SCPY 323: Quantum Mechanics II

2nd Semester 2020/2021

Lecture 9: Time-dependent Perturbation Theory Kit Matan

Mahidol University

So far, we have considered a system with a Hamiltonian \mathcal{H} independent of time t. In order to completely solve a problem in quantum mechanics, we need to

- 1. solve an eigenvalue problem for \mathcal{H} ; $\mathcal{H} |\phi_n\rangle = E_n |\phi_n\rangle$,
- 2. expand an initial state $|\psi(0)\rangle$ in terms of eigenstates $|\phi_n\rangle$ of \mathcal{H} ; $|\psi(0)\rangle = \sum_n c_n(0) |\phi_n\rangle$,
- 3. obtain the time-evolution state $|\psi(t)\rangle$;

$$\left|\psi(t)\right\rangle = U(t)\left|\psi(0)\right\rangle = e^{-i\mathcal{H}t/\hbar}\left|\psi(0)\right\rangle = \sum_{n} e^{-iE_{n}t\hbar}c_{n}(0)\left|\phi_{n}\right\rangle$$

In principle, this procedure describes any **closed** quantum mechanical system by making the system "big enough". To one extreme, you can think of the whole universe as a single quantum mechanical state. However, in most cases, we want to describe interactions of a small system with external disturbance. Therefore, we want to isolate the small system described by \mathcal{H}_0 and describe interactions with the environment through V(t), which is time-dependent.

Some examples of systems that interact with the environment.

1. Spin magnetic resonance

A spin-1/2 particle is in a region with time-varying magnetic field, where

$$\vec{B} = B_0 \hat{z} + B_1 \left(\hat{x} \cos \omega t + \hat{y} \sin \omega t \right)$$

We can describe this system using a two-state model, which we will discuss later.

2. Atom in an external electromagnetic radiation field

When an atom is inside an electromagnetic radiation field, electrons in the atom can absorb energy from the field and make transition from a lower-lying state to higher-lying state. On the other hand, the radiation field can induce the emission of photon by electrons in excited states. This phenomenon is called stimulated emission. Therefore, the radiation field can cause either absorption or stimulated emission.

Both of these phenomena can be understood by coupling quantum mechanical systems to a classical electromagnetic field. This approach is, therefore, called a semi-classical approach, since the electromagnetic field is treated classically. We also note that energy of this system is not conserved since the interaction part of the Hamiltonian is time-dependent. Energy would be conserved if we consider a "big enough" system.

There is another type of emission, which is called "spontaneous emission". In order to described the spontaneous emission, we need to quantize the electromagnetic field, which we would need *Quantum Field Theory* that is not covered in this class.

9.1 Time-dependent potential

We will use the interaction picture to describe a system that interacts with the environment. The Hamiltonian of the system is given by

$$\mathcal{H} = \mathcal{H}_0 + V(t),$$

where \mathcal{H}_0 is time-independent and exactly solvable, and V(t) is the time-dependent part and represents the interaction with the environment.

A state in the interaction picture is defined as

$$\left|\psi(t)\right\rangle_{I} = e^{i\mathcal{H}_{0}t/\hbar} \left|\psi(t)\right\rangle_{S},$$

where $\mid \rangle_S$ denotes a state in the Schrödinger picture. We note that

$$\left|\psi(t)\right\rangle_{S} = U(t) \left|\psi(0)\right\rangle = e^{-i\mathcal{H}t/\hbar} \left|\psi(0)\right\rangle.$$

Therefore, if V(t) = 0, then

$$\left|\psi(t)\right\rangle_{I} = \left|\psi(0)\right\rangle,$$

which is a state in the Heisenberg picture. Hence, if V(t) = 0, the interaction picture is the same as the Heisenberg picture. For operators, we can define the operator in the interaction picture as

$$A_I = e^{i\mathcal{H}_0 t/\hbar} A_S e^{-i\mathcal{H}_0 t/\hbar}.$$

Similarly, we can see that if V(t) = 0, then $A_I = A_H$. That is, an operator in the interaction picture is the same as the operator in the Heisenberg picture. We note that for the Heisenberg picture,

$$\left|\psi(t)\right\rangle_{H} = e^{i\mathcal{H}t/\hbar} \left|\psi(t)\right\rangle_{S}$$

and

 $A_H = e^{i\mathcal{H}t/\hbar} A_S e^{-i\mathcal{H}t/\hbar}.$

The difference between the interaction picture and the Heisenberg picture is that for the the interaction picture we use \mathcal{H}_0 but for the Heisenberg picture, \mathcal{H} is used to transform states and operators.

