Chapter 6

Applications of Perturbation Theory

6.1 Particle in an Electromagnetic Field

The Lagrangian and Hamiltonian formulation of quantum mechanics provides a systematic methods for deriving the proper Hamiltonian used to describe the behavior of a charged particle in an electromagnetic field, consistent with the classical forces. We do not provide a comprehensive overview of the Lagrangian and Hamiltonian formulation for classical mechanics here, but provide a quick summary that leads to the adequate Hamiltonian that will be used throughout this course.

6.1.1 Brief summary of the Lagrangian and Hamiltonian formulation

Lagrangian formulation starts from the least action principle, from which many classical laws of physics can be derived. Lagrangian $\mathcal{L}$ is defined as the difference between the kinetic energy and the potential energy of the system, expressed as a function of spatial coordinates, their time derivatives, and time. For a system of n particles each with mass m_i ($i = 1, 2, \ldots n$), we consider the $3n$ generalized spatial coordinates $q_i = (x_i, y_i, z_i)$

$$\mathcal{L}(q_i; \dot{q}_i; t) = T - V = \frac{1}{2} \sum_{i=1}^{n} m_i(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) - V(q_i). \tag{6.1}$$

Action $\mathcal{S}$ is defined to be the definite time integral of the Lagrangian between the initial time t_1 and the final time t_2 as

$$\mathcal{S} = \int_{t_1}^{t_2} \mathcal{L}(q_i; \dot{q}_i; t)dt. \tag{6.2}$$

The action takes a concrete value for each "path" the system can take to evolve between t_1 and t_2, where a "path" is defined as the trajectory of all 6n variables $\{q_i; \dot{q}_i\}$. The *least action principle* states that the actual path taken by the system is the one that minimizes

the action, and such condition can be found by considering the condition $\delta \mathcal{S} = 0$. Although technically this condition finds the path that satisfies the extremum (both maximum and minimum), this condition is used to derive the Lagrange equations

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) = \frac{\partial \mathcal{L}}{\partial q_i}. \tag{6.3}$$

In the Hamiltonian formulation, one first defines the conjugate momentum for a coordinate variable q_i as

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}, \tag{6.4}$$

and the (classical) Hamiltonian from these conjugate variables as

$$H(p_i; q_i; t) = \sum_i \dot{q}_i p_i - \mathcal{L}. \tag{6.5}$$

Then, the change in Hamiltonian δH is calculated as

$$\text{L.H.S} = \sum_i \left[\frac{\partial H}{\partial p_i}\delta p_i + \frac{\partial H}{\partial q_i}\delta q_i\right] + \frac{\partial H}{\partial t}\delta t \tag{6.6}$$

$$\text{R.H.S} = \sum_i [\dot{q}_i \delta p_i + p_i \delta \dot{q}_i] - \sum_i \frac{\partial \mathcal{L}}{\partial q_i}\delta q_i - \sum_i \frac{\partial \mathcal{L}}{\partial \dot{q}_i}\delta \dot{q}_i - \frac{\partial \mathcal{L}}{\partial t}\delta t \tag{6.7}$$

$$= \sum_i \dot{q}_i \delta p_i - \sum_i \left(\frac{d}{dt}p_i\right)\delta q_i - \frac{\partial \mathcal{L}}{\partial t}\delta t, \tag{6.8}$$

where we used the Lagrange equation (Eq. 6.3) and the definition of the conjugate variable (Eq. 6.4) in the last step of the second equation. Comparing the two sides, we derive the Hamilton's equations

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}, \quad \frac{\partial H}{\partial t} = -\frac{\partial \mathcal{L}}{\partial t}. \tag{6.9}$$

One notes that Hamilton's equations replaces a single second-order differential equation (Lagrange equation) with two first-order differential equation that describes the time evolution of a particle in a potential.

6.1.2　Particle in a potential well

As a first example, we consider a classical particle with mass m in a potential well of $V(\vec{r})$. The Lagrangian is given by

$$\mathcal{L} = \frac{1}{2}mv^2 - V(\vec{r}) = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right) - V(\vec{r}). \tag{6.10}$$

We also note that the force on the particle from the potential is given by

$$\vec{F}(\vec{r}) = -\nabla V(\vec{r}), \tag{6.11}$$

or more explicitly,

$$F_x = -\frac{\partial V}{\partial x}, \quad F_y = -\frac{\partial V}{\partial y}, \quad F_z = -\frac{\partial V}{\partial z}. \tag{6.12}$$

Thus, the Lagrange equation for the variable x becomes

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{x}}\right) = \frac{d}{dt}(m\dot{x}) = m\frac{d^2 x}{dt^2}, \tag{6.13}$$

$$\frac{\partial \mathcal{L}}{\partial x_i} = -\frac{\partial V}{\partial x} = F_x. \tag{6.14}$$

So, we note that the Lagrange equation corresponds to Newton's second law $m\frac{d^2\vec{r}}{dt^2} = \vec{F}(\vec{r})$.

In terms of Hamilton's formulation, we first compute the conjugate momenta and the corresponding Hamiltonian

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i} = m\dot{q}_i, \tag{6.15}$$

$$H = m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) - \mathcal{L} = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + V(\vec{r}) \tag{6.16}$$

$$= \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(\vec{r}). \tag{6.17}$$

The Hamilton's equations reads

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} = \frac{p_i}{m}, \tag{6.18}$$

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} = -\frac{\partial V}{\partial q_i} = F_i. \tag{6.19}$$

The first equation is the definition of momentum, and the second equation is Newton's second law.

6.1.3 Charged particle in an electromagnetic field

The motion of a (classical) charged particle with mass m and charge q in an electromagnetic field (consisting of both electric field $\vec{E}$ and magnetic flux density, or magnetic field $\vec{B}$) is described by the Lorentz force

$$m\frac{d^2}{dt^2}\vec{r} = q\left[\vec{E}(\vec{r},t) + \frac{d\vec{r}}{dt} \times \vec{B}(\vec{r},t)\right]. \tag{6.20}$$

From Maxwell's equations, we can express the electric and the magnetic field from the vector potential $\vec{A}(\vec{r},t)$ and the scalar potential $U(\vec{r},t)$, from which the electric and the magnetic fields can be derived as

$$\vec{E}(\vec{r},t) = -\nabla U(\vec{r},t) - \frac{\partial}{\partial t}\vec{A}(\vec{r},t), \tag{6.21}$$

$$\vec{B}(\vec{r},t) = \nabla \times \vec{A}(\vec{r},t). \tag{6.22}$$

We also note that for a given physical $\vec{E}$ and $\vec{B}$ fields, the choice of the scalar and vector potentials are not unique. For example, one can pick an arbitrary scalar function $\chi(\vec{r},t)$ and create a new pair of vector and scalar potentials such that

$$\vec{A}'(\vec{r},t) = \vec{A}(\vec{r},t) + \nabla\chi(\vec{r},t), \tag{6.23}$$

$$U'(\vec{r},t) = U(\vec{r},t) - \frac{\partial}{\partial t}\chi(\vec{r},t), \tag{6.24}$$

then these two potential will lead to identical electric and magnetic fields $\vec{E}$ and $\vec{B}$. Such transform of potential functions that keep the physical fields unchanged is known as the gauge transformation, where the choice of specific scalar function $\chi(\vec{r},t)$ defines the gauge used to describe the fields.

