Time-Dependent Perturbation Theory
Quantum Mechanics II

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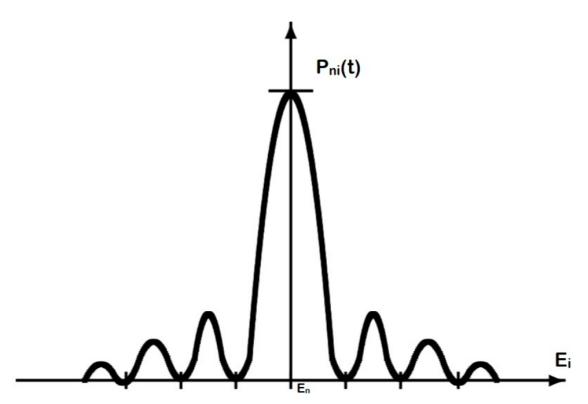


Contents

1 Time-Dependent Hamiltonians

Time-dependent Hamiltonians are essential for studying various physical processes, such as spins in time-dependent magnetic fields and atoms subject to electromagnetic radiation. The Schrödinger equation with time-dependent Hamiltonians is generally harder to solve than its time-independent counterpart.

- **Time Evolution and the Unitary Operator:** For time-dependent Hamiltonians $\hat{H}(t)$, solutions are often written in terms of a unitary operator $\mathcal{U}(t)$ that evolves any physical state over time. However, there is no simple expression for $\mathcal{U}(t)$; it can only be expressed as a formal power series involving nested integrals of time-ordered products of the Hamiltonian $\hat{H}(t)$.

- **Energy Eigenstates and Time Dependence:** A time-dependent $\hat{H}(t)$ does not have energy eigenstates. The existence of energy eigenstates relies on factorization of solutions $\Psi(\mathbf{x}, t)$ into a space-dependent part $\psi(\mathbf{x})$ and a time-dependent part, $e^{-iEt/\hbar}$, with E being the energy. This factorization is only possible for time-independent Hamiltonians. For a time-independent $\hat{H}$:

$$\hat{H}\psi(\mathbf{x}) = E\psi(\mathbf{x})$$

and

$$\Psi(\mathbf{x}, t) = \psi(\mathbf{x})e^{-iEt/\hbar}$$

solves the full Schrödinger equation:

$$i\hbar\partial_t\Psi = \hat{H}\Psi.$$

- **Instantaneous Eigenstates:** For time-dependent Hamiltonians, one might consider instantaneous eigenstates $\psi(\mathbf{x}, t)$, satisfying:

$$\hat{H}(t)\psi(\mathbf{x}, t) = E(t)\psi(\mathbf{x}, t),$$

for each value of t. These states, however, are not solutions to the time-dependent Schrödinger equation:

$$i\hbar\partial_t\Psi(\mathbf{x}, t) = \hat{H}(t)\Psi(\mathbf{x}, t).$$

- **Perturbative Approach:** We study time-dependent Hamiltonians using perturbation theory, assuming the time dependence arises as a perturbation:

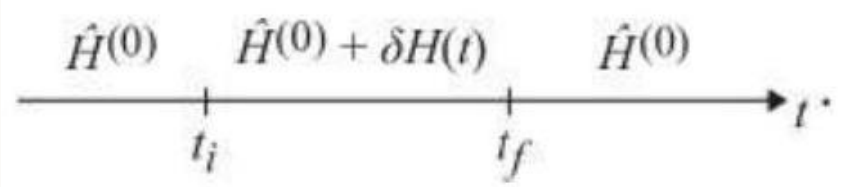
$$\hat{H}(t) = \hat{H}^{(0)} + \delta H(t),$$

where $\hat{H}^{(0)}$ is time-independent and has a well-defined spectrum, while $\delta H(t)$ introduces time dependence.

- **Time Evolution:** The goal is to solve the time-dependent Schrödinger equation (suppress the labels associated with space and other d.o.f.):

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \left(\hat{H}^{(0)} + \delta H(t)\right)|\Psi(t)\rangle.$$

- **Perturbation Timeline:** In many scenarios, $\delta H(t)$ is nonzero only within a finite time interval, as illustrated:



- **Eigenstate Basis:** For $t < t_i$, the system is in an eigenstate or a linear combination of eigenstates of $\hat{H}^{(0)}$. After the perturbation vanishes ($t > t_f$), the system can be described similarly. During the perturbation, eigenstates of $\hat{H}^{(0)}$ provide a complete basis for expressing the time-dependent state.

- **Physical Questions:** Time-dependent perturbation theory helps answer questions about transitions between eigenstates. For instance, consider a hydrogen atom initially in its ground state. An electromagnetic field is applied for a finite time interval. Time-dependent perturbation theory can determine the probabilities of finding the atom in various excited states after the perturbation ends.

2 The Interaction Picture

In order to solve efficiently for the state $|\Psi(t)\rangle$, we introduce the interaction picture of quantum mechanics. This picture combines elements of the Heisenberg and Schrödinger pictures. We use the known Hamiltonian $\hat{H}^{(0)}$ to define Heisenberg operators, and the perturbation δH to write a Schrödinger equation.

- **Time Evolution in the Heisenberg Picture:** For any Hamiltonian, the unitary operator $\mathcal{U}(t)$ generates time evolution:

$$|\Psi(t)\rangle = \mathcal{U}(t)|\Psi(0)\rangle.$$

The Heisenberg operator $\hat{A}_H$ corresponding to a Schrödinger operator $\hat{A}_S$ is defined through expectation values:

$$\langle\Psi(t)|\hat{A}_S|\Psi(t)\rangle = \langle\Psi(0)|\mathcal{U}^\dagger(t)\hat{A}_S\mathcal{U}(t)|\Psi(0)\rangle = \langle\Psi(0)|\hat{A}_H|\Psi(0)\rangle,$$

where:

$$\hat{A}_H \equiv \mathcal{U}^\dagger(t)\hat{A}_S\mathcal{U}(t).$$

- **Unitary Operator Properties:** The operator $\mathcal{U}^\dagger$ "brings states to rest":

$$\mathcal{U}^\dagger(t)|\Psi(t)\rangle = |\Psi(0)\rangle.$$

For the time-independent Hamiltonian $\hat{H}^{(0)}$, the unitary time evolution operator is:

$$\mathcal{U}_0(t) = e^{-i\hat{H}^{(0)}t/\hbar}.$$

- **Auxiliary State Definition:** To simplify the evolution problem, define the auxiliary state:

$$|\widetilde{\Psi}(t)\rangle \equiv e^{i\hat{H}^{(0)}t/\hbar}|\Psi(t)\rangle. \tag{1}$$

This auxiliary state removes the time dependence generated by $\hat{H}^{(0)}$. If $\delta H = 0$, then $|\widetilde{\Psi}(t)\rangle$ is constant. The original state can be recovered:

$$|\Psi(t)\rangle = e^{-i\hat{H}^{(0)}t/\hbar}|\widetilde{\Psi}(t)\rangle.$$

- **Initial Condition:** At $t = 0$, the auxiliary state agrees with the original state:

$$|\widetilde{\Psi}(0)\rangle = |\Psi(0)\rangle.$$

- **Schrödinger Equation in the Interaction Picture:** Differentiating the auxiliary state equation (1) and using the Schrödinger equation for $|\Psi(t)\rangle$:

$$\begin{aligned} i\hbar\frac{d}{dt}|\widetilde{\Psi}(t)\rangle &= -\hat{H}^{(0)}|\widetilde{\Psi}(t)\rangle + e^{i\hat{H}^{(0)}t/\hbar}\left(\hat{H}^{(0)}+\delta H(t)\right)|\Psi(t)\rangle \\ &= \left[-\hat{H}^{(0)} + e^{i\hat{H}^{(0)}t/\hbar}\left(\hat{H}^{(0)}+\delta H(t)\right)e^{-i\hat{H}^{(0)}t/\hbar}\right]|\widetilde{\Psi}(t)\rangle \\ &= e^{i\hat{H}^{(0)}t/\hbar}\delta H(t)e^{-i\hat{H}^{(0)}t/\hbar}|\widetilde{\Psi}(t)\rangle, \end{aligned}$$

  where terms involving $\hat{H}^{(0)}$ cancel. Thus:

$$i\hbar\frac{d}{dt}|\widetilde{\Psi}(t)\rangle = \widetilde{\delta H}(t)|\widetilde{\Psi}(t)\rangle,$$

  where:

$$\widetilde{\delta H}(t) \equiv e^{i\hat{H}^{(0)}t/\hbar}\delta H(t)e^{-i\hat{H}^{(0)}t/\hbar}.$$