We consider the time evolution of a state in the interaction picture. From the Schrödinger equation, we have

$$\begin{split} i\hbar\frac{\partial}{\partial t} |\psi(t)\rangle_{I} &= i\hbar\frac{\partial}{\partial t} \left(e^{i\mathcal{H}_{0}t/\hbar} |\psi(t)\rangle_{S} \right) \\ &= -\mathcal{H}_{0} e^{i\mathcal{H}_{0}t/\hbar} |\psi(t)\rangle_{S} + e^{i\mathcal{H}_{0}t/\hbar} \left(\mathcal{H}_{0} + V(t)\right) |\psi(t)\rangle_{S} \\ &= e^{i\mathcal{H}_{0}t/\hbar} V(t) |\psi(t)\rangle_{S} \\ &= e^{i\mathcal{H}_{0}t/\hbar} V(t) e^{-i\mathcal{H}_{0}t/\hbar} e^{i\mathcal{H}_{0}t/\hbar} |\psi(t)\rangle_{S} \\ &\Rightarrow \boxed{i\hbar\frac{\partial}{\partial t} |\psi(t)\rangle_{I} = V_{I}(t) |\psi(t)\rangle_{I}} \end{split}$$

We can see that this equation is similar to the Schrödinger equation but we replace \mathcal{H} by $V_I(t)$. Hence, the time evolution of the state in the interaction picture is governed by the interaction potential $V_I(t)$. Using the Schrödinger equation, we can also show that for an operator A,

$$\frac{dA_I}{dt} = \frac{1}{i\hbar} \left[A_I, \mathcal{H}_0 \right] + \left(\dot{A} \right)_I,$$

which is similar to the Heisenberg picture, where

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle_{H} = 0$$

$$\frac{dA_{H}}{dt} = \frac{1}{i\hbar} [A_{H}, \mathcal{H}] + \left(\dot{A}\right)_{H}$$

The interaction picture is between the Schrödinger picture and the Heisenberg picture as illustrated by the table below.

	Heisenberg	Interaction	Schrödinger
state	no change	time-evolved by V_I	time-evolved by \mathcal{H}
observable	time-evolved by \mathcal{H}	time-evolved by \mathcal{H}_0	no change

From this type of system, it is more convenient to solve the Schrödinger equation in the interaction picture by expanding $|\psi(t)\rangle_I$ using a basis of eigenstates of \mathcal{H}_0 . Given that \mathcal{H}_0 is solved

$$\mathcal{H}_0 \left| n \right\rangle = E_n \left| n \right\rangle,$$

we can expand $|\psi(t)\rangle_I$ in terms of $|n\rangle$ as

$$|\psi(t)\rangle_I = \sum_n c_n(t) |n\rangle$$

and rewrite the Schrödinger equation as $(\langle n | \times)$

$$i\hbar \frac{\partial}{\partial t} \underbrace{\langle n|\psi(t)\rangle_{I}}_{c_{n}(t)} = \sum_{m} \underbrace{\langle n|V_{I}|m\rangle}_{\text{matrix element of }V_{I}} \underbrace{\langle m|\psi(t)\rangle_{I}}_{\langle m|\psi(t)\rangle_{I}}$$

$$\Rightarrow i\hbar \dot{c}_{n}(t) = \sum_{m} V_{nm}(t) e^{i(E_{n}-E_{m})t/\hbar} c_{m}(t).$$