The Lagrangian that yields the equation of motion shown in Eq. 6.20 is given by

$$\mathcal{L}(\vec{r},\dot{\vec{r}},t) = \frac{1}{2}m\dot{\vec{r}}^2 + q\dot{\vec{r}}\cdot\vec{A}(\vec{r},t) - qU(\vec{r},t). \tag{6.25}$$

This can be confirmed by considering the Lagrange equation corresponding to each spatial coordinate. For example, the partial derivative of the Lagrangian by $\dot{x}$ and x gives

$$\frac{\partial\mathcal{L}}{\partial\dot{x}} = m\dot{x} + qA_x(\vec{r},t) \equiv p_x, \tag{6.26}$$

$$\frac{\partial\mathcal{L}}{\partial x} = q\frac{\partial}{\partial x}\left(\dot{\vec{r}}\cdot\vec{A}(\vec{r},t)\right) - \frac{\partial}{\partial x}U(\vec{r}.t), \tag{6.27}$$

We note that Eq. 6.26 defines the conjugate momentum for the coordinate x in the presence of electromagnetic field. From these partial derivatives, the Lagrange equation can be derived as

$$\frac{d}{dt}\left[m\dot{x} + qA_x(\vec{r},t)\right] = q\dot{\vec{r}}\cdot\frac{\partial}{\partial x}\vec{A}(\vec{r},t) - q\frac{\partial}{\partial x}U(\vec{r},t). \tag{6.28}$$

After some algebra taking into account the definition of fields (Eq. 6.21), we conclude that this equation is equivalent to

$$m\frac{d^2x}{dt^2} = qE_x + q(\dot{y}B_z - \dot{z}B - y) \tag{6.29}$$

$$= q[E_x + (\vec{v}\times\vec{B})_x], \tag{6.30}$$

which is equivalent to the Lorentz force given in Eq. 6.20.

The Hamiltonian describing this interaction is given by

$$
\begin{aligned}
H &= \dot{x}p_x + \dot{y}p_y + \dot{z}p_z - \mathcal{L} = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + qU(\vec{r}) \quad (6.31) \\
&= \frac{1}{2m}\left[\vec{p} - q\vec{A}(\vec{r}, t)\right]^2 + qU(\vec{r}). \quad (6.32)
\end{aligned}
$$

When the momentum $\vec{p}$ and the vector potential field $\vec{A}(\vec{r}, t)$ re replaced with quantum operators, this Hamiltonian is used to describe the behavior of a charged particle in an electromagnetic field in quantum mechanics.

6.2 The Stark Effect

When an atom is subject to a constant electric field, the energy level shifts. This is often called the (DC) Stark effect. The energy level of an atom can also shift when illuminated by an electromagnetic field whose photon energy is comparable to the atomic transition energy. This is often called the light(-induced) shift, or the AC Stark shift. The origin of the AC Stark effect is very different from the DC Stark effect. In this section, we only consider the DC Stark effect.

When a hydrogen atom is subject to a constant electric field $\vec{E} = \mathcal{E}\hat{z}$, the potential energy can be described by $U(\vec{r}) = -\mathcal{E}z$. The perturbation Hamiltonian is given by

$$
\hat{H}' = \hat{V} = -e\mathcal{E}z = -e\mathcal{E}r\cos\theta, \quad (6.33)
$$

where θ is the angle between the z-axis and the location of the electron when the origin is chosen to be at the location of the nucleus (proton in this case). The total Hamiltonian of the hydrogen atom subject to a constant electric field in the z direction is therefore given by

$$
\hat{H} = \hat{H}_0 + \hat{V} = \frac{\hat{p}_r^2}{2m_e} + \frac{\hat{L}^2}{2m_e r^2} - \frac{e^2}{r} - e\mathcal{E}r\cos\theta, \quad (6.34)
$$

where the first three terms represent the unperturbed Hamiltonian $\hat{H}_0$, and the final term is considered the perturbation Hamiltonian.

6.2.1 Ground state energy shift

The first-order energy shift of the ground state of the hydrogen atom due to this static field can be computed from using Eq. 5.12:

$$
E_1^{(1)} = \langle 100|\hat{V}|100\rangle = -e\mathcal{E}\int_0^\infty r^2 dr\ r|R_{10}(r)|^2 \int d\Omega |Y_0^0|^2 \cos\theta = 0. \quad (6.35)
$$

The integral is evaluated over the angle θ by letting $x = \cos\theta$, and noting that the θ integration boils down to $\int_0^\pi \cos\theta d(\cos\theta) = -\int_{-1}^1 x dx = 0$. So, the DC electric field does not cause a first-order shift in the ground state energy of a hydrogen atom.

The second-order correction to the ground state energy of hydrogen atom can be computed from Eq. 5.16. For the ground state, we have to consider the effects from all other possible states, by computing

$$\langle 100|\hat{V}|nlm\rangle = -e\mathcal{E}\int_0^\infty r^2 dr \, rR_{10}^*(r)R_{nl}(r)\int d\Omega Y_0^{0*}Y_l^m\cos\theta. \tag{6.36}$$

Looking at angular integration for m, we note that the φ integral vanishes unless $m = 0$. So, the only non-vanishing angular integrals are

$$\int d\Omega Y_0^{0*}Y_l^0\cos\theta = \frac{1}{2}\sqrt{2l+1}\int_{-1}^1 P_1(x)P_l(x)dx, \tag{6.37}$$

where $x = \cos\theta$, and $P_1(\cos\theta) = \cos\theta$. Due to the orthogonality of $P_l(x)$, the only non-zero integral is when $l = 1$. Noting that $\int_{-1}^1 P_m(x)P_n(x)dx = \frac{2}{2n+1}\delta_{mn}$, this integral evaluates to $1/\sqrt{3}$. Therefore, Eq. 6.36 reduces to

$$\langle 100|\hat{V}|n10\rangle = -\frac{2e\mathcal{E}}{\sqrt{3}a_0^{3/2}}\int_0^\infty r^3 dr \, e^{-r/a_0}R_{n1}(r). \tag{6.38}$$

One can evaluate this integral for each $n > 1$, and compute the ground-state energy shift from Eq. 5.16.

6.2.2 $n = 2$ state energy shift

There is no degeneracy for the $n = 1$ ground state energy for the hydrogen atom, when the electron spin degree-of-freedom is ignored (degeneracy is given by n^2). Since the electron spin does not respond to external electric field, the Stark effect for the ground state is negligible to first order. For $n = 2$ state, there is a 4-fold degeneracy, corresponding to the four states $|2, 0, 0\rangle$, $|2, 1, -1\rangle$, $|2, 1, 0\rangle$ and $|2, 1, 1\rangle$. Since these four states are degenerate, we must apply the degenerate perturbation theory. It suggests we compute the eigenstates that diagonalizes the perturbation Hamiltonian to compute the energy shift. The first-order energy shift can be calculated by considering

$$\langle 2lm|\hat{V}|2l'm'\rangle = -e\mathcal{E}\int_0^\infty r^2 dr \, rR_{2l}^*(r)R_{2l'}(r)\int d\Omega Y_l^{m*}Y_{l'}^{m'}\cos\theta. \tag{6.39}$$

From the angular integral, we note that only $m = m'$ terms contribute. We also note that when $l = l'$, the integrals are zero. Noting the recursion relation for associated Legendre polynomials

$$(2L+1)xP_l^m(x) = (l - m + 1)P_{l+1}^m(x) + (l + m)P_{l-1}^m(x), \tag{6.40}$$

we conclude that the only non-vanishing term in this integral is

$$V_{13} = -e\mathcal{E}\langle 2, 0, 0|r\cos\theta|2, 1, 0\rangle = V_{31}, \tag{6.41}$$

since the perturbation Hamiltonian is hermitian. The angular portion of the integral evaluates to

$$\int d\Omega Y_1^0(x)Y_0^0(x)x = 2\pi\int_{-1}^1\frac{\sqrt{3}}{4\pi}x^2 dx = 1/\sqrt{3}. \tag{6.42}$$

The radial integral evaluates to

$$\int_0^\infty R_{20}^*(r)R_{21}(r)r^3 dr = \frac{1}{4\sqrt{3}a_0^3}\int_0^\infty \left(1-\frac{r}{2a_0}\right)\frac{r}{a_0}e^{-r/a_0}r^3 dr \tag{6.43}$$

$$= \frac{a_0}{4\sqrt{3}}\int_0^\infty \left(1-\frac{\rho}{2}\right)\rho^4 e^{-\rho}d\rho, \tag{6.44}$$

where we define $\rho = r/a_0$. The integral can be evaluated by considering

$$\int_0^\infty e^{-a\rho}d\rho = \left[-\frac{1}{a}e^{-a\rho}\right]_0^\infty = \frac{1}{a}, \tag{6.45}$$

and noting that

$$\int_0^\infty \rho^n e^{-a\rho}d\rho = \left(-\frac{d}{da}\right)^n \int_0^\infty e^{-a\rho}d\rho = \left(-\frac{d}{da}\right)^n a^{-1} = (-1)^n n!\, a^{-n-1}. \tag{6.46}$$