- **Interpretation of $\widetilde{\delta H}(t)$:** The operator $\widetilde{\delta H}(t)$ is the Heisenberg version of $\delta H(t)$ with respect to $\hat{H}^{(0)}$. It generates the time evolution of $|\widetilde{\Psi}(t)\rangle$, which is described by a Schrödinger equation.
- **Exact Analysis:** The interaction picture allows us to simplify the Schrödinger equation

under time-dependent perturbations. If $\delta H(t) = 0$, $|\widetilde{\Psi}(t)\rangle$ remains time-independent, as it equals $|\Psi(0)\rangle$.

Example: Nuclear Magnetic Resonance with rotating magnetic field

- The Hamiltonian for a particle with a magnetic moment inside a magnetic field is:

$$\hat{H} = \boldsymbol{\omega} \cdot \hat{\mathbf{S}}$$

  where $\hat{\mathbf{S}}$ is the spin operator, and $\boldsymbol{\omega}$ is the Larmor angular velocity, a function of the magnetic field.

- The unperturbed Hamiltonian is:

$$\hat{H}^{(0)} = \omega_0 S_z = \frac{\hbar}{2}\omega_0 \sigma_z$$

  which corresponds to a magnetic field in the z-direction. In NMR applications, longitudinal magnetic fields are of the order of a tesla, and Larmor frequencies $\omega_0 \approx 100\,\mathrm{MHz}$ are common.

- To this unperturbed Hamiltonian, we add the effect of a magnetic field in the (x, y)-plane, rotating with the Larmor frequency ω_0:

$$\delta H(t) = \Omega \left(\hat{S}_x \cos \omega_0 t + \hat{S}_y \sin \omega_0 t \right)$$

where Ω is another frequency determined by the strength of the rotating magnetic field. This is a specific case of the general NMR problem, where the system is at resonance.

- In the interaction picture, the perturbation $\widetilde{\delta H}(t)$ is defined as:

$$\widetilde{\delta H}(t) = \exp\left[i\omega_0 t\frac{\sigma_z}{2}\right]\Omega\left(\hat{S}_x\cos\omega_0 t + \hat{S}_y\sin\omega_0 t\right)\exp\left[-i\omega_0 t\frac{\sigma_z}{2}\right]$$

- The right-hand side has zero time derivative, and thus (**Exercise**):

$$\widetilde{\delta H}(t) = \Omega\hat{S}_x$$

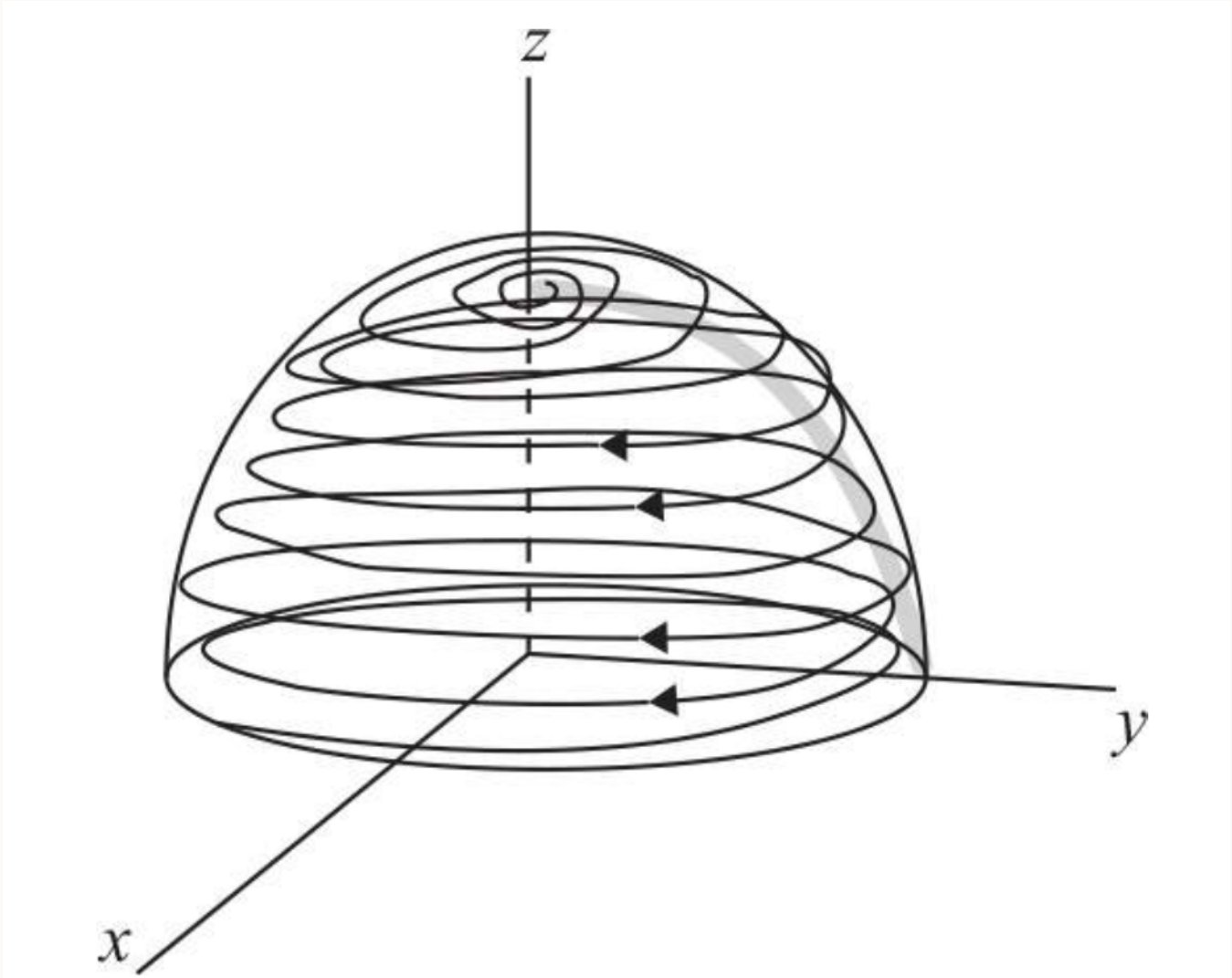
- Since $\widetilde{\delta H}(t)$ is time-independent, the Schrödinger equation for $|\widetilde{\Psi}(t)\rangle$ is:

$$|\widetilde{\Psi}(t)\rangle = \exp\left[-i\frac{\widetilde{\delta H}t}{\hbar}\right]|\widetilde{\Psi}(0)\rangle = \exp\left[-i\Omega t\frac{\sigma_x}{2}\right]|\Psi(0)\rangle$$

- The complete solution for the state evolution is:

$$|\Psi(t)\rangle = \exp\left[-\frac{i\hat{H}^{(0)}t}{\hbar}\right]|\widetilde{\Psi}(t)\rangle = \exp\left[-i\omega_0 t\frac{\sigma_z}{2}\right]\exp\left[-i\Omega t\frac{\sigma_x}{2}\right]|\Psi(0)\rangle$$

- The spin, aligned along $\hat{z}$ at $t = 0$, will move toward the x, y-plane with angular velocity Ω while simultaneously rotating around the z-axis with angular velocity ω_0.


z
y
x

Interaction picture as seen in a basis

- Consider an orthonormal basis $|n\rangle$ for the Hamiltonian $\hat{H}^{(0)}$:

$$\hat{H}^{(0)}|n\rangle = E_n|n\rangle$$

  where the states $|n\rangle$ and their energies E_n remain unperturbed.