For the matrix element of V_I in the $|n\rangle$ basis, we note that

$$\langle n | V_I | m \rangle = \left\langle n \left| e^{i\mathcal{H}_0 t/\hbar} V_S(t) e^{-i\mathcal{H}_0 t/\hbar} \right\rangle \right.$$

$$= e^{iE_n t/\hbar} \cdot e^{-iE_m t/\hbar} \underbrace{\left\langle n \mid V_S(t) \mid m \right\rangle}_{V_{nm}(t)}$$

$$= e^{i(E_n - E_m)t/\hbar} V_{nm}(t).$$

Therefore, we have

$$i\hbar\dot{c}_n(t) = \sum_m V_{nm}(t)e^{i\omega_{nm}t}c_m(t)$$

where $\omega_{nm} = \frac{E_n - E_m}{\hbar} = -\omega_{mn}$. In a matrix form, this equation can be explicitly rewritten as

	$\begin{bmatrix} \dot{c}_1 \end{bmatrix}$		V_{11}	$V_{12}e^{i\omega_{12}t}$	$V_{13}e^{i\omega_{13}t}$		c	1
	\dot{c}_2		$V_{21}e^{i\omega_{21}t}$	V_{22}	$V_{23}e^{i\omega_{23}t}$		c	2
$i\hbar$	\dot{c}_3	=	$V_{31}e^{i\omega_{31}t}$	$V_{32}e^{i\omega_{32}t}$	V_{33}	• • •		3
	:		÷	÷	÷	·		:

Any system that interacts with the environment through V(t), that is governed by the Hamiltonian $\mathcal{H} = \mathcal{H}_0 + V(t)$, can be describes by this equation. However, in general this equation is difficult to solve, especially for a high dimensional Hilbert space. In the next section we will consider one of the simplest problems that is exactly solvable in the interaction picture.

9.2 Two-state system

The two-state problem can be solved exactly. The Hamiltonian for this system can be described by

$$\mathcal{H}_{0} = E_{1} |1\rangle \langle 1| + E_{2} |2\rangle \langle 2|$$

$$V(t) = \gamma e^{i\omega t} |1\rangle \langle 2| + \gamma e^{-i\omega t} |2\rangle \langle 1|$$

In a matrix form, we can rewrite the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + V(t) = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + \begin{bmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{bmatrix}$$

In the interaction picture, the time derivative of the coefficients $c_n(t)$ is described by a set of equations we have derived in the previous section,

$$i\hbar\dot{c}_{1} = \sum_{m=1}^{2} V_{1m}e^{i\omega_{im}t}c_{m}(t) = \gamma e^{i\omega t} \cdot e^{i(E_{1}-E_{2})t/\hbar}c_{2}(t) = \gamma e^{i(\omega-\omega_{21})t}c_{2}(t)$$
$$i\hbar\dot{c}_{2} = \sum_{m=1}^{2} V_{2m}e^{i\omega_{im}t}c_{m}(t) = \gamma e^{-i\omega t} \cdot e^{i(E_{2}-E_{1})t/\hbar}c_{1}(t) = \gamma e^{-i(\omega-\omega_{21})t}c_{1}(t)$$

We have two coupled differential equations, which are solvable. In a matrix form, this equation can be rewritten as

$$\begin{bmatrix} \dot{c}_1 \\ \dot{c}_2 \end{bmatrix} = \gamma \begin{bmatrix} 0 & e^{i(\omega - \omega_{21})t} \\ e^{-i(\omega - \omega_{21})t} & 0 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$$\Rightarrow \quad \frac{dC(t)}{dt} = \gamma \begin{bmatrix} 0 & e^{i(\omega - \omega_{21})t} \\ e^{-i(\omega - \omega_{21})t} & 0 \end{bmatrix} C(t),$$

where $C(t) = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$. This equation is called the Rabi's formula. We will solve these coupled differential equations by taking the derivative and substituting c_2 for c_1 or vice versa.

$$i\hbar\ddot{c}_{1} = i\left(\omega - \omega_{21}\right)\gamma e^{i(\omega - \omega_{21})t/\hbar}c_{2} + \gamma e^{i(\omega - \omega_{21})t/\hbar}\dot{c}_{2}$$
$$= i\left(\omega - \omega_{21}\right)\left(i\hbar\dot{c}_{1}\right) + \gamma e^{i(\omega - \omega_{21})t/\hbar} \cdot \frac{1}{i\hbar}\gamma e^{-i(\omega - \omega_{21})t/\hbar}c_{1}$$
$$\Rightarrow \ddot{c}_{1} = i\left(\omega - \omega_{21}\right)\dot{c}_{1} - \frac{\gamma^{2}}{\hbar^{2}}c_{1}$$