Letting $a = 1$ allows us to evaluate the integral to be $(-1)^n n!$. Using this result, the energy correction term in Eq. 6.39 reduces to

$$V_{13} = e\mathcal{E}\frac{36a_0}{4\sqrt{3}}\frac{1}{\sqrt{3}} = 3e\mathcal{E}a_0 \equiv \mathbb{E}. \tag{6.47}$$

This interaction Hamiltonian can be diagonalized. The secular equation yields three eigenvalues, $\pm\mathbb{E}$ and 0 (with two degenerate eigenstates). The two states $|2,1,\pm1\rangle$ have eigenvalues of 0 and the energy remains unchanged at $E_2^{(0)}$. For the remaining two states $|2,0,0\rangle$ and $|2,1,0\rangle$, they form new eigenstates with energy shifts

$$E_2^{(0)} + \mathbb{E}: \quad |\varphi_+\rangle = \frac{1}{\sqrt{2}}(|2,0,0\rangle - |2,1,0\rangle) \tag{6.48}$$

$$E_2^{(0)} - \mathbb{E}: \quad |\varphi_-\rangle = \frac{1}{\sqrt{2}}(|2,0,0\rangle + |2,1,0\rangle). \tag{6.49}$$

6.3 Hyperfine Interaction

6.3.1 Hamiltonian for hyperfine interaction

Hyperfine interaction is a magnetic interaction between the electron and the spin of the nucleus (proton, in the case of hydrogen atom). We denote the proton spin with an angular momentum operator $\hat{\boldsymbol{I}}$. The magnetic moment of the proton is given by

$$\vec{\mu}_I = g_p\mu_N\vec{I}/\hbar, \tag{6.50}$$

where $g_p = 2 \times 2.79$ is the Landé g-factor for proton, and μ_N is the nuclear magneton, as discussed in Eq. 3.37. The nuclear magneton is about 1,836 times smaller than the Bohr magneton for the electron, which is the ratio between the electron and the proton mass. If

we let $\hat{\boldsymbol{A}}_I(\vec{r})$ and $U_I(\vec{r})$ as the (time-independent) vector and scalar potential arising from the nuclear spin, the total Hamiltonian for the electron becomes

$$\hat{H} = \frac{1}{2m_e}\left(\hat{\boldsymbol{p}} - q\hat{\boldsymbol{A}}_I(\vec{r})\right)^2 + qU_I(\vec{r}) - 2\mu_B\left(\frac{\hat{\boldsymbol{S}}}{\hbar}\right)\cdot[\nabla \times \hat{\boldsymbol{A}}_I(\vec{r})]. \tag{6.51}$$

As for the scalar potential $U_D(\vec{r})$, the zeroth order expansion of this is simply the Coulomb term given by $V(\vec{r} = -Ze^2/r$, contributing to the unperturbed Hamiltonian $\hat{H}_0 = \hat{\boldsymbol{p}}^2/2m_e + V_0(\vec{r})$. Since the proton has spin $I = 1/2$ and thus no spin quadrupole, the second order correction is zero. It turns out that there are no higher order multi-poles either, so there are no further corrections from the scalar potential.

The remaining interaction arises from the interaction with the vector potential. With the magnetic dipole moment of the proton $\vec{\mu}_I$, the vector potential can be written as

$$\hat{\boldsymbol{A}}_I(\vec{r}) = \frac{\mu_0}{4\pi}\frac{\vec{\mu}_I \times \vec{r}}{r^3}, \tag{6.52}$$

where μ_0 is the magnetic permeability of vacuum. We treat the vector potential as a small correction term to the Hamiltonian. Then, the first-order terms on $\hat{\boldsymbol{A}}_I(\vec{r})$ gives

$$\hat{H}_{\text{hf}} = -\frac{q}{2m_e}(\hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{A}}_I + \hat{\boldsymbol{A}}_I\cdot\hat{\boldsymbol{p}}) - 2\mu_B\left(\frac{\hat{\boldsymbol{S}}}{\hbar}\right)\cdot[\nabla \times \hat{\boldsymbol{A}}_I(\vec{r})]. \tag{6.53}$$

The first two terms denote the interaction of the electron's orbital angular momentum with the nuclear spin, while the third term describes the interaction of the electron spin and the nuclear spin. Using the expression Eq. 6.52 for the vector potential, we note that

$$\hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{A}}_I + \hat{\boldsymbol{A}}_I\cdot\hat{\boldsymbol{p}} = \frac{\mu_0}{4\pi}\left[\hat{\boldsymbol{p}}\cdot(\vec{\mu}_I \times \vec{r})\frac{1}{r^3} + \frac{1}{r^3}(\vec{\mu}_I \times \vec{r})\cdot\hat{\boldsymbol{p}}\right]. \tag{6.54}$$

Using the cyclic property $\vec{A}\cdot(\vec{B}\times\vec{C}) = \vec{B}\cdot(\vec{C}\times\vec{A})$, the definition $\hat{\boldsymbol{L}} = \vec{r}\times\hat{\boldsymbol{p}}$ and noting that $[\hat{\boldsymbol{L}}, 1/r^3] = 0$, the Hamiltonian corresponding to these terms reduce to

$$-\frac{q}{2m_e}(\hat{\boldsymbol{p}}\cdot\hat{\boldsymbol{A}}_I + \hat{\boldsymbol{A}}_I\cdot\hat{\boldsymbol{p}}) = -\frac{\mu_0}{4\pi}\frac{q}{2m_e}\frac{2\vec{\mu}_I \times \hat{\boldsymbol{L}}}{r^3} \equiv -\vec{\mu}_I\cdot\vec{B}_{\text{eff}}, \tag{6.55}$$

where it describes the magnetic interaction between the nuclear magnetic moment $\vec{\mu}_I$ and the effective magnetic field $\vec{B}_{\text{eff}} = \frac{\mu_0}{4\pi}\frac{q\hat{\boldsymbol{L}}}{m_e r^3}$ created by the orbiting electrons felt by the nucleus.

The third term in Eq. 6.53 is given by considering the magnetic dipole field generated by the proton spin oriented along the $\hat{z}$-direction ($\vec{\mu}_I = \mu_I\hat{z}$), at the location of the electron

$$\vec{B}_{\text{dip}}(\vec{r}) = \frac{\mu_0}{4\pi r^3}[3(\vec{\mu}_I \cdot \hat{r})\hat{r} - \vec{\mu}_I] = \frac{\mu_0\mu_I}{4\pi r^3}\left[\frac{3z(x\hat{x} + y\hat{y} + z\hat{z}) - r^2\hat{z}}{r^2}\right]. \tag{6.56}$$

The third term in Eq. 6.53, which we term the dipole term, is then given by

$$\hat{H}_{\text{hf}}^{\text{dip}} = -\frac{\mu_0}{4\pi}\frac{2\mu_B}{\hbar r^3}\left[3(\vec{\mu}_I \cdot \hat{r})(\hat{\boldsymbol{S}} \cdot \hat{r}) - \hat{\boldsymbol{S}} \cdot \vec{\mu}_I\right]. \tag{6.57}$$

If we consider the average value of this dipole term over the atomic state $\langle nlmm_s|\hat{H}_{\text{hf}}^{\text{dip}}|nlmm_s\rangle$ near the origin $r = 0$, the radial integral is given by

$$\int_0^\infty r^l r^l \frac{1}{r^3} r^2 dr = \frac{1}{2l-1}\left[r^{2l}\right]_0^\infty. \tag{6.58}$$

This term is identically zero when $2l \geq 2$, or when $l \geq 1$. For the wavefunctions with $l = 0$, the electronic wavefunction given by Eq. 2.47 is constant near $r = 0$. Therefore, the integral very close to the origin $(r \leq \rho_0)$ becomes

$$\iint_{r\leq\rho_0} d^3 r \psi_{nlm}^* \psi_{nlm} \sim \frac{4\pi\rho_0^3}{3}|\psi_{nlm}(0)|^2. \tag{6.59}$$

The dipole Hamiltonian term near $r = 0$ integrates to a constant value in this case, known as the "contact term"

$$W_{\text{hf}}^c = -\frac{\mu_0}{4\pi}\frac{8\pi}{3}\vec{\mu}_I \cdot \left(\frac{2\mu_B\hat{\boldsymbol{S}}}{\hbar}\right)\delta(\vec{r}). \tag{6.60}$$