- **Ansatz**: The interaction-picture state can be written as:

$$|\widetilde{\Psi}(t)\rangle = \sum_n c_n(t)|n\rangle$$

  where the $c_n(t)$ are time-dependent coefficients.

- The original wavefunction in terms of the interaction picture is:

$$|\Psi(t)\rangle = e^{-i\hat{H}^{(0)}t/\hbar}|\widetilde{\Psi}(t)\rangle = \sum_n c_n(t)e^{-iE_nt/\hbar}|n\rangle$$

- Substituting the ansatz into the interaction picture Schrödinger equation gives:

$$i\hbar\frac{d}{dt}\sum_m c_m(t)|m\rangle = \widetilde{\delta H}(t)\sum_n c_n(t)|n\rangle$$

- Resolving the identity on the right-hand side:

$$\sum_m i\hbar\dot{c}_m(t)|m\rangle = \sum_{m,n} \widetilde{\delta H}_{mn}(t)c_n(t)|m\rangle$$

  where the matrix elements are defined as:

$$\widetilde{\delta H}_{mn}(t) = \langle m|\widetilde{\delta H}(t)|n\rangle$$

- Equating coefficients of $|m\rangle$, the evolution equations for the coefficients are:

$$i\hbar\dot{c}_m(t) = \sum_n \widetilde{\delta H}_{mn}(t)c_n(t)$$

- The matrix elements $\widetilde{\delta H}_{mn}(t)$ in terms of the original variables are:

$$\widetilde{\delta H}_{mn}(t) = e^{i(E_m - E_n)t/\hbar}\langle m|\delta H(t)|n\rangle$$

- Defining the frequency difference:

$$\omega_{mn} \equiv \frac{E_m - E_n}{\hbar}$$

  we write:

$$\widetilde{\delta H}_{mn}(t) = e^{i\omega_{mn}t}\delta H_{mn}(t)$$

- The coupled differential equations for $c_m(t)$ are:

$$i\hbar\dot{c}_m(t) = \sum_n e^{i\omega_{mn}t}\delta H_{mn}(t)c_n(t)$$

- Once the coefficients $c_m(t)$ are determined, the state is given by:

$$|\Psi(t)\rangle = \sum_n c_n(t)e^{-iE_nt/\hbar}|n\rangle$$

- These equations are exact and hold for arbitrary $\delta H(t)$, whether small or large.

Example: Transitions in a two-state system

- Consider a two-state system with basis states $|1\rangle$ and $|2\rangle$, which are eigenstates of $\hat{H}^{(0)}$ with energies E_1 and E_2, respectively. The off-diagonal perturbation $\delta H(t)$ is defined as:

$$\delta H(t) = \begin{pmatrix} 0 & f(t) \\ f^*(t) & 0 \end{pmatrix}$$

  where $f(t)$ is only nonzero for $-T < t < T$ and vanishes for $t \leq -T$ and $t \geq T$.

- An example of the function $f(t)$ is shown in the figure below:

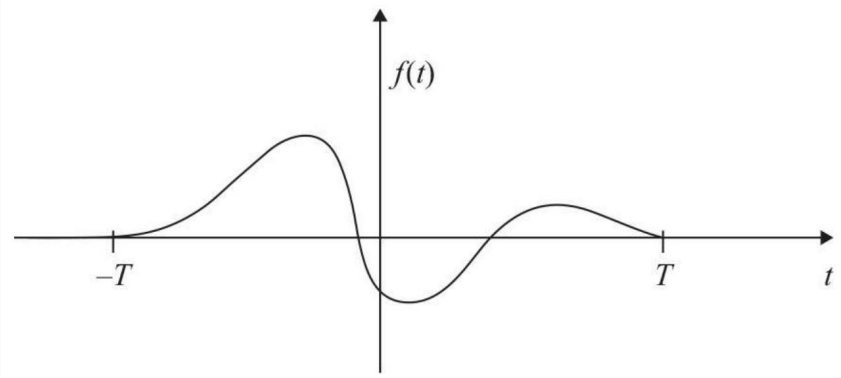


Figure 1: A function $f(t)$ that vanishes for $t > |T|$.

- If the system is in $|1\rangle$ at $t = -\infty$, the state evolves as:

$$|\Psi(t)\rangle = e^{-iE_1 t/\hbar}|1\rangle, \quad \text{for } -\infty < t \leq -T$$

- If the state at $t = T$ is

$$|\Psi(T)\rangle = \gamma_1|1\rangle + \gamma_2|2\rangle$$

with γ_1 and γ_2 constants, then the state for any time $t > T$ will be

$$|\Psi(t)\rangle = \gamma_1|1\rangle e^{-iE_1(t-T)/\hbar} + \gamma_2|2\rangle e^{-iE_2(t-T)/\hbar}$$

and the probability of finding the system in $|2\rangle$ is:

$$p_2(t) = |\langle 2|\Psi(t)\rangle|^2 = |\gamma_2|^2$$

which is time-independent for $t > T$.

- The state during the perturbation interval is written as:

$$|\Psi(t)\rangle = c_1(t)e^{-iE_1 t/\hbar}|1\rangle + c_2(t)e^{-iE_2 t/\hbar}|2\rangle$$

with initial conditions:

$$c_1(-T) = 1, \quad c_2(-T) = 0$$

- The coupled differential equations for the coefficients are:

$$i\hbar\dot{c}_1(t) = e^{i\omega_{12}t}\delta H_{12}(t)c_2(t)$$
$$i\hbar\dot{c}_2(t) = e^{i\omega_{21}t}\delta H_{21}(t)c_1(t)$$

  where $\omega_{12} = -\omega_{21} \equiv (E_1 - E_2)/\hbar$. The couplings are off-diagonal because $\delta H_{11} = \delta H_{22} = 0$. Using the form of the δH matrix elements, we find that

$$i\hbar\dot{c}_1(t) = e^{i\omega_{12}t}f(t)c_2(t)$$

$$i\hbar\dot{c}_2(t) = e^{-i\omega_{12}t}f^*(t)c_1(t)$$

- These equations, along with the initial conditions, determine the solution for $t > -T$. Numerical or perturbative methods may be used to solve them.
- Once the solution is obtained, the probability of finding the state in $|2\rangle$ at $t = \infty$ is:

$$p_2(\infty) = |c_2(T)|^2$$

3 Perturbative Solution in the Interaction Picture

- To develop a perturbative solution to the interaction picture Schrödinger equation:

$$i\hbar\frac{d}{dt}|\widetilde{\Psi}(t)\rangle = \widetilde{\delta H}(t)|\widetilde{\Psi}(t)\rangle$$

- Introduce a small parameter λ to systematically expand the perturbation in the time-dependent Hamiltonian:

$$\hat{H}(t) = \hat{H}^{(0)} + \lambda\delta H(t)$$

- The interaction picture Schrödinger equation becomes:

$$i\hbar\frac{d}{dt}|\widetilde{\Psi}(t)\rangle = \lambda\widetilde{\delta H}(t)|\widetilde{\Psi}(t)\rangle$$

- Expand the state $|\widetilde{\Psi}(t)\rangle$ in powers of λ:

$$|\widetilde{\Psi}(t)\rangle = \left|\widetilde{\Psi}^{(0)}(t)\right\rangle + \lambda\left|\widetilde{\Psi}^{(1)}(t)\right\rangle + \lambda^2\left|\widetilde{\Psi}^{(2)}(t)\right\rangle + \mathcal{O}\left(\lambda^3\right)$$

