_{\mathbf{k}\sigma} + \hat{c}^\dagger_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}\sigma}\right) \quad + \quad \text{constant}. \tag{5.89}$$

(The constant is infinite, but this can be dealt with by standard regularization tricks.) Now $\hat{H}$ describes two species of fermions—b-type electrons, which we simply call "electrons", and positrons—both carrying positive energy. We can also deduce, via similar reasoning, that the positron created by $\hat{c}^\dagger_{\mathbf{k}\sigma}$ has momentum $\hbar\mathbf{k}$ (not $-\hbar\mathbf{k}$, due to how we defined $|\mathbf{k}, -, \sigma\rangle$), and a positive electric charge $+e$.

The state $|\varnothing\rangle$, defined in Eq. (5.85), no longer serves as the vacuum for this reinterpreted Hamiltonian. Its vacuum state $|\varnothing'\rangle$ should satisfy

$$\hat{b}_{\mathbf{k}\sigma}|\varnothing'\rangle = \hat{c}_{\mathbf{k}\sigma}|\varnothing'\rangle = 0. \tag{5.90}$$

Such a state can be constructed from $|\varnothing\rangle$ (or vice versa):

$$|\varnothing'\rangle = \prod_{\mathbf{k}\sigma} \hat{c}_{\mathbf{k}\sigma}|\varnothing\rangle = \prod_{\mathbf{k}\sigma} \hat{d}^\dagger_{\mathbf{k}\sigma}|\varnothing\rangle. \tag{5.91}$$

Thus, from the viewpoint of the b, d operators, $|\varnothing'\rangle$ is the "Dirac sea" state, formed by occupying all the negative-energy states. From the viewpoint of the b, c operators, it is simply a state of no particles.

The next step is to interpret the multi-particle system as a quantum field. This must be done with some care, due to the peculiar relationship between the electron and positron operators. When formulating bosonic field theory in Chapter 4, we defined a field operator

$$\hat{\psi}(\mathbf{r}) = \int d^3k\; \varphi_{\mathbf{k}}(\mathbf{r})\,\hat{a}_{\mathbf{k}}, \tag{5.92}$$

where $\hat{a}_{\mathbf{k}}$ is a bosonic annihilation operator, and $\varphi_{\mathbf{k}}(\mathbf{r})$ denotes the corresponding single-particle wavefunction. In our case, the single-particle wavefunctions have the form

$$\langle \mathbf{r}, n|\mathbf{k}, +, \sigma\rangle = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}}\, u^n_{\mathbf{k}\sigma} \tag{5.93}$$

$$\langle \mathbf{r}, n|\mathbf{k}, -, \sigma\rangle = \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}}\, v^n_{-\mathbf{k},\sigma} \tag{5.94}$$

where $n = 1, \ldots, 4$ indexes the spinor components. In Eq. (5.94), the sign of the exponent corresponds to momentum $-\hbar\mathbf{k}$, matching our earlier definition. For each $\mathbf{k}$, $u_{\mathbf{k}\sigma}$ and $v_{\mathbf{k},\sigma}$ are normalized eigenvectors of a single 4×4 Hamiltonian matrix, so they are orthogonal,

$$\sum_n \left(u^n_{\mathbf{k}\sigma}\right)^* u_{\mathbf{k}\sigma'} = \delta_{\sigma\sigma'}, \quad \sum_n \left(v^n_{\mathbf{k}\sigma}\right)^* v_{\mathbf{k}\sigma'} = \delta_{\sigma\sigma'}, \quad \sum_n \left(u^n_{\mathbf{k}\sigma}\right)^* v_{\mathbf{k}\sigma'} = 0, \tag{5.95}$$

and satisfy the resolution of the identity,

$$\sum_\sigma \left[u^n_{\mathbf{k}\sigma}\left(u^{n'}_{\mathbf{k}\sigma}\right)^* + v^n_{\mathbf{k}\sigma}\left(v^{n'}_{\mathbf{k}\sigma}\right)^*\right] = \delta_{nn'}. \tag{5.96}$$