This contact term exists only for the atomic orbitals satisfying $l = 0$. Therefore, the final form of the Hamiltonian describing the hyperfine interaction becomes

$$\hat{H}_{\text{hf}} = -\frac{\mu_0}{4\pi}\frac{2g_p\mu_B\mu_N}{\hbar^2}\left[\frac{\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{L}}}{r^3} + 3\frac{(\hat{\boldsymbol{I}}\cdot\hat{r})(\hat{\boldsymbol{S}}\cdot\hat{r})}{r^3} - \frac{\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{S}}}{r^3} + \frac{8\pi}{3}\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{S}}\delta(\vec{r})\right] \tag{6.61}$$

The first term denotes the interaction between the nuclear magnetic moment with the magnetic field created at the location of the nucleus by the orbital motion of the electron. The second and the third term denote the dipole-dipole interaction between the electron and nuclear magnetic moments when the electron is away from the location of the nucleus. The final term, often called "Fermi's contact term" arises from the singularity of the magnetic field created by the nuclear magnetic moment at the origin $r = 0$. This term describes the interaction of the magnetic moment of the electron spin with the magnetic field inside the proton, and is non-zero only when the electron wavefunction has a non-zero value at the origin (corresponding to the cases where the orbital angular momentum of the electron $l = 0$).

The order-of-magnitude of the hyperfine interaction is given by

$$E_{\text{hf}} \sim \frac{\mu_0}{4\pi}\frac{2g_p\mu_B\mu_N}{\hbar^2 r^3}\hbar^2 \sim \frac{\mu_0}{4\pi}2\cdot2\cdot2.79\frac{q\hbar}{2m_e}\frac{q\hbar}{2M_p} \sim \frac{e^2\hbar^2}{m_eM_pc^2r^3}, \tag{6.62}$$

where we used $\mu_0 = 1/\varepsilon_0 c^2$ and $e^2 = q^2/4\pi\varepsilon_0$. The order-of-magnitude for the fine structure is given by

$$E_{\text{f}} \sim \alpha^2\mathbb{R} \sim \frac{e^4}{\hbar^2 c^2}\frac{\hbar^2}{2m_e a_0^2} \sim \frac{e^2\hbar^2}{2m_e^2 c^2 a_0^3}, \tag{6.63}$$

where we used the definition of the Bohr radius $a_0 = \hbar^2/m_e e^2$. Given that the distance between the electron and the nucleus $r \sim a_0$ for the hydrogen atom, the ratio of the two

terms is given by $E_{\text{hf}}/E_{\text{f}} \sim m_e/M_p \sim 1/2,000$, so the hyperfine structure has energy scale about three orders of magnitude smaller than that of the fine structure. One can also check that the Fermi's contact term is about three orders of magnitude smaller than the Darwin term, which has the same order-of-magnitude energy as the fine structure splitting.

In the event the nuclear spin I is larger than $1/2$, there will be higher order multipole expansion. This will lead to higher order electric and magnetic moments from the nucleus, that that will result in further corrections for the orbital variable (for the case of electric moment) and orbital and spin variables (for the case of magnetic moment). The hyperfine structure can get quite complicated for nucleus with complex spin I.

6.3.2   Hyperfine structure of the hydrogen ground state

For the ground state of a hydrogen atom ($|n, l, m\rangle = |1, 0, 0\rangle$ state), the spin-orbit coupling does not lead to an energy splitting. The relativistic correction term (Eq. 4.36) and the Darwin term (Eq. 4.39) leads to an energy shift, corresponding to the values

$$\langle \hat{H}_{rc} \rangle = -\frac{5}{4}\mathbb{R}\alpha^2 = -\frac{5}{8}\mu c^2 \alpha^4, \tag{6.64}$$

$$\langle \hat{H}_D \rangle = \frac{\pi e^2 \hbar^2}{2\mu^2 c^2}|\psi(0)|^2 = \frac{1}{2}\mu c^2 \alpha^4, \tag{6.65}$$

where μ is the reduced mass of the electron, α is the fine structure constant, and we used Eq. 2.50 to evaluate $\psi(0)$. The total energy shift of the ground state due to these two effects is $-\mu c^2 \alpha^4/8$. However, the fine structure interaction does not provide any further structure to the ground state of the hydrogen atom.

The possible basis states of the ground state of the hydrogen atom when electron and nucleus spin are included are $\{|n = 1, l = 0, m = 0, m_s = \pm 1/2, m_I = \pm 1/2\rangle\}$. The hyperfine interaction between the nuclear spin and the electron spin is given by Eq. 6.61. We consider the contribution of each term in this hyperfine Hamiltonian.

We can easily see that the first term is zero for the ground state, since it is proportional to $\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{L}}$, and $\langle l = 0, m = 0|\hat{\boldsymbol{L}}|l = 0, m = 0\rangle = 0$ because $l = 0$.

The second and third term (dipole-dipole interaction term) also averages to zero because the electron wavefunction is spherically symmetric around the nucleus. The the explicit algebra showing this is a bit complicated but relatively straightforward. We consider the case where nuclear spin is aligned along the z-axis, and use spherical coordinates (r, θ, φ) to describe the location of the electron. In this case, we note that

$$\hat{\boldsymbol{I}} \cdot \hat{r} = \hat{I}_z \cos\theta + \sin\theta(\hat{I}_x \cos\varphi + \hat{I}_y \sin\varphi) \tag{6.66}$$

$$= \hat{I}_z \cos\theta + \frac{1}{2}\sin\theta(\hat{I}_+ e^{-i\varphi} + \hat{I}_- e^{i\varphi}), \tag{6.67}$$

$$\hat{\boldsymbol{S}} \cdot \hat{r} = \hat{S}_z \cos\theta + \frac{1}{2}\sin\theta(\hat{S}_+ e^{-i\varphi} + \hat{S}_- e^{i\varphi}), \tag{6.68}$$

$$\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}} = \hat{I}_z \hat{S}_z + \frac{1}{2}(\hat{I}_+ \hat{S}_- + \hat{I}_- \hat{S}_+). \tag{6.69}$$

Therefore, the dipole-dipole interaction terms are given as the sum of the following terms:

$$\hat{H}_{\mathrm{hf}}^{\mathrm{dip}} = -\frac{\mu_0}{4\pi} \frac{2g_p \mu_B \mu_N}{\hbar^2 r^3} \left[T_0 + T_0' + T_1 + T_{-1} + T_2 + T_{-2} \right], \tag{6.70}$$

where

$$T_0 = (3\cos^2\theta - 1)\hat{I}_z \hat{S}_z \quad \propto \quad Y_2^0(\theta, \varphi) \tag{6.71}$$

$$T_0' = \left[\frac{3}{4}\sin^2\theta - \frac{1}{2} \right] (\hat{I}_+ \hat{S}_- + \hat{I}_- \hat{S}_+)$$

$$= -\frac{1}{4}(3\cos^2\theta - 1)(\hat{I}_+ \hat{S}_- + \hat{I}_- \hat{S}_+) \quad \propto \quad Y_2^0(\theta, \varphi) \tag{6.72}$$

$$T_1 = \frac{3}{2}\sin\theta\cos\theta e^{i\varphi}(\hat{I}_z \hat{S}_- + \hat{I}_- \hat{S}_z) \quad \propto \quad Y_2^1(\theta, \varphi) \tag{6.73}$$

$$T_{-1} = \frac{3}{2}\sin\theta\cos\theta e^{-i\varphi}(\hat{I}_z \hat{S}_+ + \hat{I}_+ \hat{S}_z) \quad \propto \quad Y_2^{-1}(\theta, \varphi) \tag{6.74}$$

$$T_2 = \frac{3}{4}\sin^2\theta e^{2i\varphi}\hat{I}_- \hat{S}_- \quad \propto \quad Y_2^2(\theta\varphi) \tag{6.75}$$

$$T_{-2} = \frac{3}{4}\sin^2\theta e^{-2i\varphi}\hat{I}_+ \hat{S}_+ \quad \propto \quad Y_2^{-2}(\theta\varphi). \tag{6.76}$$

We note that each of these terms is proportional to a spherical harmonic with $l = 2$. Therefore, the expectation value for each of these terms for the ground state wavefunction is proportional to

$$\int Y_0^{0*}(\theta, \varphi) Y_2^m(\theta, \varphi) Y_0^0(\theta, \varphi) d\Omega \quad \propto \quad \int Y_0^{0*}(\theta, \varphi) Y_2^m(\theta, \varphi) d\Omega = 0, \tag{6.77}$$

since $Y_0^0(\theta, \varphi)$ is constant, and due to the orthonormality of the spherical harmonics.