- Insert the expansion into the Schrödinger equation. Equating terms of like powers of λ,

we get:

$$
\begin{aligned}
i\hbar\partial_t \left|\widetilde{\Psi}^{(0)}(t)\right\rangle &= 0, \\
i\hbar\partial_t \left|\widetilde{\Psi}^{(1)}(t)\right\rangle &= \widetilde{\delta H} \left|\widetilde{\Psi}^{(0)}(t)\right\rangle, \\
i\hbar\partial_t \left|\widetilde{\Psi}^{(2)}(t)\right\rangle &= \widetilde{\delta H} \left|\widetilde{\Psi}^{(1)}(t)\right\rangle, \\
&\vdots = \quad \vdots \\
i\hbar\partial_t \left|\widetilde{\Psi}^{(n+1)}(t)\right\rangle &= \widetilde{\delta H} \left|\widetilde{\Psi}^{(n)}(t)\right\rangle.
\end{aligned}
$$

- The origin of this pattern lies in the explicit λ multiplying the right-hand side of the Schrödinger equation. Thus, the time derivative of the nth-order ket is coupled to the perturbation $\widetilde{\delta H}$ acting on the $(n-1)$th-order ket.
- $|\tilde{\Psi}(t)\rangle$ and $|\Psi(t)\rangle$ agree at $t = 0$:

$$
|\widetilde{\Psi}(0)\rangle = |\Psi(0)\rangle = \left|\widetilde{\Psi}^{(0)}(0)\right\rangle + \lambda \left|\widetilde{\Psi}^{(1)}(0)\right\rangle + \lambda^2 \left|\widetilde{\Psi}^{(2)}(0)\right\rangle + \mathcal{O}(\lambda^3)
$$

- Matching terms for all powers of λ gives:

$$
\left|\widetilde{\Psi}^{(0)}(0)\right\rangle = |\Psi(0)\rangle, \quad \left|\widetilde{\Psi}^{(n)}(0)\right\rangle = 0, \quad n \geq 1
$$

- Solving the first equation in the perturbation series:

$$\left|\widetilde{\Psi}^{(0)}(t)\right\rangle = \left|\widetilde{\Psi}^{(0)}(0)\right\rangle = |\Psi(0)\rangle$$

- For the $\mathcal{O}(\lambda)$ term:

$$i\hbar\partial_t \left|\widetilde{\Psi}^{(1)}(t)\right\rangle = \widetilde{\delta H}(t)|\Psi(0)\rangle$$

- Its solution is:

$$\left|\widetilde{\Psi}^{(1)}(t)\right\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}|\Psi(0)\rangle\, dt'$$

- For the $\mathcal{O}(\lambda^2)$ term:

$$i\hbar\partial_t \left|\widetilde{\Psi}^{(2)}(t)\right\rangle = \widetilde{\delta H}(t) \left|\widetilde{\Psi}^{(1)}(t)\right\rangle$$

- The solution becomes:

$$\left|\widetilde{\Psi}^{(2)}(t)\right\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar} \left|\widetilde{\Psi}^{(1)}(t')\right\rangle\, dt'$$

- Substituting $\left|\widetilde{\Psi}^{(1)}(t')\right\rangle$, the nested integral form is:

$$\left|\widetilde{\Psi}^{(2)}(t)\right\rangle = \int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}\, dt' \int_0^{t'} \frac{\widetilde{\delta H}(t'')}{i\hbar}|\Psi(0)\rangle\, dt''$$

- The complete solution is:

$$|\Psi(t)\rangle = e^{-i\hat{H}^{(0)}t/\hbar}\left(|\Psi(0)\rangle + \left|\widetilde{\Psi}^{(1)}(t)\right\rangle + \left|\widetilde{\Psi}^{(2)}(t)\right\rangle + \cdots\right)$$

- Transition probability $P_{m\leftarrow n}(t)$ from $|n\rangle$ to $|m\rangle$ with $m \neq n$:

$$P_{m\leftarrow n}(t) = |\langle m|\Psi(t)\rangle|^2$$

- Using the perturbative expansion:

$$P_{m\leftarrow n}(t) = \left|\langle m|\left(|\Psi(0)\rangle + \left|\widetilde{\Psi}^{(1)}(t)\right\rangle + \left|\widetilde{\Psi}^{(2)}(t)\right\rangle + \cdots\right)\right|^2$$

- For $m \neq n$, and keeping only the first-order term:

$$P^{(1)}_{m\leftarrow n}(t) = \left|\langle m|\int_0^t \frac{\widetilde{\delta H}(t')}{i\hbar}|n\rangle\, dt'\right|^2 = \left|\int_0^t \frac{\langle m|\widetilde{\delta H}(t')|n\rangle}{i\hbar}\, dt'\right|^2$$

- Recalling the relation between matrix elements of $\widetilde{\delta H}$ and δH:

$$P^{(1)}_{m\leftarrow n}(t) = \left|\int_0^t e^{i\omega_{mn}t'}\frac{\delta H_{mn}(t')}{i\hbar}\, dt'\right|^2, \quad m \neq n$$

- This is the key result for transition probabilities to first order in perturbation theory.

Perturbative solution in a basis

- To describe the state evolution, we use the expansion:

$$|\widetilde{\Psi}(t)\rangle = \sum_n c_n(t)|n\rangle$$

- The initial condition reads:

$$|\Psi(0)\rangle = \sum_n c_n(0)|n\rangle = \left|\widetilde{\Psi}^{(0)}(0)\right\rangle$$

- Writing each order term:

$$\left|\widetilde{\Psi}^{(k)}(t)\right\rangle = \sum_n c_n^{(k)}(t)|n\rangle, \quad k = 0, 1, 2, \ldots$$

- The perturbative expansion of the state:

$$|\widetilde{\Psi}(t)\rangle = \left|\widetilde{\Psi}^{(0)}(t)\right\rangle + \lambda \left|\widetilde{\Psi}^{(1)}(t)\right\rangle + \lambda^2 \left|\widetilde{\Psi}^{(2)}(t)\right\rangle + \mathcal{O}\left(\lambda^3\right)$$

- Coefficients for the expansion:

$$c_n(t) = c_n^{(0)}(t) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \cdots$$

- Since $\left|\widetilde{\Psi}^{(0)}(t)\right\rangle$ is constant:

$$\left|\widetilde{\Psi}^{(0)}(t)\right\rangle = \sum_n c_n^{(0)}(t)|n\rangle = |\Psi(0)\rangle = \sum_n c_n(0)|n\rangle$$

- We conclude:

$$c_n^{(0)}(t) = c_n^{(0)}(0) = c_n(0)$$

- The expansion simplifies:

$$c_n(t) = c_n(0) + \lambda c_n^{(1)}(t) + \lambda^2 c_n^{(2)}(t) + \cdots$$

- For $n \geq 1$, initial conditions give:

$$c_n^{(k)}(0) = 0, \quad k \geq 1$$

- Using the solution for $\left|\widetilde{\Psi}^{(1)}(t)\right\rangle$:

$$\left|\widetilde{\Psi}^{(1)}(t)\right\rangle = \sum_n c_n^{(1)}(t)|n\rangle = \int_0^t \frac{\widetilde{\delta H}\,(t')}{i\hbar} dt' \sum_n c_n(0)|n\rangle$$

- Projecting onto $\langle m|$, we find:

$$c_m^{(1)}(t) = \sum_n \int_0^t \frac{\langle m|\widetilde{\delta H}\left(t'\right)|n\rangle}{i\hbar} c_n(0) dt'$$

- Expressing in terms of δH:

$$c_m^{(1)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'} \frac{\delta H_{mn}\left(t'\right)}{i\hbar} c_n(0)$$

- The probability of being in state $|m\rangle$ at time t:

$$P_m(t) = |\langle m \mid \Psi(t)\rangle|^2 = |\langle m \mid \widetilde{\Psi}(t)\rangle|^2 = |c_m(t)|^2$$

- Using the expansion of $c_m(t)$:

$$P_m(t) = \left|c_m(0) + c_m^{(1)}(t) + \mathcal{O}\left((\delta H)^2\right)\right|^2$$

- If $c_m(0) \neq 0$:

$$P_m(t) = |c_m(0)|^2 + c_m(0)^* c_m^{(1)}(t) + c_m^{(1)}(t)^* c_m(0) + \mathcal{O}\left(\delta H^2\right)$$

- If $c_m(0) = 0$:

$$P_m(t) = \left| c_m^{(1)}(t) \right|^2 + \mathcal{O}\left((\delta H)^3 \right)$$

- This is equivalent to earlier results when $|n\rangle$ is the initial state.