Therefore, the differential equation for c_1 is

$$\ddot{c}_1 - i(\omega - \omega_{21})\dot{c}_1 + \frac{\gamma^2}{\hbar^2}c_1 = 0$$

Similarly, for c_2 we have

$$\ddot{c}_2 + i(\omega - \omega_{21})\dot{c}_2 + \frac{\gamma^2}{\hbar^2}c_2 = 0$$

We can solve both of these equations by considering the characteristic polynomial

$$\lambda^2 - i\left(\omega - \omega_{21}\right)\lambda + \frac{\gamma^2}{\hbar^2} = 0.$$

Solutions of this equation are

$$\lambda_{1,2} = i \left(\frac{\omega - \omega_{21}}{2} \pm \sqrt{\frac{\left(\omega - \omega_{21}\right)^2}{4} + \frac{\gamma^2}{\hbar^2}} \right)$$

Therefore,

$$c_1(t) = Ae^{\lambda_1 t} + Be^{\lambda_2 t} = e^{i(\omega - \omega_{21})t/2} \left(Ae^{i\Omega t} + Be^{-i\Omega t} \right)$$

where $\Omega = \sqrt{\frac{(\omega - \omega_{21})^2}{4} + \frac{\gamma^2}{\hbar^2}}$, and we can find $c_2(t)$ using

$$i\hbar\dot{c}_1 = \gamma e^{i(\omega-\omega_{21})t/2}c_2(t)$$

$$\Rightarrow c_2(t) = \frac{\hbar}{\gamma} \left[-\left(\frac{\omega-\omega_{21}}{2} + \Omega\right)Ae^{i\Omega t} - \left(\frac{\omega-\omega_{21}}{2} - \Omega\right)Be^{-i\Omega t} \right].$$

We can find A and B using the initial condition that $c_1(0) = 1$ and $c_2(0) = 0$. That is, all particles are in the ground state at t = 0.

$$A + B = 1$$
$$-\left(\frac{\omega - \omega_{21}}{2} + \Omega\right)A - \left(\frac{\omega - \omega_{21}}{2} - \Omega\right)B = 0$$

We can solve for A and B, and obtain

$$\Rightarrow A = \frac{\Omega - (\omega - \omega_{21})/2}{2\Omega}$$
$$B = \frac{\Omega + (\omega - \omega_{21})/2}{2\Omega}$$

Therefore, $c_2(t)$ is equal to

$$c_{2}(t) = \frac{\hbar}{\gamma} \left(-\frac{\Omega^{2} - (\omega - \omega_{21})^{2}/4}{2\Omega} e^{i\Omega t} + \frac{\Omega^{2} - (\omega - \omega_{21})^{2}/4}{2\Omega} e^{-i\Omega t} \right)$$
$$= \frac{\hbar}{\gamma} \frac{\Omega^{2} - (\omega - \omega_{21})^{2}/4}{\Omega} \cdot i \sin \Omega t$$
$$\Rightarrow c_{2}(t) = \frac{i\gamma/\hbar}{\sqrt{(\omega - \omega_{21})^{2}/4 + \gamma^{2}/\hbar^{2}}} \cdot \sin \Omega t.$$

The probability of being in the E_2 state is therefore equal to

$$|c_2(t)|^2 = \frac{\gamma^2/\hbar^2}{(\omega - \omega_{21})^2/4 + \gamma^2/\hbar^2} \cdot \sin^2 \Omega t$$

and the probability of being in the E_1 state is

$$|c_1(t)|^2 = 1 - |c_2(t)|^2$$
.

We can think of $|c_2(t)|^2$ as a probability that a particle is excited and makes a transition from the E_1 to E_2 state. Therefore, $|c_2(t)|^2$ represents the absorption probability. On the other hand, $|c_1(t)|^2$ represents the

stimulated emission probability. At the resonance, where $\omega = \omega_{21}$, the maximum probability of $|c_2(t)|^2$ is equal to one while the minimum probability of $|c_1(t)|^2$ can reach zero as shown in the figure below.