The final term in the hyperfine interaction (Fermi's contact term) is the only non-zero term in the hyperfine Hamiltonian. This term is evaluated in the basis states as

$$\mathcal{A} \langle m_s', m_I' | \hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}} | m_s, m_I \rangle, \tag{6.78}$$

where the coefficient is given by

$$\mathcal{A} = \frac{g_p e^2}{2m_e M_p c^2} \frac{8\pi}{3} \langle n = 1, l = 0, m = 0 | \delta(\vec{r}) | n = 1, l = 0, m = 0 \rangle$$

$$= \frac{4\pi}{3} \frac{g_p e^2}{m_e M_p c^2} \frac{1}{\pi a_0^3} \int e^{-2r/a_0} \delta(\vec{r}) d^3\vec{r}$$

$$= \frac{4}{3} \frac{g_p e^2}{m_e M_p c^2 a_0^3}$$

$$= \frac{4}{3} g_p \frac{m_e}{M_p} m_e c^2 \alpha^4 \left(1 + \frac{m_e}{M_p} \right)^{-3} \frac{1}{\hbar^2}. \tag{6.79}$$

We note that compared to the fine structure energy scale of $m_e c^2 \alpha^4$, this energy scale is smaller by a factor of $\sim m_e/M_p$. The Fermi's contact term for the hyperfine interaction Hamiltonian is given by $\mathcal{A}\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}}$.

In order to evaluate this Hamiltonian, we should move to a new basis set corresponding to the joint angular momentum of the electron and nuclear spins $\hat{\boldsymbol{F}} = \hat{\boldsymbol{I}} + \hat{\boldsymbol{S}}$. In this basis, the four quantum numbers are $\{s, I, F, m_F\}$, where $s = I = 1/2$, F is 0 or 1, and m_F runs from $-F$ to F in increments of 1. The Fermi's contact term is expressed by

$$\mathcal{A}\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}} = \frac{\mathcal{A}}{2}(\hat{\boldsymbol{F}}^2 - \hat{\boldsymbol{I}}^2 - \hat{\boldsymbol{S}}^2). \tag{6.80}$$

The eigenvalue equation for this operator are

$$\mathcal{A}\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}} |F = 1, m_F\rangle = \frac{\mathcal{A}\hbar^2}{2}\left[2 - \frac{3}{4} - \frac{3}{4}\right]|F = 1, m_F\rangle = \frac{\mathcal{A}\hbar^2}{4}|F = 1, m_F\rangle, \tag{6.81}$$

$$\mathcal{A}\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}} |F = 0, m_F\rangle = \frac{\mathcal{A}\hbar^2}{2}\left[0 - \frac{3}{4} - \frac{3}{4}\right]|F = 0, m_F\rangle = -\frac{3\mathcal{A}\hbar^2}{4}|F = 0, m_F\rangle. \tag{6.82}$$

So, the three $F = 1$ states (corresponding to $M_F = -1$, 0, 1) and the one $F = 0$ states are split in energy by $\mathcal{A}\hbar^2 \sim \frac{4}{3}g_p \frac{m_e}{M_p} m_e c^2 \alpha^4$.

It turns out that the hyperfine splitting of the atomic ground state is very stable. For hydrogen atom, the frequency of this splitting is given by

$$\frac{\mathcal{A}\hbar}{2\pi} = 1\ 420\ 405\ 751.\ 768 \pm 0.001 \text{ Hz}. \tag{6.83}$$

This splitting corresponds to a wave length of 21 cm, and is known as the "21 cm line". It is widely used to study hydeogen atoms in interstellar space. The spontaneous emission between these two levels is known to be negligible, with a lifetime of $\sim 3 \times 10^{15}$s, which is about 10^7 years. The hyperfine splitting of a Cs atom that is perfectly isolated from the environment is used to *define* the second, to be *exactly* 9 192 631 770 Hz.

6.4   The Zeeman Effect

When the atom is subject to an external magnetic field, certain energy levels move depending on the strength of the field. Such dependence of energy levels on external magnetic field is called the *Zeeman* effect. For an external magnetic field applied along the z-axis chosen as the "quantization axis" $\vec{B}_0 = B_0\hat{z}$, the Hamiltonian describing the coupling between the atomic levels and the field is given by

$$\hat{H}_Z = -\vec{B}_0 \cdot (\vec{\mu}_L + \vec{\mu}_S + \vec{\mu}_I) = \omega_0(\hat{L}_z + 2\hat{S}_z) + \omega_n\hat{I}_z, \tag{6.84}$$

where

$$\omega_0 = -\frac{q}{2m_e}B_0, \quad \omega_n = \frac{q}{2M_p}g_pB_0 \tag{6.85}$$

are the Larmor frequency corresponding to the electron and the nucleus, respectively, and $\omega_0 \gg \omega_n$. For the ground state of the hydrogen atom ($n = 1$, and therefore $l = m = 0$), the contribution from $\hat{L}_z$ is zero, so the total Hamiltonian describing the energy levels in the presence of the external magnetic field is given by

$$\hat{H}_{\text{hf}} + \hat{H}_Z = \mathcal{A}\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}} + 2\omega_0\hat{S}_z + \omega_n\hat{I}_z \simeq \mathcal{A}\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{S}} + 2\omega_0\hat{S}_z, \tag{6.86}$$

since $\omega_n \ll \omega_0$.

6.4.1 Weak-field Zeeman effect

When the magnetic field is weak, the energy level shift is small compared to the hyperfine splitting $\hbar\omega_0 \ll \mathcal{A}\hbar^2$. In this limit, we diagonalize the $F = 1$ states and the $F = 0$ state separately, as the magnetic field is not strong enough to create mixing between these two sets of states. The description of two spins is described in Section 4.1.3. The triplet states are given by

$$
\begin{aligned}
|F = 1, m_F = 1\rangle &= |m_I = \tfrac{1}{2}, m_s = \tfrac{1}{2}\rangle, \\
|F = 1, m_F = 0\rangle &= (|m_I = -\tfrac{1}{2}, m_s = \tfrac{1}{2}\rangle + |m_I = \tfrac{1}{2}, m_s = -\tfrac{1}{2}\rangle)/\sqrt{2}, \\
|F = 1, m_F = -1\rangle &= |m_I = -\tfrac{1}{2}, m_s = -\tfrac{1}{2}\rangle,
\end{aligned}
\tag{6.87}
$$

and the singlet state is given by

$$
|F = 0, m_F = 0\rangle = (|m_I = -\tfrac{1}{2}, m_s = \tfrac{1}{2}\rangle - |m_I = \tfrac{1}{2}, m_s = -\tfrac{1}{2}\rangle)/\sqrt{2}.
\tag{6.88}
$$

We note that the application of $\hat{S}_z$ operator on these states yields

$$
\hat{S}_z |F = 1, m_F = 1\rangle = \frac{\hbar}{2} |F = 1, m_F = 1\rangle,
\tag{6.89}
$$

$$
\hat{S}_z |F = 1, m_F = 0\rangle = \frac{\hbar}{2} |F = 0, m_F = 0\rangle,
\tag{6.90}
$$

$$
\hat{S}_z |F = 1, m_F = -1\rangle = -\frac{\hbar}{2} |F = 1, m_F = -1\rangle,
\tag{6.91}
$$

$$
\hat{S}_z |F = 0, m_F = 0\rangle = \frac{\hbar}{2} |F = 1, m_F = 0\rangle.
\tag{6.92}
$$

Since in the weak field limit the states with different F numbers do not mix, we consider projection of the states back into the $F = 1$ and $F = 0$ manifolds. Letting $\hat{P}_i$ be projection operators onto the $F = i$ states ($i = 0,\ 1$), we note that $\hat{P}_1 \hat{S}_z \hat{P}_1 = \frac{1}{2} \hat{P}_1 \hat{F}_z \hat{P}_1$. For the states in $F = 1$ and $F = 0$, the application of the Zeeman Hamiltonian $2\omega_0 \hat{S}_z$ would therefor yield energy eigenvalues of

$$
|F = 1, m_F = 1\rangle \leftrightarrow \frac{\mathcal{A}\hbar^2}{4} + \hbar\omega_0
\tag{6.93}
$$

$$
|F = 1, m_F = 0\rangle \leftrightarrow \frac{\mathcal{A}\hbar^2}{4}
\tag{6.94}
$$

$$
|F = 1, m_F = -1\rangle \leftrightarrow \frac{\mathcal{A}\hbar^2}{4} - \hbar\omega_0
\tag{6.95}
$$

$$
|F = 0, m_F = 0\rangle \leftrightarrow -\frac{3\mathcal{A}\hbar^2}{4}
\tag{6.96}
$$

We see that the degeneracy of the three states in $F = 1$ manifold is lifted by the external magnetic field.