NMR at resonance in perturbation theory

- Consider the case of NMR at resonance, where the rotating magnetic field is treated as a perturbation. The spin-state evolution is obtained to first order in the perturbation.
- In the previous example, we determined the exact solution for the state $|\widetilde{\Psi}(t)\rangle$, given by:

$$|\widetilde{\Psi}(t)\rangle = \exp\left[-\frac{i}{\hbar}\Omega\hat{S}_x t\right]|\Psi(0)\rangle = \exp\left[-i\Omega t\frac{\sigma_x}{2}\right]|\Psi(0)\rangle$$

- To check consistency with first-order perturbation theory, we use:

$$\left|\widetilde{\Psi}^{(1)}(t)\right\rangle = \int_0^t \frac{\widetilde{\delta H}\,(t')}{i\hbar}|\Psi(0)\rangle dt'$$

- Substituting $\widetilde{\delta H}(t) = \Omega\hat{S}_x$, we compute:

$$\left|\widetilde{\Psi}^{(1)}(t)\right\rangle = -\frac{i}{\hbar}\Omega t\hat{S}_x|\Psi(0)\rangle = -i\Omega t\frac{\sigma_x}{2}|\Psi(0)\rangle$$

- This result corresponds to the first nontrivial term in the Taylor expansion of the exact solution:

$$|\widetilde{\Psi}(t)\rangle = \exp\left[-i\Omega t\frac{\sigma_x}{2}\right]|\Psi(0)\rangle$$

- The first-order result is an accurate description of the system for short times, where $\Omega t \ll 1$. However, for arbitrarily long times, this approximation becomes less reliable.

4 Constant Perturbations

- Consider a constant perturbation, where the Hamiltonian is time-independent, but we use time-dependent perturbation theory for analysis. The perturbed Hamiltonian is given by:

$$\hat{H} = \hat{H}^{(0)} + V$$

- Assuming the initial state at $t = 0$ is an eigenstate of $\hat{H}^{(0)}$, the effect of the perturbation V at a later time t_0 can be studied using first-order time-dependent perturbation theory. The transition amplitude to first order is:

$$c_m^{(1)}(t) = \sum_n \int_0^t dt' e^{i\omega_{mn}t'} \frac{V_{mn}}{i\hbar} c_n(0)$$

- Representing the initial state $|i\rangle$ at $t = 0$, with $c_n(0) = \delta_{n,i}$, the transition amplitude to a final state $|f\rangle$ at $t = t_0$ is:

$$\begin{aligned} c_f^{(1)}(t_0) &= \frac{1}{i\hbar} \int_0^{t_0} V_{fi} e^{i\omega_{fi}t'} dt' \\ &= \frac{V_{fi}}{E_f - E_i} \left(1 - e^{i\omega_{fi}t_0}\right) = \frac{V_{fi} e^{i\omega_{fi}t_0/2}}{E_f - E_i} (-2i) \sin\left(\frac{\omega_{fi}t_0}{2}\right) \end{aligned} \tag{2}$$

- The transition probability from $|i\rangle$ at $t = 0$ to $|f\rangle$ at $t = t_0$ is:

$$P_{f\leftarrow i}(t_0) = \frac{|V_{fi}|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega_{fi} t_0}{2}\right)}{\left(\frac{E_f - E_i}{2\hbar}\right)^2}$$

- This result is expected to be accurate as long as $P_{f\leftarrow i}(t_0) \ll 1$. For large probabilities, higher-order corrections must be considered.
- The transition probability can also be expressed as:

$$P_{f\leftarrow i}(t_0) = \frac{|V_{fi}|^2}{\hbar^2} F(\omega_{fi}; t_0) \tag{3}$$

  where $F(\omega; t)$ is defined as:

$$F(\omega; t) = \frac{\sin^2\left(\frac{\omega t}{2}\right)}{\left(\frac{\omega}{2}\right)^2}$$

- In the limit $\omega \to 0$, the function $F(\omega; t)$ behaves as:

$$\lim_{\omega \to 0} F(\omega; t) = t^2$$

- A plot of $F(\omega; t)$ as a function of ω for a fixed t shows a central lobe and smaller side lobes. The width of the main lobe, denoted $(\Delta\omega)_t$, is defined as the distance between the

two nearest zeroes and is given by:

$$(\Delta\omega)_t = \frac{4\pi}{t}$$

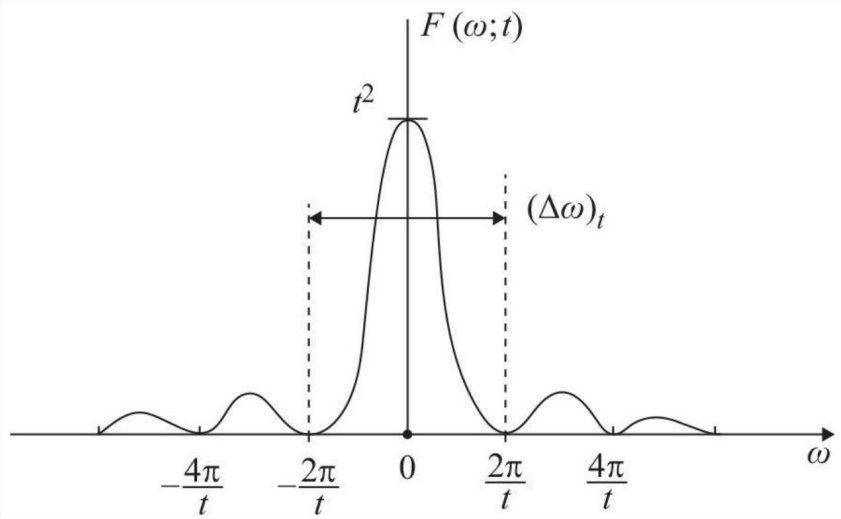


Figure 2: Plot of $F(\omega; t)$ as a function of ω for a fixed t. The function features a central lobe and smaller side lobes. As t grows, the width of the main lobe decreases as $1/t$, while the peak value at $\omega = 0$ grows as t^2.

- The function $F(\omega; t)$ is suppressed for $|\omega| > (\Delta\omega)_t$, meaning that transitions are most likely within the main lobe.

- To understand the main features of the transition probability, we examine its behavior for different values of the final energy E_f.
- If $E_f \neq E_i$, the transition is termed energy nonconserving. This does not contradict energy conservation, as the time-dependent perturbation effectively changes the energy. The energy is supplied or absorbed by the source generating the term V. When V is turned off, the state can be re-expressed as a superposition of $\hat{H}^{(0)}$ eigenstates, allowing a range of energy values.
- If $E_f = E_i$, the transition is energy conserving. Both energy nonconserving and energy conserving transitions are possible and are considered below.

1. $E_f \neq E_i$: The associated transition probability $P_{f\leftarrow i}(t_0)$, given in (3), is shown below. This probability is periodic in t_0 with period $2\pi/\left|\omega_{fi}\right|$. The condition for the first-order transition probability to remain accurate for all times t_0 is:

$$\frac{4\left|V_{fi}\right|^2}{\left(E_f - E_i\right)^2} \ll 1$$

In this case, the amplitude remains small for all times. The amplitude decreases as $\left|E_f - E_i\right|$ increases, indicating that the larger the energy "violation," the smaller the transition probability. This occurs because a perturbation that turns on, remains constant, and then turns off is not an efficient source of energy.