By analogy with Eq. (5.92), we can use Eqs. (5.93)–(5.94) to define the field operator

$$\hat{\psi}_n(\mathbf{r}) = \int d^3k \sum_\sigma \left[\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}}\, u^n_{\mathbf{k}\sigma}\hat{b}_{\mathbf{k}\sigma} + \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{(2\pi)^{3/2}}\, v^n_{-\mathbf{k},\sigma}\hat{d}^\dagger_{\mathbf{k}\sigma}\right]. \tag{5.97}$$

Like the single-particle wavefunctions, the field operator at each point $\mathbf{r}$ has four components (i.e., it consists of four distinct operators), indexed by n. Next, in the second term of the integrand, let us replace the d operators with c operators, and change variables $k \to -k$:

$$\hat{\psi}_n(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^{3/2}} \sum_\sigma e^{i\mathbf{k}\cdot\mathbf{r}} \left(u^n_{\mathbf{k}\sigma}\hat{b}_{\mathbf{k}\sigma} + v^n_{\mathbf{k},\sigma}\hat{c}^\dagger_{-\mathbf{k},\sigma}\right). \tag{5.98}$$

Using the electron and positron anticommutation relations (5.87), and the spinor property (5.96), we can now prove that

$$\left\{\hat{\psi}_n(\mathbf{r}),\, \hat{\psi}^\dagger_{n'}(\mathbf{r}')\right\} = \delta_{nn'}\,\delta^3(\mathbf{r}-\mathbf{r}'), \tag{5.99}$$

$$\left\{\hat{\psi}_n(\mathbf{r}),\, \hat{\psi}_{n'}(\mathbf{r}')\right\} = \left\{\hat{\psi}^\dagger_n(\mathbf{r}),\, \hat{\psi}^\dagger_{n'}(\mathbf{r}')\right\} = 0. \tag{5.100}$$

These imply that $\hat{\psi}_n(\mathbf{r})$ and $\hat{\psi}^\dagger_n(\mathbf{r})$ act as creation/annihilation operators at a local point $\mathbf{r}$. However, neither field operator acts on electrons or positrons alone: $\hat{\psi}_n(\mathbf{r})$ annihilates an electron or creates a positron [Eq. (5.98)], and conversely $\hat{\psi}^\dagger_n(\mathbf{r})$ creates an electron or annihilates a positron.

The fermionic quantum field theory can thus be interpreted in two ways: (i) in terms of electrons and positrons carrying positive energies, with $|\varnothing'\rangle$ referring to a vacuum state of no particles, or (ii) in terms of electrons that can carry positive or negative energies, with $|\varnothing'\rangle$ referring to a Dirac sea in which all negative-energy states are filled. The former picture is arguably theoretically "cleaner", whereas the latter picture has the advantage of mapping directly to Dirac's original single-particle theory.

There are many more details about the Dirac field theory that we will not discuss here, including the expression of the Hamiltonian in terms of the field operators, and the issue of how the particles transform under Lorentz boosts and other changes in coordinate system. For such matters, the reader is referred to Ref. [1].

5.3. QUANTIZING THE ELECTROMAGNETIC FIELD

Up to now, we have treated the electromagnetic field as a classical entity not subject to quantum mechanics. At a fundamental level, however, the electromagnetic field must behave as a quantum field. We have already, in Chapter 4, discussed the quantization of a simple scalar boson field: the classical field is decomposed into normal modes, each mode is assigned a set of quantum mechanical creation and annihilation operators, and these are used to construct quantum observables (particularly the Hamiltonian and field variables). We can use the same approach, with only minor adjustments, to quantize the electromagnetic field.