Figure 9.1: $|c_1(t)|^2$ and $|c_2(t)|^2$ off resonance (left) and on resonance (right).

The amplitude of the probability $|c_2(t)|^2$ as a function of ω is described by a Lorentzian, as shown below, where $\Delta = \frac{4\gamma}{\hbar}$ is full-width-at-half-maximum (FWHM). The amplitude peaks at the resonance where $\omega = \omega_{21}$, and the width of the amplitude around the resonance is proportional to γ , which represents the strength of the interaction.



This two-state problem shows a basic principle of absorption and stimulated emission. In general, we can simplify an atom, which has many energy levels, into a two-state system. This atom then interacts with a background radiation field at frequency ω . The interaction part of the Hamiltonian can be described by

$$V(t) = \gamma \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix}.$$

When ω is near $\omega_{21} = \frac{E_2 - E_1}{\hbar}$, the atom can absorb photons from the radiation field most efficiently.

Examples of 2-state systems

1. Spin magnetic resonance

We consider a spin-1/2 particle in a time-varying magnetic field described by

$$\vec{B} = B_0 \hat{z} + B_1 \left(\hat{x} \cos \omega t + \hat{y} \sin \omega t \right).$$

This magnetic field rotates around the z-axis as depicted below.



The Hamiltonian for this system can be described by

$$\mathcal{H} = -g\mu_B \frac{\vec{S}}{\hbar} \cdot \vec{B} = -\frac{1}{2}g\mu_B \left[\sigma_z B_0 + B_1 \left(\sigma_x \cos \omega t + \sigma_y \sin \omega t\right)\right] = \mathcal{H}_0 + V(t),$$

where $\mu_B = \frac{e\hbar}{2mc}$. In a matrix from, we have

$$\mathcal{H}_0 = -\frac{e\hbar B_0}{2m_e c} \begin{pmatrix} 1 & 0\\ 0 & -1 \end{pmatrix}$$
$$V(t) = -\frac{eB_1\hbar}{2m_e c} \begin{pmatrix} 0 & e^{-i\omega t}\\ e^{i\omega t} & 0 \end{pmatrix}$$

We can see right away that this Hamiltonian is that of the two-state system, where we have $E_1 = -\frac{eB_0\hbar}{2m_ec}$, $E_2 = \frac{eB_0\hbar}{2m_ec}$, and $\gamma = -\frac{eB_1\hbar}{2m_ec}$. Therefore, we can apply the results of the two-state system to this problem.

If $B_1 = 0$ (no interaction between the two states), a spin will precesses around the z-axis due to the constant magnetic field B_0 along the z-axis with the angular frequency

$$\omega_{21} = \frac{E_2 - E_1}{\hbar} = \frac{|e| B_0}{m_e c}.$$

The probability $|c_{\pm}|^2$ are unchanged with time. Therefore, the system remains in the eigenstates with rotating phase. There is no transition between $|+\rangle \longleftrightarrow |-\rangle$. The expectation value of $S_z \langle S_z \rangle$ is unchanged but since the spin rotates in the xy-plane, $\langle S_x \rangle$ and $\langle S_y \rangle$ change. We have already solved this problem.

If $B_1 \neq 0$, there is an oscillation between the probability $|c_{\pm}|^2$, which means that the spin can make the transition between $|+\rangle \longleftrightarrow |-\rangle$. We can think of the state $|1\rangle$ in the two-state system as $|-\rangle$ and

 $|2\rangle$ as $|+\rangle$. We call this transition "spin-flops". We can calculate the probability of "spin-flops" using the results from the two-state system.

Classically, we can think of the spin-flop transition as spin precessing around the *t*-dependent axis, which rotates around the *z*-axis. At the resonance where $\omega = \omega_{21} = \frac{|e|B_0}{m_e c}$, \vec{B} rotates around the *z*-axis at the precessing frequency ω_{21} . This gives rise to the complete spin flop transition. That is, $|c_-|_{min}^2 = 0$ and $|c_+|_{max}^2 = 1$. Here, we assume that initially the spin is in $|-\rangle$, and the frequency of the spin-flop is $\Omega \sim B_1$. If the system is not at the resonance, the spin-flop is then not complete. The figure below shows the spin-flop transition due to the magnetic field B_1 in the *xy*-plane.