6.4.2 Strong-field Zeeman effect

When the magnetic field is very strong so that the Zeeman energy shift is much larger than the hyperfine splitting ($\hbar\omega_0 \gg \mathcal{A}\hbar^2$), then we note that the Zeeman term is diagonal

in the $|m_I, m_s\rangle$ basis, and $2\omega_0\hat{S}_z|m_i, m_s\rangle = 2m_s\hbar\omega_0|m_I, m_s\rangle$. In this case, the hyperfine interaction is considered a perturbation to the electron spin subspaces $|m_I, \frac{1}{2}\rangle$ and $|m_I, -\frac{1}{2}\rangle$, which has Zeeman shifts of $\hbar\omega_0$ and $-\hbar\omega_0$, respectively. The hyperfine perturbation $\mathcal{A}\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{S}} = \frac{\mathcal{A}}{2}(\hat{\boldsymbol{F}}^2 - \hat{\boldsymbol{I}}^2 - \hat{\boldsymbol{S}}^2)$ commutes with $\hat{F}_z$, and therefore each subspace is diagonal in

$$\mathcal{A}\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{S}} = \mathcal{A}\left[\hat{I}_z\hat{S}_z + \frac{1}{2}(\hat{I}_+\hat{S}_- + \hat{I}_-\hat{S}_+)\right]. \tag{6.97}$$

For each subspace with fixed m_s, the only relevant term in this Hamiltonian is $\mathcal{A}\hat{I}_z\hat{S}_z$. The perturbation term is evaluated as

$$\langle m_I, m_s|\mathcal{A}\hat{\boldsymbol{I}}\cdot\hat{\boldsymbol{S}}|m_I m_s\rangle = \langle m_I, m_s|\mathcal{A}\hat{I}_z\hat{S}_z|m_I m_s\rangle = \mathcal{A}\hbar^2 m_I m_s. \tag{6.98}$$

Therefore, in the strong field limit, the eigenstates and the eigenvectors are given by

$$|m_I = 1/2, m_s = 1/2\rangle \quad \leftrightarrow \quad \hbar\omega_0 + \frac{\mathcal{A}\hbar^2}{4} \tag{6.99}$$

$$|m_I = -1/2, m_s = 1/2\rangle \quad \leftrightarrow \quad \hbar\omega_0 - \frac{\mathcal{A}\hbar^2}{4} \tag{6.100}$$

$$|m_I = 1/2, m_s = -1/2\rangle \quad \leftrightarrow \quad -\hbar\omega_0 - \frac{\mathcal{A}\hbar^2}{4} \tag{6.101}$$

$$|m_I = -1/2, m_s = -1/2\rangle \quad \leftrightarrow \quad -\hbar\omega_0 + \frac{\mathcal{A}\hbar^2}{4}. \tag{6.102}$$

6.4.3   Intermediate-field Zeeman effect

We note that the states $|F = 1, m_F = 1\rangle = |m_I = 1/2, m_s = 1/2\rangle$ and $|F = 1, m_F = -1\rangle = |m_I = -1/2, m_s = -1/2\rangle$ are eigenstates of the Hamiltonian for both strong and weak field regimes. We have to diagonalize the remaining states by noting the two equations 6.90 and 6.92. In the space of the two states $|F = 1, m_F = 0\rangle$ and $|F = 0, m_F = 0\rangle$, the matrix corresponding to the total Hamiltonian is given by

$$\begin{pmatrix} \frac{\mathcal{A}\hbar^2}{4} & \hbar\omega_0 \\ \hbar\omega_0 & \frac{\mathcal{A}\hbar^2}{4} \end{pmatrix}. \tag{6.103}$$

Diagonalizing this matrix, the two eigenvalues are given by

$$E = -\frac{\mathcal{A}\hbar^2}{4} \pm \sqrt{\left(\frac{\mathcal{A}\hbar^2}{4}\right)^2 + \hbar^2\omega_0^2}. \tag{6.104}$$

One can readily confirm that these energy levels reduce to the weak- and strong-field Zeeman effect in the appropriate limit.

6.5   Derivation of Fermi's Golden Rule

It is possible to use time-dependent perturbation theory to derive an expected transition rate out of an initial state to a continuum of states due to a weak perturbation. Recall the

explicit result from time-dependent perturbation theory (Eq. 5.66), and renaming our initial state with the subscript i and our final state with the subscript f:

$$i\hbar\frac{d}{dt}b_f(t) = \lambda\sum_i e^{i\omega_{fi}t}\hat{V}_{fi}(t)b_i(t). \qquad (6.105)$$

where the b_n coefficients implicity have λ dependence.

We now consider a constant perturbation where $V_{fi}(t) = V_0$ for $t \geq 0$ and zero otherwise. We will then determine the state at a later time τ. We assume that we start in a particular initial energy eigenstate $|i\rangle$, such that $b_k^{(0)}(0) = \delta_{ik}$. From Eq. 5.68 we then see that $b_k^{(0)}(t) = b_k^{(0)}(0) = \delta_{ik}$. We then insert this into Eq. 5.69 (using $r = 1$ to obtain the λ^1 corrections) to obtain:

$$i\hbar\frac{db_f^{(1)}}{dt} = e^{i\omega_{fi}t}V_0 \qquad (6.106)$$

This expression can be trivially integrated to obtain:

$$b_f^{(1)}(t) = \frac{V_0}{i\hbar}\int_0^t e^{i\omega_{fi}t'}dt' = \frac{2V_0}{i\hbar}e^{i\omega_{fi}t/2}\frac{\sin(\omega_{fi}t/2)}{\omega_{fi}} \qquad (6.107)$$

The probability of being found in the $|f\rangle$ state after some time t is therefore:

$$P_{f\leftarrow i}(t) = |b_f^{(1)}(t)|^2 = \frac{4|V_0|^2}{\hbar^2\omega_{fi}^2}\sin^2(\omega_{fi}t/2) \qquad (6.108)$$

This equation shows that the solution is oscillatory in time. In the frequency domain, however, the function is sharply peaked around $\omega_{fi} = 0$, especially if t is large. In fact we can show that

$$\begin{aligned}
\int_{-\infty}^{\infty} dx\frac{\sin^2(tx/2)}{tx^2} &= \frac{1}{2}\int_{-\infty}^{\infty} d\left(\frac{tx}{2}\right)\frac{\sin^2(tx/2)}{t^2x^2/4} \\
&= \frac{1}{2}\int_{-\infty}^{\infty} d(u)\frac{\sin^2(u)}{u^2} \\
&= \frac{\pi}{2}
\end{aligned} \qquad (6.109)$$

which is independent of t. We also know that, as t increases, this function's peak increases linearly with t, whereas it's width scales as $1/t$. We therefore conclude that:

$$\lim_{t\to\infty}\frac{\sin^2(tx/2)}{tx^2} = \frac{\pi}{2}\delta(x) \qquad (6.110)$$

combining this result with Eq. 6.108, we get:

$$\lim_{t\to\infty}P_{f\leftarrow i}(t) = \frac{2\pi}{\hbar^2}|V_0|^2t\delta(\omega_{fi}) \qquad (6.111)$$