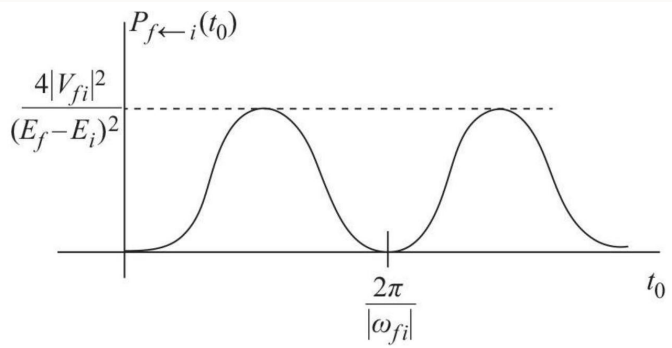


Figure 3: The transition probability $P_{f\leftarrow i}(t_0)$ for constant perturbations, shown as a function of time.

2. $E_f = E_i$: The result for the transition probability in this case is obtained by taking the $\omega_{fi} \to 0$ limit of the probability expression. Using the limit condition for small ω, we find:

$$P_{f\leftarrow i}(t_0)\Big|_{E_f=E_i} = \frac{|V_{fi}|^2}{\hbar^2} t_0^2$$

The probability for energy-conserving transitions grows quadratically in time without bound. However, this result is only valid for small t_0 such that $P_{f\leftarrow i}(t_0) \ll 1$.

3. Note that quadratic growth of $P_{f\leftarrow i}$ is also observed in the energy nonconserving case for small times t_0. Using the earlier probability expression, we have:

$$\lim_{t_0\to 0} P_{f\leftarrow i}(t_0) = \frac{|V_{fi}|^2}{\hbar^2} t_0^2, \quad E_f \neq E_i$$

This behavior can be noted near the origin in the above figure. In this case, the quadratic growth eventually transitions to oscillatory behavior.

5 Harmonic Perturbations

- Having studied the effect of constant perturbations, we now consider truly time-dependent perturbations. A harmonic perturbation is one in which $\delta H(t)$ is periodic in time with some frequency ω. Such a perturbation can efficiently trigger transitions between discrete energy levels separated by an energy approximately equal to $\hbar\omega$.
- The perturbation can cause a transition from the lower to the higher level, where the system absorbs energy from the perturbation. It can also cause a transition from the higher level to the lower level, where the system releases energy to the perturbation. In the latter case, the system does not release the energy spontaneously; it is the perturbation that stimulates the release of the energy.

- For harmonic perturbations, we write

$$\hat{H}(t) = \hat{H}^{(0)} + \delta H(t),$$

where the perturbation $\delta H(t)$ takes the form

$$\delta H(t) = \begin{cases} 0, & \text{for } t \leq 0 \\ 2H' \cos \omega t, & \text{for } t > 0 \end{cases}$$

- Here, by definition,

$$\omega > 0,$$

and H' is some time-independent Hamiltonian. The inclusion of an extra factor of two in the relation between δH and H' is convenient.

- We consider transitions from an initial state $|i\rangle$ with energy E_i to a final state $|f\rangle$ with energy E_f. The transition amplitude follows from

$$c_f^{(1)}(t_0) = \frac{1}{i\hbar} \int_0^{t_0} dt' e^{i\omega_{fi}t'} \delta H_{fi}(t').$$

- Using the explicit form of $\delta H(t)$, the integral can be evaluated:

$$c_f^{(1)}(t_0) = \frac{1}{i\hbar} \int_0^{t_0} e^{i\omega_{fi}t'} 2H'_{fi} \cos \omega t' dt'.$$

- Expanding the cosine, we have:

$$c_f^{(1)}(t_0) = \frac{H'_{fi}}{i\hbar} \int_0^{t_0} \left(e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'} \right) dt'.$$

- Evaluating the integrals, we find:

$$c_f^{(1)}(t_0) = -\frac{H'_{fi}}{\hbar} \left[\frac{e^{i(\omega_{fi}+\omega)t_0} - 1}{\omega_{fi} + \omega} + \frac{e^{i(\omega_{fi}-\omega)t_0} - 1}{\omega_{fi} - \omega} \right].$$

- **Comments:**

1. The amplitude takes the form of a factor multiplying the sum of two terms, each one a fraction. As $t_0 \to 0$, each fraction goes to it_0. For finite t_0, which is our case of interest, each numerator is a complex number of bounded absolute value that oscillates in time from zero up to two. In comparing the two terms, the relevant one is the one with the smallest denominator. This is how we compare any two waves that are superposed: the one with larger amplitude is more relevant, even though at some special times-as it crosses the value of zero, for example-it is smaller than the other wave.
2. The second term is relevant for $\omega_{fi} \simeq \omega$-that is, when $E_f \simeq E_i + \hbar\omega$. Since $\omega > 0$,

we have $E_f > E_i$. Energy is transferred from the perturbation to the system, and we have a process of energy "absorption" in which the system moves to a higher-energy state. This is shown on the left in the figure below.

3. The first term is relevant for $\omega_{f\mathrm{i}} \simeq -\omega$-that is, when $E_f = E_i - \hbar\omega$. Since $\omega > 0$, we have $E_i > E_f$. Here, the system begins on the higher-energy state E_i, and we have a process of stimulated emission in which the source has stimulated the system into a transition that gives away energy $\hbar\omega$. This is shown on the right in figure below.

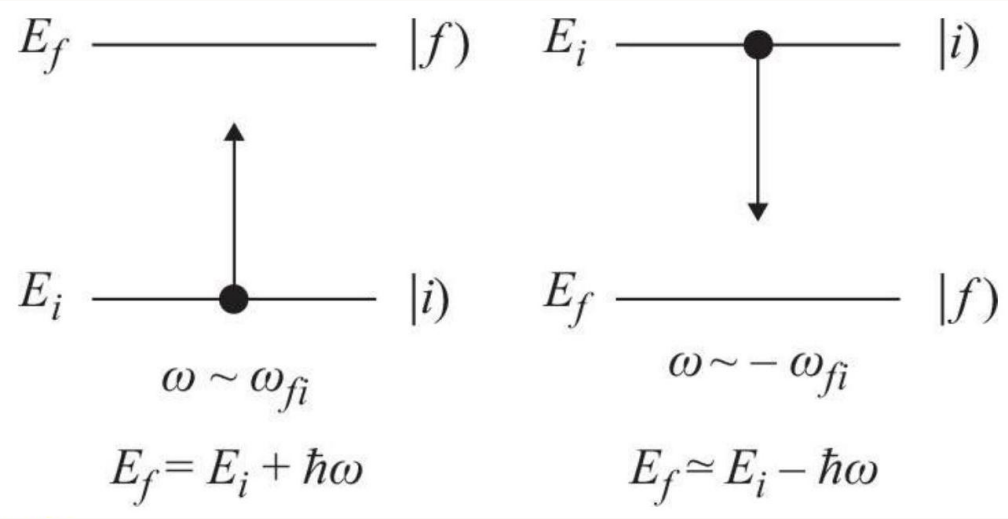


Figure 4: Left: Absorption process in which the source supplies the energy for the transition from the lower-energy state $|i\rangle$ into the higher-energy state $|f\rangle$. Right: Stimulated emission process in which the source stimulates the system to transition from the higher-energy state $|i\rangle$ into the lower-energy state $|f\rangle$ while releasing energy.