First, consider a "source-free" electromagnetic field—i.e., with no electric charges and currents. Without sources, Maxwell's equations (in SI units, and in a vacuum) reduce to:

$$\nabla \cdot \mathbf{E} = 0 \tag{5.101}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{5.102}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \tag{5.103}$$

$$\nabla \times \mathbf{B} = \frac{1}{c^2}\frac{\partial \mathbf{E}}{\partial t}. \tag{5.104}$$

Once again, we introduce the scalar potential Φ and vector potential $\mathbf{A}$:

$$\mathbf{E} = -\nabla\Phi - \frac{\partial \mathbf{A}}{\partial t} \tag{5.105}$$

$$\mathbf{B} = \nabla \times \mathbf{A}. \tag{5.106}$$

With these relations, Eqs. (5.102) and (5.103) are satisfied automatically via vector identities. The two remaining equations, (5.101) and (5.104), become:

$$\nabla^2\Phi = -\frac{\partial}{\partial t}\nabla \cdot \mathbf{A} \tag{5.107}$$

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{A} = \nabla\left[\frac{1}{c^2}\frac{\partial}{\partial t}\Phi + \nabla \cdot \mathbf{A}\right]. \tag{5.108}$$

In the next step, we choose a convenient gauge called the **Coulomb gauge**:

$$\Phi = 0, \quad \nabla \cdot \mathbf{A} = 0. \tag{5.109}$$

(To see that we can always make such a gauge choice, suppose we start out with a scalar potential Φ_0 and vector potential $\mathbf{A}_0$ not satisfying (5.109). Perform a gauge transformation with $\Lambda(\mathbf{r}, t) = \int^t dt'\, \Phi_0(\mathbf{r}, t')$. The new potentials satisfy

$$\Phi = \Phi_0 - \dot{\Lambda} = \Phi_0 - \Phi_0 = 0 \tag{5.110}$$

$$\nabla \cdot \mathbf{A} = \nabla \cdot \mathbf{A}_0 + \nabla^2\Lambda = \nabla \cdot \mathbf{A}_0 + \int^t dt'\, \nabla^2\Phi_0(\mathbf{r}, t'). \tag{5.111}$$

Plugging Eq. (5.107) into Eq. (5.111), we find that $\nabla \cdot \mathbf{A} = 0$.)

In the Coulomb gauge, Eq. (5.107) is automatically satisfied. The sole remaining equation, (5.108), simplifies to

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\mathbf{A} = 0. \tag{5.112}$$

This has plane-wave solutions of the form

$$\mathbf{A}(\mathbf{r},t) = \left(\mathcal{A}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + \text{c.c.}\right)\mathbf{e}, \tag{5.113}$$

where $\mathcal{A}$ is a complex number (the **mode amplitude**) that specifies the magnitude and phase of the plane wave, $\mathbf{e}$ is a real unit vector (the **polarization vector**) that specifies which direction the vector potential points along, and "c.c." denotes the complex conjugate of the first term. Referring to Eq. (5.112), the angular frequency ω must satisfy

$$\omega = c|\mathbf{k}|. \tag{5.114}$$

Moreover, since $\nabla \cdot \mathbf{A} = 0$, it must be the case that

$$\mathbf{k}\cdot\mathbf{e} = 0. \tag{5.115}$$

In other words, the polarization vector is perpendicular to the propagation direction. For any given $\mathbf{k}$, we can choose (arbitrarily) two orthogonal polarization vectors.

Now suppose we put the electromagnetic field in a box of volume $V = L^3$, with periodic boundary conditions (we will take $L \to \infty$ at the end). The $\mathbf{k}$ vectors form a discrete set:

$$k_j = \frac{2\pi n_j}{L}, \quad n_j \in \mathbf{Z}, \quad \text{for} \quad j = 1, 2, 3. \tag{5.116}$$

Then the vector potential field can be decomposed as a superposition of plane waves,

$$\mathbf{A}(\mathbf{r},t) = \sum_{\mathbf{k}\lambda}\left(\mathcal{A}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \text{c.c.}\right)\mathbf{e}_{\mathbf{k}\lambda}, \quad \text{where} \quad \omega_{\mathbf{k}} = c|\mathbf{k}|. \tag{5.117}$$

Here, λ is a two-fold polarization degree of freedom indexing the two possible orthogonal polarization vectors for each $\mathbf{k}$. (We won't need to specify how exactly these polarization vectors are defined, so long as the definition is used consistently.)