While this may look strange at first glance, we interpret this equation by realizing that we have a constant transition rate multiplied by the interaction time t. The transition rate is then given by:

$$R_{f \leftarrow i} = \frac{1}{t} \lim_{t \to \infty} P_{f \leftarrow i}(t) = \frac{2\pi}{\hbar^2} |V_0|^2 \delta(\omega_{fi}) \tag{6.112}$$

The interaction Hamiltonian usually allows transitions out of the initial state to a number of final states. To obtain the total transition rate out of the initial state we need to sum the transition rate over all the possible final states. We define the density of states $\rho(E)$ such that $\rho(E)dE$ is the number of states whose energy lies in the interval from E to $E + dE$.

$$\Gamma_{f \leftarrow i} = \sum_f R_{f \leftarrow i} \tag{6.113}$$

$$= \int dE_f \rho(E_f) \frac{2\pi}{\hbar^2} |V_0|^2 \delta\left(\frac{E_f - E_i}{\hbar}\right) \tag{6.114}$$

We rescale the delta function using $\delta(x/a) = a\delta(x)$, and perform the integral to obtain:

$$\Gamma_{f \leftarrow i} = \frac{2\pi}{\hbar} \rho(E_f) |\langle f^{(0)} | V | i^{(0)} \rangle|^2 \tag{6.115}$$

which is a famous result known as *Fermi's golden rule*.

6.6 Time-dependent Harmonic Perturbation

Consider now the time-dependent perturbation theory problem of the following Hamiltonian:

$$\hat{V}(t) = \begin{cases} 2\hat{V}' \cos(\omega t) & \text{for } 0 \leq t \leq \tau \\ 0 & \text{otherwise} \end{cases} \tag{6.116}$$

where we assume that $\hat{V}'$ is time-independent, and $\omega \geq 0$. As in Sec. 6.5, we will assume that we are going to start in state $|i^{(0)}\rangle$, such that the $b_k(0) = \delta_{ik}$. The λ^0 does not depend on the perturbation Hamiltonian, and so we again find that $b_k^{(0)}(t) = b_k^{(0)}(0) = \delta_{ik}$. However, for the λ^1 term we now have:

$$i\hbar \frac{d}{dt} b_f^{(1)}(t) = e^{i\omega_{fi} t} 2V_{fi}' \cos(\omega t) \tag{6.117}$$

Writing the cosine term as a sum of complex exponentials, we see that:

$$\frac{d}{dt} b_f^{(1)}(t) = \frac{V_{fi}'}{i\hbar} \left(e^{i(\omega_{fi} + \omega)t} + e^{i(\omega_{fi} - \omega)t} \right) \tag{6.118}$$

Since we are turning on the perturbation for a duration τ, we can integrate this expression to obtain the expression for $b_f^{(1)}(t)$:

$$b_f^{(1)}(\tau) = \frac{V_{fi}'}{i\hbar} \int_0^\tau \left(e^{i(\omega_{fi} + \omega)t} + e^{i(\omega_{fi} - \omega)t} \right) dt$$

$$= -\frac{V_{fi}'}{\hbar} \left[\frac{e^{i(\omega_{fi} + \omega)\tau} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi} - \omega)\tau} - 1}{\omega_{fi} - \omega} \right] \tag{6.119}$$

The two terms on the right-hand side of Eq. 6.119 encapsulate two different physical processes. Note, first of all, that the numerators of both terms are bounded, i.e. their magnitude lies between 0 and 2 at all times and for any frequency. The denominators, however, can be made near-zero. Recall that $\hbar\omega_{fi} = E_f - E_i$, and therefore the first term is largest when $E_f = E_i - \hbar\omega = 0$. In other words, the perturbation causes the system to give $\hbar\omega$ of its energy to the perturbation, lowering its own internal energy. This process is usually referred to as *stimulated emission.* It is stimulated because it would not happen without the perturbation present.

Likewise, the second term in Eq. 6.119 is largest when $E_f = E_i + \hbar\omega$. This process involves the system taking an amount of energy $\hbar\omega$ from the perturbation, increasing its internal energy, in a process known as *absorption.*

It should be clear that if the conditions are such that either absorption or stimulated emission are large, then the other process is strongly suppressed due to the large denominator value. The probability of absorption or stimulated emission can therefore be expressed by only considering the norm squared of the process in question:

$$P_{f\leftarrow i}^{\pm}(\tau) = \frac{4|V_{fi}'|^2}{\hbar^2} \frac{\sin^2[(\omega_{fi} \pm \omega)\tau/2]}{(\omega_{fi} \pm \omega)^2} \tag{6.120}$$

This equation is almost identical to Eq. 6.108, except that now the function is peaked around $\omega_{fi} = \pm\omega$.

6.6.1 Long-time limit

We can again take the delta-function limit, assuming that the perturbation time τ is long enough for the distribution to become sharply peaked, to get a transition rate

$$R_{f\leftarrow i}^{\pm} = \frac{1}{t}\lim_{t\to\infty} P_{f\leftarrow i}^{\pm}(t) = \frac{2\pi}{\hbar^2}|V_{fi}'|^2\delta(\omega_{fi} \pm \omega) \tag{6.121}$$

using the relationship

$$\delta(\omega) = \frac{2}{\pi}\lim_{t\to\infty} \frac{\sin^2(\omega t/2)}{t\omega^2}. \tag{6.122}$$

Summing over all final states gives us a very similar expression for the transition probability out of the initial state:

$$\Gamma_{f\leftarrow i}^{\pm} = \sum_f P_{f\leftarrow i}(\tau) \tag{6.123}$$

$$= \int dE_f \rho(E_f)\frac{2\pi}{\hbar^2}|V_{fi}'|^2\delta\left(\frac{E_f - E_i}{\hbar} \pm \omega\right) \tag{6.124}$$

$$= \frac{2\pi}{\hbar}\rho(E_f = E_i \pm \hbar\omega)|\langle f|V'|i\rangle|^2 \tag{6.125}$$

where the $(+)$ case is for absorption, and the $(-)$ case is for stimulated emission. The only difference with Eq. 6.115 is in the evaluation of the density of states.

6.6.2   Short-time limit

When the interaction time with the perturbative Hamiltonian is short such that $(\omega_{fi} \pm \omega)t \ll 1$, then the numerator in Eq. 6.120 approximates to

$$\sin(\omega_{fi} \pm \omega)\tau \simeq (\omega_{fi} \pm \omega)\tau, \tag{6.126}$$

and therefore, the transition probability reduces to

$$P^{\pm}_{f \leftarrow i}(\tau) = \frac{|V'_{fi}|^2}{\hbar^2}\tau^2. \tag{6.127}$$

The transition rate in this case becomes

$$R^{\pm}_{f \leftarrow i} = \frac{|V'_{fi}|^2}{\hbar^2}t, \tag{6.128}$$

which increases linearly in time t.

6.7   Einstein's Derivation of Planck Radiation Formula

One of the challenges of classical electromagnetic theory in the early 20th century was the Rayleigh-Jeans law, that predicted that the amount of radiation emitted by a black body increases as the frequency increases. This classical model is inconsistent with the physical reality, as it predicts all matter will lose all of its energy by black body radiation. This inconsistency is called the Rayleigh-Jeans catastrophe, or sometimes the ultraviolet catastrophe. The solution to this theoretical problem led to the emergence of Planck's theory of radiation, where the quantization of energy of electromagnetic radiation was introduced, and signals the beginning of the quantum mechanics.