- Both absorption and stimulated emission are of interest. Let us do the calculations for the case of absorption; the answer for the case of stimulated emission will be completely analogous. Since $\omega_{fi} \simeq \omega$, the second term in the last line of the equation is much more important than the first as long as

$$|\omega - \omega_{fi}| \ll |\omega_{fi}|$$

Keeping only the second term, we find that

$$c_f^{(1)}(t_0) = -\frac{H'_{fi}}{\hbar} \frac{e^{\frac{i}{2}(\omega_{fi}-\omega)t_0}}{\omega_{fi}-\omega} 2i \sin\left(\frac{\omega_{fi}-\omega}{2} t_0\right),$$

and the transition probability is

$$P_{f\leftarrow i}(\omega; t_0) = \frac{\left|H'_{fi}\right|^2}{\hbar^2} \frac{\sin^2\left(\frac{\omega_{fi}-\omega}{2} t_0\right)}{\left(\frac{\omega_{fi}-\omega}{2}\right)^2}$$

- The transition probability depends on the frequency ω of the perturbation. Note that at this point both E_i and E_f are held fixed. The transition probability is exactly the same as that for constant perturbations with V replaced by H' and ω_{fi} replaced by $\omega_{fi} - \omega$. A sketch of $P_{f-i}(\omega; t)$ as a function of ω is shown below.

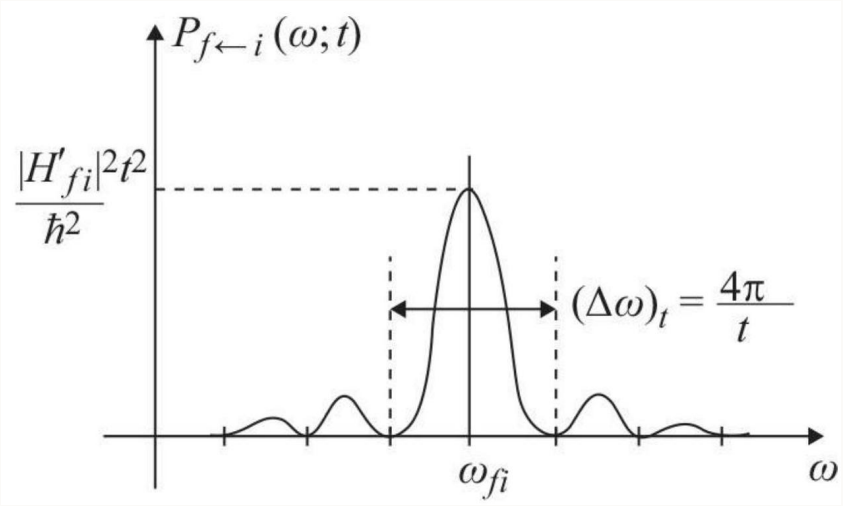


Figure 5: The ω dependence of the transition probability $P_{f-i}(\omega;t)$ from a state $|i\rangle$ of energy E_i at $t=0$ to a state $|f\rangle$ of energy E_f at time t, under a harmonic perturbation with frequency ω. The probability peaks when $\omega = \omega_{fi} = (E_f - E_i)/\hbar$.

- Conditions on t_0 for the above transition probability to be valid:
  1. Consider the neglect of the first wave in the transition amplitude, the term peaking for $\omega_{fi} \simeq -\omega$. That wave, if included, would contribute to $P_{f-i}(\omega;t_0)$ by itself and through interference with the wave we kept. The width $(\Delta\omega)_t$ of the main lobe should

be small compared to the distance $2|\omega_{fi}|$ between the peaks:

$$\frac{4\pi}{t_0} \ll 2|\omega_{fi}|$$

Since $\omega_{fi} \simeq \omega$, we see that

$$t_0 \gg \frac{1}{|\omega_{fi}|} \simeq \frac{1}{\omega}$$

This ensures t_0 includes enough periods of the wave to identify the perturbation as oscillatory.

2. Preventing $P_{f-i}(\omega; t_0)$ from becoming too large: For resonance, $\omega = \omega_{fi}$, the condition

$$P_{f\leftarrow i}(\omega_{fi}; t_0) = \frac{\left|H'_{fi}\right|^2}{\hbar^2} t_0^2 \ll 1$$

gives

$$t_0 \ll \frac{\hbar}{\left|H'_{fi}\right|}$$

- Combining the two conditions on t_0:

$$\frac{1}{|\omega_{fi}|} \ll t_0 \ll \frac{\hbar}{\left|H'_{fi}\right|}$$

For a suitable range of t_0 to exist, the constraint

$$\frac{1}{|\omega_{fi}|} \ll \frac{\hbar}{\left|H'_{fi}\right|} \Rightarrow \left|H'_{fi}\right| \ll \hbar|\omega_{fi}|$$

ensures that the matrix element of the perturbation remains much smaller than the $\hat{H}^{(0)}$ energy separating the two levels.

6 Fermi's Golden Rule

- Consider transitions where the initial state of the system is discrete, but the final state belongs to a continuum. A common example is the ionization of a hydrogen atom: the initial state can be a bound state, while the final state involves a free electron, effectively a momentum eigenstate in a continuum of nonnormalizable states. Such a spectrum is depicted on the left side of the figure below.

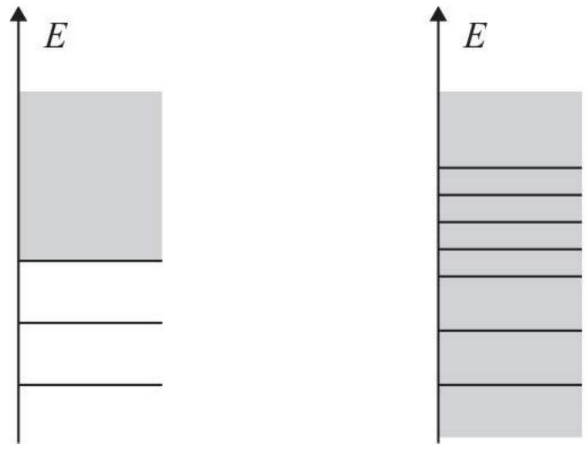


Figure 6: Left: A spectrum with discrete states separate from a continuum. Right: A spectrum in which discrete states are present at energies within the continuum.

- If the final state is in a continuum, the probability of transition from a discrete initial state no longer exhibits periodic time dependence. Instead, an integral over final continuum states is required, resulting in a transition probability that **grows linearly in time**. From this, we can define a **constant transition rate**.
- The transition rate to the continuum is given by **Fermi's golden rule**. For both constant and harmonic perturbations, we know the time-dependent transition probabilities from an initial state with energy E_i to a final state with energy E_f. The next step is to learn how to integrate these probabilities over the continuum of final states.

Continuum States

- To handle continuum states, we consider placing the system in a large cubic box of side L with periodic boundary conditions. Although any boundary conditions would work, periodic ones are simplest. Since physical effects should be insensitive to the distant walls of a very large box, taking $L \to \infty$ removes any influence of the box.
- In this approach, the originally continuous part of the spectrum becomes discrete, with energy levels spaced very closely as L increases. For large L, the box has negligible effect on the discrete part of the spectrum, but the continuum is now represented by a dense set of states.
- For large energies and short-range potentials, momentum eigenstates form a suitable representation of the continuum. Introducing L as a regulator helps us handle infinite quantities like the number of continuum states. At the end of the calculation, L will drop out, ensuring consistency.

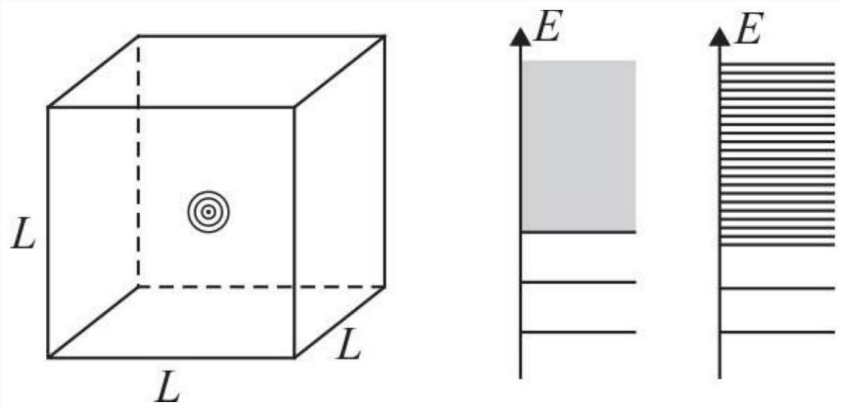


Figure 7: A large cubic box of side L imposes boundary conditions that discretize the continuum states. As $L \to \infty$, the states become densely packed.