To convert the classical field theory into a quantum field theory, for each $(\mathbf{k},\lambda)$ we define an independent set of creation and annihilation operators:

$$\left[\hat{a}_{\mathbf{k}\lambda}, \hat{a}^\dagger_{\mathbf{k}'\lambda'}\right] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'}, \quad \left[\hat{a}_{\mathbf{k}\lambda}, \hat{a}_{\mathbf{k}'\lambda'}\right] = \left[\hat{a}^\dagger_{\mathbf{k}\lambda}, \hat{a}^\dagger_{\mathbf{k}'\lambda'}\right] = 0. \tag{5.118}$$

Then the Hamiltonian for the electromagnetic field is

$$\hat{H} = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}}\, \hat{a}^\dagger_{\mathbf{k}\lambda}\hat{a}_{\mathbf{k}\lambda}, \quad \text{where} \quad \omega_{\mathbf{k}} = c|\mathbf{k}|. \tag{5.119}$$

The vector potential is now promoted into a Hermitian operator in the Heisenberg picture:

$$\hat{\mathbf{A}}(\mathbf{r},t) = \sum_{\mathbf{k}\lambda} \mathcal{C}_{\mathbf{k}\lambda}\left(\hat{a}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \text{h.c.}\right)\mathbf{e}_{\mathbf{k}\lambda}. \tag{5.120}$$

Here, $\mathcal{C}_{\mathbf{k}\lambda}$ is a constant to be determined, and "h.c." denotes the Hermitian conjugate. The creation and annihilation operators in this equation are Schrödinger picture ($t = 0$) operators. The particles they create/annihilate are **photons**—elementary particles of light.

To find $\mathcal{C}_{\mathbf{k}\lambda}$, we compare the quantum and classical energies. Suppose the electromagnetic field is in a coherent state $|\alpha\rangle$ such that for any $\mathbf{k}$ and λ,

$$\hat{a}_{\mathbf{k}\lambda}|\alpha\rangle = \alpha_{\mathbf{k}\lambda}|\alpha\rangle \tag{5.121}$$

for some $\alpha_{\mathbf{k}\lambda} \in \mathbb{C}$. From this and Eq. (5.120), we identify the corresponding classical field

$$\mathbf{A}(\mathbf{r},t) = \sum_{\mathbf{k}\lambda} \left(\mathcal{A}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \text{c.c.} \right) \mathbf{e}_{\mathbf{k}\lambda}, \quad \text{where} \quad \mathcal{C}_{\mathbf{k}\lambda}\alpha_{\mathbf{k}\lambda} = \mathcal{A}_{\mathbf{k}\lambda}. \tag{5.122}$$

For each $\mathbf{k}$ and λ, Eqs. (5.105)–(5.106) give the electric and magnetic fields

$$\mathbf{E}_{\mathbf{k}\lambda} = \left(i\omega_{\mathbf{k}} \mathcal{A}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \text{c.c.} \right) \mathbf{e}_{\mathbf{k}\lambda} \tag{5.123}$$

$$\mathbf{B}_{\mathbf{k}\lambda} = \left(i\mathcal{A}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \text{c.c.} \right) \mathbf{k} \times \mathbf{e}_{\mathbf{k}\lambda}. \tag{5.124}$$

In the classical theory of electromagnetism, Poynting's theorem tells us that the total energy carried by a classical plane electromagnetic wave is

$$\begin{aligned} E &= \int_V d^3r\, \frac{\epsilon_0}{2} \left(\left|\mathbf{E}_{\mathbf{k}\lambda}\right|^2 + c^2 \left|\mathbf{B}_{\mathbf{k}\lambda}\right|^2 \right) \\ &= 2\,\epsilon_0\, \omega_{\mathbf{k}}^2\, |\mathcal{A}_{\mathbf{k}\lambda}|^2\, V. \end{aligned} \tag{5.125}$$