We note that

- (a) The transitions $|+\rangle \longleftrightarrow |-\rangle$ occur for any finite value of B_1 at the resonance, since at the resonance the strength of amplitude of spin-flop is independent of B_1 . Therefore, we obtain the complete spin flop at the resonance but the time it takes for the spin to flop is very large for small B_1 ($\Omega \sim B_1$).
- (b) In an experiment, it is easier to apply

$$\vec{B} = (0, B_1 \sin \omega t, B_0)$$

than rotating B_1 in the xy-plane. However, there is relatively small contribution from a term $e^{-i\omega t}$ near the resonance. Therefore, near the resonance, only $\omega = \omega_{21}$ from a term $e^{i\omega t}$ is relevant.

2. MASER (Microwave Amplification by Stimulated Emission of Radiation)

For the next example, we consider an ammonia molecule NH₃, which has two nearby states. These two states are eigenstates of parity $P: \vec{x} \to -\vec{x}$, which we will called $|S\rangle$ for a symmetric state and $|A\rangle$ for an anti-symmetric state, where

$$P |S\rangle = |S\rangle, \quad P |A\rangle = -|A\rangle.$$

The eigenenergies for $|S\rangle$ and $|A\rangle$ are E_S and E_A , respectively, where $E_S \leq E_A$. Therefore, the unperturbed Hamiltonian is described by

$$\mathcal{H}_0 = \begin{pmatrix} E_S & 0\\ 0 & E_A \end{pmatrix}.$$

We also note that the electron density near nitrogen is greater than near hydrogen creating the displacement of charge in NH₃ resulting in the electric dipole. Let $\vec{\mu}_{el}$ be an operator for the electric dipole. $\vec{\mu}_{el} \sim \vec{x}$ is odd under parity, *i.e.* $P\vec{\mu}_{el}P = -\vec{\mu}_{el}$. Therefore,

$$\langle A | \vec{\mu}_{el} | A \rangle = \langle S | \vec{\mu}_{el} | S \rangle = 0.$$

On the the other hand,

$$\langle A | \vec{\mu}_{el} | S \rangle = \langle S | \vec{\mu}_{el} | A \rangle \neq 0$$

In the presence of an time-varying electric field, the electric dipole can interact with the field giving rise to the time-varying potential

$$V(t) = -\vec{\mu}_{el} \cdot \vec{E}(t),$$

where $\vec{E}(t) = E_0 \hat{z} \cos \omega t$. Therefore, the time-varying perturbed potential is equal to

$$\Rightarrow \quad V(t) = \gamma \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix},$$

where γ is a function of the matrix element of $\vec{\mu}_{el}$ and E_0 . As you can see, this problem also has a Hamiltonian of the two-state problem. We can, therefore, use the results we obtained from the two-state problem to describe this system.

So, how does MASER work?

- (a) We take a beam of NH₃ with a mixing state of $|S\rangle$ and $|A\rangle$.
- (b) We select only the antisymmetric state |A⟩ by passing the beam through inhomogeneous electric field. The different electric dipole of |A⟩ and |S⟩ will result in different forces acting on the two states.
- (c) We take the state $|A\rangle$ to go through a cavity with the microwave radiation field with $\omega = \omega_{21} = \frac{E_A E_S}{\hbar}$. At the resonance, the frequency of the transition is equal to $\Omega = \frac{\gamma}{\hbar}$. Therefore, to obtain the complete stimulated emission from the transition $|A\rangle \rightarrow |S\rangle$, we need to vary the time at which the beam spends inside the cavity to be equal to $\frac{\pi}{2\Omega} = \frac{\pi\hbar}{2\gamma}$ by adjusting the velocity of the NH₃ beam.

This procedure will amplify the microwave field from the (stimulated) emitted photons with $\omega = \omega_{21}$ from NH₃ molecules. Note that we can also make hydrogen MASER using the hyperfine transition with wavelength equal to 21 cm; this hyperfine transition is known to an accuracy of one part in 10⁶.