- Momentum eigenstates in the box are given by

$$\psi(\mathbf{x}) = \frac{1}{\sqrt{L^3}} e^{ik_x x} e^{ik_y y} e^{ik_z z},$$

with $\mathbf{k} = (k_x, k_y, k_z)$. The normalization is correct since

$$\int_{\text{box}} |\psi(\mathbf{x})|^2 d^3x = \frac{1}{L^3} \int_{\text{box}} d^3x = 1.$$

- Periodic boundary conditions impose

$$\psi(x + L, y, z) = \psi(x, y + L, z) = \psi(x, y, z + L) = \psi(x, y, z),$$

which quantize the components of $\mathbf{k}$:

$$k_x L = 2\pi n_x, \quad k_y L = 2\pi n_y, \quad k_z L = 2\pi n_z.$$

- From these relations, an increment d^3k in momentum space corresponds to $dn_x dn_y dn_z$ in the discrete indices. It follows that

$$dn_x dn_y dn_z = \left(\frac{L}{2\pi}\right)^3 d^3k.$$

- The density of states in momentum space is uniform. Expressing d^3k in spherical coordinates,

$$d^3k = k^2 dk\, d\Omega,$$

where $d\Omega$ is the solid angle element.

- The energy of a free particle is related to k by

$$E = \frac{\hbar^2 k^2}{2m} \implies k dk = \frac{m}{\hbar^2} dE.$$

- Substituting this into d^3k, we get

$$d^3k = k\frac{m}{\hbar^2} dE\, d\Omega.$$

- Thus, the number of states in the energy interval dE and solid angle $d\Omega$ is

$$dN = \left(\frac{L}{2\pi}\right)^3 k\frac{m}{\hbar^2}d\Omega\, dE.$$

- Define the density of states $\rho(E)$ such that $dN = \rho(E)dE$. Then

$$\rho(E) = \left(\frac{L}{2\pi}\right)^3 \frac{m}{\hbar^2}kd\Omega.$$

- For large L, a sum over continuum states can be converted into an integral using this density:

$$\sum_{\text{states}} \to \int \rho(E)dE.$$

- With this formalism, we are ready to integrate over final continuum states when calculating transition amplitudes. We consider the case of constant perturbations, where this approach will be applied.

Constant perturbations

- Recall that the Hamiltonian is $\hat{H}(t) = \hat{H}^{(0)} + V$, with V a constant perturbation. We consider transitions from an initial discrete state $|i\rangle$ with energy E_i into any state $|f\rangle$ in the continuum. The transition probability $P_{f\leftarrow i}(t_0)$ for a single final state f was obtained previously.
- To find the total probability of transitioning into the continuum, we sum over all final continuum states:

$$\sum_f P_{f\leftarrow i}(t_0) = \int P_{f\leftarrow i}(t_0)\rho(E_f)\,dE_f = \int \frac{|V_{fi}|^2}{\hbar^2}\rho(E_f)F(\omega_{fi};t_0)\,dE_f \tag{4}$$

- The function $F(\omega_{fi};t_0)$ is large only for ω_{fi} near zero, corresponding to E_f near E_i. Thus, the integral is dominated by energies close to E_i. Define

$$K(E_f) \equiv |V_{fi}|^2\rho(E_f) \tag{5}$$

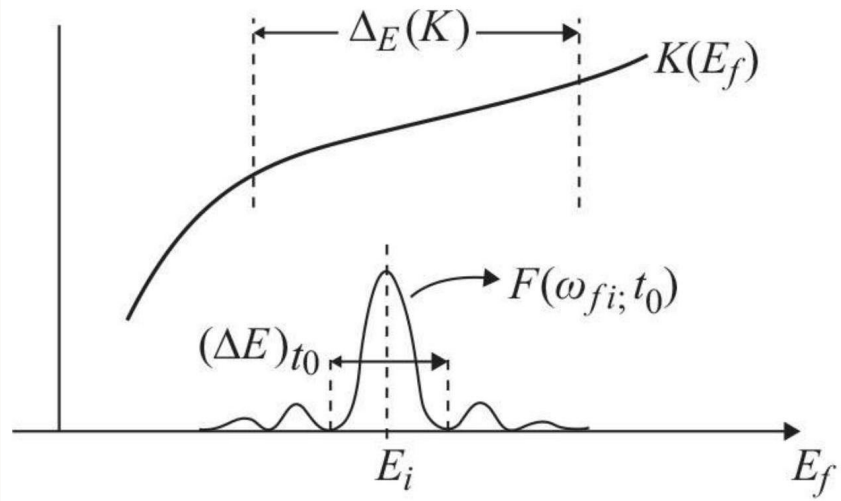


Figure 8: Two plots in one, both functions of the energy E_f. The function $F(\omega_{fi}; t_0)$ has a main lobe centered at E_i of width $(\Delta E)_{t_0}$. The other function is the product $K(E_F) = |V_{fi}|^2 \rho(E_f)$. We indicate the width $\Delta_E(K)$ over which K changes appreciably.

If $K(E_f)$ varies slowly with E_f, we approximate it as nearly constant over the narrow energy range that contributes. Evaluating it at $E_f = E_i$ and taking it out of the integral:

$$\sum_f P_{f\leftarrow i}(t_0) \simeq \frac{|V_{fi}|^2}{\hbar^2}\rho(E_f = E_i)I(t_0) \tag{6}$$

- Consider

$$I(t_0) \equiv \int F(\omega_{fi}; t_0)\, dE_f \tag{7}$$

Since $dE_f = \hbar d\omega_{fi}$, we have

$$I(t_0) = \hbar \int F(\omega_{fi}; t_0)\, d\omega_{fi} \tag{8}$$

- The function $F(\omega_{fi}; t_0) = \frac{\sin^2(\omega_{fi}t_0/2)}{(\omega_{fi}/2)^2}$ is peaked around $\omega_{fi} = 0$. Extending the integral to infinity:

$$I(t_0) = \hbar \int_{-\infty}^{\infty} \frac{\sin^2(\omega_{fi}t_0/2)}{(\omega_{fi}/2)^2}\, d\omega_{fi} \tag{9}$$

Change variables $u = \omega_{fi}t_0/2$:

$$I(t_0) = 2\hbar t_0 \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2}\, du \tag{10}$$

The integral of $\sin^2 u/u^2$ from $-\infty$ to ∞ is π, giving:

$$I(t_0) = 2\pi\hbar t_0 \tag{11}$$

- Substituting $I(t_0)$ back:

$$\sum_f P_{f\leftarrow i}(t) \simeq \frac{|V_{fi}|^2}{\hbar^2}\rho(E_f = E_i)2\pi\hbar t = \frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_f = E_i)t \tag{12}$$

For sufficiently large t, the transition probability grows linearly in time. Defining a transition rate w:

$$w \equiv \frac{1}{t}\sum_f P_{f\leftarrow i}(t) \tag{13}$$

- Thus:

$$w = \frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_f = E_i) \tag{14}$$

This is Fermi's golden rule for constant perturbations.

- Note that $|V_{fi}|^2 \sim L^{-3}$, while $\rho(E) \sim L^3$, so the dependence on the size L of the box cancels out, ensuring a finite, well-defined rate.
- In terms of $K(E)$:

$$w = \frac{2\pi}{\hbar}K(E_i) \tag{15}$$