Here, V is the volume of the enclosing box, and we have used the fact that terms like $e^{2i\mathbf{k}\cdot\mathbf{r}}$ vanish when integrated over $\mathbf{r}$. Hence, we make the correspondence

$$2\,\epsilon_0\, \omega_{\mathbf{k}}^2\, |\mathcal{C}_{\mathbf{k}\lambda}\alpha_{\mathbf{k}\lambda}|^2\, V = \hbar\omega_{\mathbf{k}} |\alpha_{\mathbf{k}\lambda}|^2 \quad \Rightarrow \quad \mathcal{C}_{\mathbf{k}\lambda} = \sqrt{\frac{\hbar}{2\epsilon_0\omega_{\mathbf{k}}V}}. \tag{5.126}$$

We thus arrive at the result

$$\begin{aligned} \hat{H} &= \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}}\, \hat{a}^\dagger_{\mathbf{k}\lambda}\hat{a}_{\mathbf{k}\lambda} \\ \hat{\mathbf{A}}(\mathbf{r},t) &= \sum_{\mathbf{k}\lambda} \sqrt{\frac{\hbar}{2\epsilon_0\omega_{\mathbf{k}}V}} \left(\hat{a}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \text{h.c.} \right) \mathbf{e}_{\mathbf{k}\lambda} \\ \omega_{\mathbf{k}} &= c|\mathbf{k}|, \quad \left[\hat{a}_{\mathbf{k}\lambda}, \hat{a}^\dagger_{\mathbf{k}'\lambda'}\right] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'}, \quad \left[\hat{a}_{\mathbf{k}\lambda}, \hat{a}_{\mathbf{k}'\lambda'}\right] = 0. \end{aligned} \tag{5.127}$$

To describe infinite free space rather than a finite-volume box, we take the $L \to \infty$ limit and re-normalize the creation and annihilation operators by the replacement

$$\hat{a}_{\mathbf{k}\lambda} \to \sqrt{\frac{(2\pi)^3}{V}}\, \hat{a}_{\mathbf{k}\lambda}. \tag{5.128}$$

Then the sums over $\mathbf{k}$ become integrals over the infinite three-dimensional space:

$$\begin{aligned}
\hat{H} &= \int d^3k \sum_\lambda \hbar\omega_{\mathbf{k}}\, \hat{a}^\dagger_{\mathbf{k}\lambda}\hat{a}_{\mathbf{k}\lambda} \\
\hat{\mathbf{A}}(\mathbf{r},t) &= \int d^3k \sum_\lambda \sqrt{\frac{\hbar}{16\pi^3\epsilon_0\omega_{\mathbf{k}}}} \left(\hat{a}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + \text{h.c.}\right) \mathbf{e}_{\mathbf{k}\lambda} \\
\omega_{\mathbf{k}} &= c|\mathbf{k}|, \quad \left[\hat{a}_{\mathbf{k}\lambda}, \hat{a}^\dagger_{\mathbf{k}'\lambda'}\right] = \delta^3(\mathbf{k}-\mathbf{k}')\delta_{\lambda\lambda'}, \quad \left[\hat{a}_{\mathbf{k}\lambda}, \hat{a}_{\mathbf{k}'\lambda'}\right] = 0.
\end{aligned} \tag{5.129}$$

5.4. THE ELECTRON-PHOTON INTERACTION

Having derived fully quantum mechanical theories for both the electron and the electromagnetic field, we are now able to describe a range of phenomena involving the absorption and/or emission of light by matter. As an example, we will model how an excited atom decays by emitting a photon.

Consider a single electron orbiting an atomic nucleus. It is described by a single-particle Hilbert space $\mathscr{H}_{\text{e}}$, while the electromagnetic field has Hilbert space $\mathscr{H}_{\text{EM}}$. The combined system has Hilbert space $\mathscr{H}_e \otimes \mathscr{H}_{\text{EM}}$, and is described by a Hamiltonian of the form

$$H = H_e + H_{\text{EM}} + H_{\text{int}}. \tag{5.130}$$

Here, H_e is the electron's Hamiltonian in the absence of the electromagnetic field, H_{EM} is the Hamiltonian for the source-free electromagnetic field, and H_{int} is an "interaction Hamiltonian" describing how the electron and electromagnetic field affect each other.