Einstein later derived the Planck's model from the consideration of an optical cavity in thermal equilibrium of two-level atoms, which we briefly discuss here. We consider the decay rate R_{kl} of atoms, from level k to level l, due to spontaneous and stimulated emission process, the former of which is only proportional to the number of atoms N_k in state k and the latter proportional to both the number of atoms in state k and the photon energy density $u(\nu)$;

$$R_{kl} = A_{kl}N_k + B_{kl}u(\nu)N_k \equiv r_{kl}N_k, \tag{6.129}$$

where r_{kl} is the transition probability rate per atom. Similarly, the (stimulated) absorption rate of the atoms is given by

$$R_{lk} = B_{lk}u(\nu)N_l \equiv r_{lk}N_l. \tag{6.130}$$

In thermal equilibrium, the transition probability rate from k to l has to equal the transition probability rate from l to k, i.e., $R_{kl} = R_{lk}$. From this condition and the assumptions of Boltzmann distribution where the the number of atoms goes as $N_k \propto e^{-E_k/e_B T}$ (k_B is the Boltzmann constant and T is the temperature in Kelvin), we get

$$\frac{N_l}{N_k} = \frac{A_{kl} + B_{kl}u(\nu)}{B_{lk}u(\nu)} = e^{(E_k - E_l)/k_B T} = e^{h\nu/k_B T}. \tag{6.131}$$

From this condition, we can solve for the photon energy density as

$$u(\nu) = \frac{A_{kl}}{B_{lk}e^{h\nu/k_BT} - B_{kl}}. \tag{6.132}$$

From perturbation theory, if the interaction Hamiltonian for the dipole transition is given by $\hat{H}' = -\vec{d}\cdot\vec{\mathcal{E}} = -2\vec{d}\cdot\vec{\mathcal{E}}_0\cos\omega t$, the transition probability rate per atom would be given by

$$r_{lk} = \frac{2\pi}{\hbar^2}|\langle l|\vec{\mathcal{E}}_0\cdot\vec{d}|k\rangle|^2\delta(\omega_{kl} - \omega). \tag{6.133}$$

For isotropic electric field (random orientation), which is relevant for atoms in a cavity modeling black body radiation, the ensemble average for arbitrary orientations is given by

$$|\langle\vec{\mathcal{E}}_0\cdot\vec{d}\rangle|^2 = \frac{1}{3}\langle\mathcal{E}_0^2\rangle|d_{lk}|^2, \tag{6.134}$$

where $d_{lk} = \langle l|\vec{d}|k\rangle$ is the average of the dipole moment between the states l and k. If the density of the modes $u(\omega) = \langle\vec{\mathcal{E}}_0\rangle/2\pi$ is introduced, the transition probability rate per atom is reduced to

$$r_{lk} = \frac{4\pi^2}{3\hbar^2}u(\omega)|d_{lk}|^2\delta(\omega_{kl} - \omega) = B_{lk}u(\omega)\delta(\omega_{kl} - \omega), \tag{6.135}$$

from which we deduce that $B_{lk} = \frac{4\pi^2}{3\hbar^2}|\langle l|\vec{d}|k\rangle|^2$. Noting that $|\langle l|\vec{d}|k\rangle|^2 = |\langle k|\vec{d}|l\rangle|^2$, we conclude that $B_{lk} = B_{kl} \equiv B$. Thus, Eq. 6.132 reduces to

$$u(\nu) = \frac{A/B}{e^{h\nu/k_BT} - 1}, \tag{6.136}$$

where we removed the dependence k from A as well for isotropic case. In order to recover the remaining coefficient A/B, we look at the limit $h \to 0$ and make sure it matches the classical Rayleigh-Jeans law for the photon energy density $u_{RJ} = \frac{8\pi\nu^2}{c^3}k_BT$, derived from Maxwell's equations. In this limit, one notes that $\exp(h\nu/k_BT) \simeq 1 + h\nu/k_BT$, and we derive $A/B = 8\pi h\nu^3/c^3$. Therefore, we correctly derive the Planck's expression for the photon energy density

$$u(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_BT} - 1}. \tag{6.137}$$

6.8 Adiabatic Theorem

Adiabatic theorem is a basic principle by which one can understand how a quantum state evolves when subject to a slowly varying Hamiltonian. Consider a case where the perturbation Hamiltonian $\hat{H}'$ is turned on very slowly ("adiabatically"). Mathematically, this is defined by the condition that the rise time t over which the perturbation is turned on is long compared to the difference between any internal energy levels of the unperturbed system, or the frequency ω corresponding to the turn-on timescale satisfies

$$\omega = t^{-1} \ll \omega_{kl}, \tag{6.138}$$

where ωkl indicates the natural frequency differences between energy levels in the unperturbed system.

The core conclusion of the adiabatic theorem is that under these conditions, the energy uncertainty introduced to the quantum system due to the turn-on of the perturbation Hamiltonian is not large enough to induce any meaningful transition of the initial state to a different state, and it remains in the eigenstate of the total Hamiltonian after the perturbation is fully turned on. The adiabatic theorem guarantees that the final state of the quantum system after the adiabatic transition will remain in the corresponding state before the perturbation is turned on. This can be seen by considering the coefficient

$$
\begin{aligned}
c_k(t) &= \frac{1}{i\hbar} \int_{-\infty}^{t} H'_{kl}(t') e^{i\omega_{kl}t'} dt' \\
&= \left[-\frac{1}{\hbar\omega_{kl}} H'_{kl}(t') e^{i\omega_{kl}t'} \right]_{-\infty}^{t} + \frac{1}{\hbar\omega_{kl}} \int_{-\infty}^{t} e^{i\omega_{kl}t'} \frac{\partial}{\partial t} H'_{kl}(t') dt' \\
&= -\frac{1}{\hbar\omega_{kl}} \left[H'_{kl}(t) e^{i\omega_{kl}t} - \int_{-\infty}^{t} e^{i\omega_{kl}t'} \frac{\partial}{\partial t} H'_{kl}(t') dt' \right] \\
&\simeq -\frac{1}{\hbar\omega_{kl}} H'_{kl}(t) e^{i\omega_{kl}t} = -\frac{\langle k|\hat{H}'(t)|l\rangle}{E_k^{(0)} - E_l^{(0)}} e^{i\omega_{kl}t},
\end{aligned}
\tag{6.139}
$$

where, in moving to the final line, we used the adiabatic condition that the time derivative of $H'_{kl}(t)$ is negligible and therefore ignored. The resulting state is given by

$$
\psi(\vec{r}, t) = \psi_l + \sum_{k \neq l} c_k \psi_k,
\tag{6.140}
$$

where ψ_k are the eigenstates of the (time-independent) unperturbed Hamiltonian, and ψ_l is the initial state. Defining $\varphi_k = e^{i\omega_k t}\psi_k$, we note that the final state is given by

$$
\varphi(\vec{r}) = e^{i\omega_l t}\psi(\vec{r}, t) = \varphi_l + \sum_{k \neq l} \frac{H'_{kl}\varphi_k}{E_k^{(0)} - E_l^{(0)}}.
\tag{6.141}
$$

We note that this equation looks almost identical to the first-order solution to the time-independent perturbation theory given in Eq. 5.17, except that this state corresponds to the first-order corrected, l-th eigenstate of the perturbed Hamiltonian $\hat{H}_0 + \hat{H}'(t)$. This indicates that *the system in the l-th eigenstate of an unperturbed Hamiltonian will, at the end of an adiabatic perturbation, be found in the l-th eigenstate of the new Hamiltonian*, in other words, the system "remains in the l-th state." The expectation of the energy is, to first order, given by $E_l = E_l^{(0)} + H'_{ll}(t)$, which is the l-th eigenenergy of the final Hamiltonian $\hat{H}_0 + \hat{H}'(t)$. This is known as the **adiabatic theorem**.

6.8.1   Domain of validity

The approximation in the final line of Eq. 6.139 stems from dropping the second term with respect to the first term in the previous line. This approximation is valid when

$$
\left| \int_0^t e^{i\omega_{kl}t'} \frac{\partial H'_{kl}}{\partial t'} dt' \right| \;\simeq\; \left| \frac{\partial H'_{kl}}{\partial t'} \right| \left| \int_0^t e^{i\omega_{kl}t'} dt' \right|
$$

$$
\simeq\; \left| \frac{2}{\omega_{kl}} \frac{\partial H'_{kl}}{\partial t'} \right| \left| \sin \frac{\omega_{kl}t}{2} \right| \ll |H'_{kl}|, \tag{6.142}
$$

which can be rewritten as

$$
\left| \frac{\partial H'_{kl}}{H'_{kl}} \right| \ll \frac{\partial t}{2}\omega_{kl}, \tag{6.143}
$$

or, equivalently,

$$
|\omega_{kl} H'_{kl}| \gg 2 \left| \frac{\partial H'_{kl}}{\partial t} \right|. \tag{6.144}
$$