9.3 Time-dependent Perturbation Theory

The two-state system is one example of the problems that can be solved exactly. In general, there is no analytic solution for the Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + V(t).$$

Therefore, we must use the perturbation analysis to expand $c_n(t)$ in a power series of V(t) assuming that V(t) is small.

$$\Rightarrow \quad c_n(t) = c_n^{(0)} + c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots,$$

where $c_n^{(0)}$ represents the overlap with the initial state and is time-independent. In order to calculate $c_n(t)$, we will use the propagator in the interaction picture $U_I(t; t_0)$, where

$$|\alpha, t_0; t\rangle_I = U_I(t; t_0) |\alpha, t_0\rangle_I$$

and $U_I(t; t_0)$ must satisfy the following Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} U_I(t;t_0) = V_I(t)U_I(t;t_0)$$

with the initial condition

$$U_I(t_0;t_0) = \mathbb{1}.$$

We can solve this differential equation and obtain

$$U_{I}(t;t_{0}) = \mathbb{1} - \frac{i}{\hbar} \int_{t_{0}}^{t} V_{I}(t') U_{I}(t';t_{0}) dt'.$$

The problem here is that the solution contain itself on the right hand side of the equation. Therefore, we can obtain $U_I(t; t_0)$ using an iterative method.

$$\Rightarrow \quad U_{I}(t;t_{0}) = \mathbb{1} - \frac{i}{\hbar} \int_{t_{0}}^{t} V_{I}(t_{1}) dt_{1} - \frac{1}{\hbar^{2}} \int_{t_{0}}^{t} dt_{1} \int_{t_{0}}^{t_{1}} dt_{2} V_{I}(t_{1}) V_{I}(t_{2}) + \cdots + \left(-\frac{i}{\hbar}\right)^{n} \int_{t_{0}}^{t} dt_{1} \int_{t_{0}}^{t_{1}} dt_{2} \cdots \int_{t_{0}}^{t_{n-1}} dt_{n} V_{I}(t_{1}) V_{I}(t_{2}) \cdots V_{n}(t_{n}) + \cdots U_{I}(t;t_{0}) = \mathbb{1} + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^{n} \int_{t_{0}}^{t} dt_{1} \int_{t_{0}}^{t_{1}} dt_{2} \cdots \int_{t_{0}}^{t_{n-1}} dt_{n} V_{I}(t_{1}) V_{I}(t_{2}) \cdots V_{n}(t_{n}).$$

We can rewrite this expression using the time-ordering operator.

$$\Rightarrow \quad U_I(t;t_0) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{i}{\hbar}\right)^n \Gamma\left[\int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \cdots \int_{t_0}^t dt_n V_I(t_1) V_I(t_2) \cdots V_n(t_n)\right].$$

This series is called "Dyson series". Now in order to calculate $c_n(t)$, we will consider the time-evolution of a state. We start with the initial state $|i\rangle$ at $t = t_0$.

$$\begin{aligned} |i, t_0; t\rangle_I &= U_I(t; t_0) |i, t_0\rangle_I \\ &= \sum_n |n\rangle \underbrace{\langle n | U_I(t; t_0) | i\rangle}_{c_n(t)} \end{aligned}$$

Therefore, to the second-order in V(t), we can take $U_I(t;t_0)$ and substitute it into $c_n(t) = \langle n|U_I(t;t_0)|I\rangle$.

$$\Rightarrow \quad c_n(t) \quad = \quad \delta_{ni} - \frac{i}{\hbar} \int_{t_0}^t dt_1 \left\langle n | V_I(t_1) | i \right\rangle - \frac{1}{\hbar^2} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \sum_m \left\langle n | V_I(t_1) | m \right\rangle \left\langle m | V_I(t_2) | i \right\rangle.$$

We can evaluate each term and obtain

$$\begin{aligned} c_n^{(0)} &= \delta_{ni} \\ c_n^{(1)}(t) &= -\frac{i}{\hbar} \int_{t_0}^t dt_1 \langle n | \underbrace{V_I(t_1)}_{=e^{i\mathcal{H}_0 t/\hbar V(t)} e^{-i\mathcal{H}_0 t/\hbar}} |i\rangle \\ &= -\frac{i}{\hbar} \int_{t_0}^t dt_1 e^{i\omega_{ni}t_1} \underbrace{V_{ni}(t_1)}_{=\langle n|V(t)|i\rangle} \\ c_n^{(2)}(t) &= -\frac{1}{\hbar^2} \sum_m \int_{(t_0)}^t dt_1 \int_{t_0}^{t_1} dt_2 \ e^{i\omega_{nm}t_1} e^{i\omega_{mi}t_2} V_{nm}(t_1) V_{mi}(t_2) \end{aligned}$$