We assume $\hat{H}_e$ has a ground state of energy E_0 and an excited state of energy $E_1 > E_0$:

$$\begin{aligned}
\hat{H}_e|1\rangle &= E_1|1\rangle \\
\hat{H}_e|0\rangle &= E_0|0\rangle.
\end{aligned} \tag{5.131}$$

We initialize the electron in the excited state $|1\rangle$, and the electromagnetic field in the vacuum state $|\varnothing\rangle$. Thus, the initial state of the combined system is

$$|\psi_i\rangle = |1\rangle \otimes |\varnothing\rangle. \tag{5.132}$$

If $\hat{H}_{\text{int}} = 0$, then $|\psi_i\rangle$ is an energy eigenstate, so the electron would remain in the excited state for all time. But if $\hat{H}_{\text{int}}$ is a non-vanishing operator, the electron can decay to $|0\rangle$ by emitting a photon. The post-decay state of the combined system has the form

$$|\psi_{\mathbf{k}\lambda}\rangle = |0\rangle \otimes \left(\hat{a}^\dagger_{\mathbf{k}\lambda}|\varnothing\rangle\right). \tag{5.133}$$

There are many such final states, of different photon wavevector $\mathbf{k}$ and polarization λ.

The decay rate κ can be estimated using Fermi's Golden Rule (see Chapter 2):

$$\kappa = \frac{2\pi}{\hbar}\, \overline{|\mathcal{W}|^2}\, \mathcal{D}, \tag{5.134}$$

where

$$\mathcal{W} = (2\pi)^{3/2}\langle\psi_{\mathbf{k}\lambda}|\hat{H}_{\rm int}|\psi_i\rangle \tag{5.135}$$

$$\mathcal{D} = 2\int \frac{d^3k}{(2\pi)^3}\,\delta(\hbar\omega - \hbar c|\mathbf{k}|). \tag{5.136}$$

Here, we have set the spatial dimension to $d = 3$, $\overline{(\cdots)}$ denotes the average over final states, and $\mathcal{D}$ is the density of photon states, with the prefactor of 2 accounting for the polarization degree of freedom. Eqs. (5.135)–(5.136) are to be evaluated at the resonance energy:

$$\hbar\omega = \hbar c|\mathbf{k}| = E_1 - E_0. \tag{5.137}$$

To calculate the transition amplitude (5.135), we need the interaction Hamiltonian $\hat{H}_{\rm int}$. Let us adopt the Coulomb gauge (see Section 5.3), so that the scalar potential vanishes, and the vector potential acts on the electron via the substitution (see Section 5.1.1):

$$\hat{\mathbf{p}} \to \hat{\mathbf{p}} + e\mathbf{A}(\hat{\mathbf{r}}, t). \tag{5.138}$$

Previously, we have treated the $\mathbf{A}$ field in Eq. (5.138) as a classical entity; although the electron's position operator $\hat{\mathbf{r}}$ slots into it, the field itself lacks quantum dynamics. Now, we make this a quantum field by replacing $\mathbf{A}$ with the operator derived in Section 5.3:

$$\hat{\mathbf{A}}(\hat{\mathbf{r}}) = \int d^3k \sum_\lambda \sqrt{\frac{\hbar}{16\pi^3\epsilon_0\omega_{\mathbf{k}}}}\left(\hat{a}_{\mathbf{k}\lambda}\, e^{i\mathbf{k}\cdot\hat{\mathbf{r}}} + \text{h.c.}\right)\mathbf{e}_{\mathbf{k}\lambda}. \tag{5.139}$$

Here, we are using the expression for infinite space and the Schrodinger picture, equivalent to setting $t = 0$ in Eq. (5.129). Note that the position in Eq. (5.139) is not a vector, but the electron's position operator; hence, $\hat{\mathbf{A}}(\hat{\mathbf{r}}, t)$ acts nontrivially on both $\mathscr{H}_e$ and $\mathscr{H}_{\rm EM}$.

For a non-relativistic electron, the Hamiltonian (5.25) yields the interaction Hamiltonian

$$H_{\rm int} = \frac{e}{2m}\left(\hat{\mathbf{p}}\cdot\hat{\mathbf{A}} + \hat{\mathbf{A}}\cdot\hat{\mathbf{p}}\right). \tag{5.140}$$

Combining this with Eq. (5.139), we can calculate

$$\begin{aligned}\langle\psi_{\mathbf{k}\lambda}|\hat{H}_{\rm int}|\psi_i\rangle &= \frac{e}{2m}\int d^3k' \sum_{j\lambda'}\sqrt{\frac{\hbar}{16\pi^3\epsilon_0\omega_{\mathbf{k}'}}}\langle 0|\{\hat{p}_j, e^{-i\mathbf{k}'\cdot\hat{\mathbf{r}}}\}|1\rangle\; e^j_{\mathbf{k}'\lambda'}\;\langle\varnothing|\hat{a}_{\mathbf{k}\lambda}\hat{a}^\dagger_{\mathbf{k}'\lambda'}|\varnothing\rangle \\ &= \frac{e}{2m}\sqrt{\frac{\hbar}{16\pi^3\epsilon_0\omega_{\mathbf{k}}}}\sum_j \langle 0|\{\hat{p}_j, e^{-i\mathbf{k}\cdot\hat{\mathbf{r}}}\}|1\rangle\; e^j_{\mathbf{k}\lambda}\end{aligned} \tag{5.141}$$

We can make two further simplifications. Firstly, note that for atomic transitions in the visible light regime, the optical wavelength is around 10^{-6} m (i.e., $|\mathbf{k}| \sim 10^6\,\text{m}^{-}1$), whereas the size of a typical atomic orbital is around 10^{-9} m. Hence, we can take $\exp(-i\mathbf{k}\cdot\hat{\mathbf{r}}) \approx 1$. Secondly, note that if the electron's Hamiltonian has the generic form

$$\hat{H}_e = |\hat{\mathbf{p}}|^2/2m + V(\mathbf{r}), \tag{5.142}$$

then $[\hat{H}_e, \hat{\mathbf{r}}] = -i\hbar\mathbf{p}/m$, and hence

$$\langle 0|\hat{p}_j|1\rangle = -\frac{im(E_1 - E_0)\mathbf{d}}{\hbar}, \quad \mathbf{d} = \langle 0|\mathbf{r}|1\rangle. \tag{5.143}$$

We call $\mathbf{d}$, which is easily calculated from the orbital wavefunctions, the **transition dipole moment**. Putting these simplifications into Eq. (5.141) yields

$$\langle \psi_{\mathbf{k}\lambda}|\hat{H}_{\text{int}}|\psi_i\rangle \approx -ie\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{16\pi^3\epsilon_0}}\,\mathbf{d}\cdot\mathbf{e}_{\mathbf{k}\lambda}. \tag{5.144}$$

According to Fermi's Golden Rule, Eq. (5.134), we need to take the absolute square and average over photon states. It can be shown (via a standard angular integration) that

$$\overline{|\mathbf{d}\cdot\mathbf{e}_{\mathbf{k}\lambda}|^2} = \frac{|\mathbf{d}|^2}{3}. \tag{5.145}$$

Hence,

$$\overline{|\mathcal{W}|^2} = (2\pi)^3\overline{|\langle\psi_{\mathbf{k}\lambda}|\hat{H}_{\text{int}}|\psi_i\rangle|^2} \tag{5.146}$$

$$= \frac{e^2\hbar\omega}{6\epsilon_0}\,|\mathbf{d}|^2, \tag{5.147}$$

where $\omega = (E_1 - E_0)/\hbar$ is the resonance frequency.

Finally, we calculate the density of states, Eq. (5.136), which results in (see Exercise 3):

$$\mathcal{D}(\hbar\omega) = \frac{\omega^2}{\pi^2\hbar c^3}. \tag{5.148}$$

Plugging Eq. (5.147) and (5.148) into Eq. (5.134), we obtain

$$\kappa = \frac{e^2\omega^3|\mathbf{d}|^2}{3\pi\epsilon_0\hbar c^3} \tag{5.149}$$

We can make this look nicer by defining the dimensionless **fine-structure constant**

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137}. \tag{5.150}$$

Hence,

$$\kappa = \frac{4}{3}\frac{\alpha\omega^3\,|\mathbf{d}|^2}{c^2}. \tag{5.151}$$

This rate of spontaneous emission is called the **Einstein A coefficient**. It can be observed directly in experiments, by measuring the line-widths of atomic spectral lines. In the figure below, we present a comparison of the theoretical result, Eq. (5.151), to the experimentally-observed decay rates of the simplest excited states of hydrogen, lithium, and sodium. In theoretical result, we simply take the transition dipole moment to be $|\mathbf{d}| \approx 10^{-10}\,\text{m}$ (i.e., the length scale of an atomic orbital), rather than doing a more precise calculation using the actual orbital wavefunctions. Despite this rather crude approximation, it can be seen that the decay rates produced by Fermi's Golden Rule are within striking distance of the experimental values.

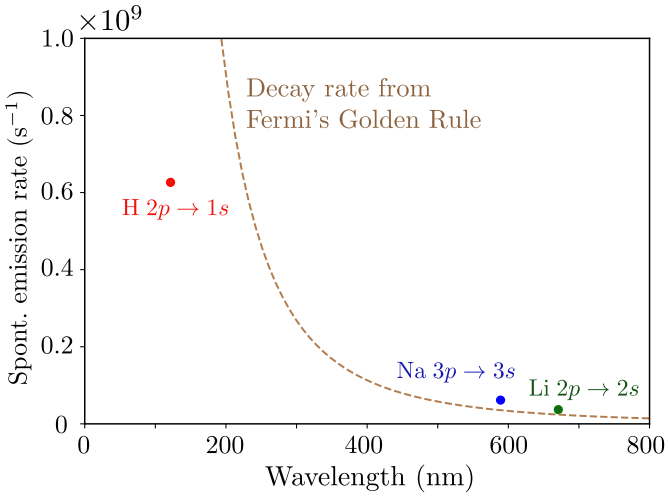


FIG. 1. Spontaneous emission rates (Einstein A coefficients) for the $2p \to 1s$ transition in hydrogen, the $2p \to 2s$ transition in lithium, and the $3p \to 3s$ transition in sodium. Data points extracted from the NIST Atomic Spectra Database (https://www.nist.gov/pml/atomic-spectra-database). The dashed curve shows the decay rate based on Fermi's Golden Rule, with $|\mathbf{d}| \approx 10^{-10}$ m.

EXERCISES

1. In Section 5.3, we derived the vector potential operator, in an infinite volume, to be

$$\hat{\mathbf{A}}(\mathbf{r}, t) = \int d^3k \sum_\lambda \sqrt{\frac{\hbar}{16\pi^3 \epsilon_0 \omega_\mathbf{k}}} \left(\hat{a}_{\mathbf{k}\lambda}\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega_\mathbf{k} t)} + \text{h.c.} \right) \mathbf{e}_{\mathbf{k}\lambda}. \tag{5.152}$$

   Since $[\hat{a}_{\mathbf{k}\lambda}, \hat{a}^\dagger_{\mathbf{k}'\lambda'}] = \delta^3(\mathbf{k} - \mathbf{k}')\delta_{\lambda\lambda'}$, the creation and annihilation operators each have units of $[x^{3/2}]$. Prove that $\hat{\mathbf{A}}$ has the same units as the classical vector potential.

2. Repeat the spontaneous decay rate calculation from Section 5.4 using the finite-volume versions of the creation/annihilation operators and the vector potential operator (5.139). Show that it yields the same result (5.150).

3. The density of photon states at energy E is defined as

$$\mathcal{D}(E) = 2 \int \frac{d^3k}{(2\pi)^3}\, \delta(E - E_\mathbf{k}), \tag{5.153}$$

   where $E_\mathbf{k} = \hbar c|\mathbf{k}|$. Note the factor of 2 accounting for the polarizations. Prove that

$$\mathcal{D}(E) = \frac{E^2}{\pi^2 \hbar^3 c^3}. \tag{5.154}$$

FURTHER READING

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