Suppose we want to calculate the transition probability from $|i\rangle \longrightarrow |n\rangle$, where $n \neq i$.

$$P(i \to n) = |c_n(t)|^2 = \left|c_n^{(0)} + c_n^{(1)}(t) + c_n^{(2)}(t) + \cdots\right|^2.$$

$$P(i \to i) = 1 - \sum_{n} P(i \to n) \quad \forall n \neq i.$$

Transition amplitude and Feynman diagram

There is an alternative way to derive the transition amplitude using Feynman diagram. We can rewrite the transition probability as

$$|c_n(t)|^2 = |\langle n|U_I(t;t_0)\rangle|^2 = |\langle n|U(t;t_0)|i\rangle|^2,$$

since the difference between $U(t;t_0)$ and $U_I(t;t_0) = e^{i\mathcal{H}_0 t/\hbar} U(t;t_0) e^{-i\mathcal{H}_0 t/\hbar}$ is just the phase. We can calculate $\langle n|U(t;t_0)|i\rangle$ in a series of V(t) with the help of Feynman diagram. Then, we can use the fact that

$$c_n(t) = \langle n | U_I(t;t_0) | i \rangle = e^{iE_n t/\hbar - iE_i t/\hbar} \langle n | U(t;t_0) | i \rangle$$

to calculate $c_n(t)$. The graphical depiction of $\langle n|U(t;t_0)|i\rangle$ using the Feynman diagram is shown in the figure below.



The propagator is represented by a line segment, while the vortex represents the interaction part, which involves a matrix element connecting two states.

Implicit integrals $\int dt_i$ and sums $\sum_{m'}$ are performed for variables that are not fixed such as t_i and m_i in the diagram above. Using the Feynman diagram, we can write the first-order term of $\langle n|U(t;t_0)|i\rangle$ as

$$\langle n|U(t;t_0)|i\rangle = -\frac{i}{\hbar} \int dt_1 \ e^{-iE_i(t_1-t_0)/\hbar} \langle n|V(t_1)|i\rangle \ e^{-iE_n(t-t_1)/\hbar}.$$

We can then use this to calculate

$$\begin{aligned} c_n^{(1)}(t) &= \langle n | U_I(t;t_0) | i \rangle = e^{iE_n t/\hbar - iE_i t/\hbar} \langle n | U(t;t_0) | i \rangle \\ &= -\frac{i}{\hbar} \int dt_1 \ e^{iE_n t_1/\hbar - iE_i t_1/\hbar} \langle n | V(t) | i \rangle \\ \Rightarrow \quad c_n^{(1)}(t) &= -\frac{i}{\hbar} \int_{t_0}^t dt_1 \ e^{i\omega_{ni} t_1} V_{ni}(t_1), \end{aligned}$$

which is the same as what we have previous derived.

9.3.1 First-order perturbation calculations

In this section, we will apply the equation of the first-order perturbation theory to a simple perturbed potential. From the previous section, we have

$$c_n^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t dt_1 \ e^{i\omega_{ni}t_1} V_{ni}(t_1),$$

and the transition probability is equal to

$$P_{i \to n}^{(1)} = \left| c_n^{(1)}(t) \right|^2,$$

assuming that $n \neq i$. In this class, we will only consider two special and simple cases, where the perturbed potential is a harmonic or constant perturbation. We will first assume that the perturbation is harmonic, where

$$V(t) = V\sin\omega t,$$

and n matrix element of V(t) in a basis of the eigenstates of $\mathcal{H}_0 |n\rangle$ is

$$V_{ni}(t) = \langle n | V(t) | i \rangle = \frac{1}{2i} V_{ni}(t) \left(e^{i\omega t} - e^{-i\omega t} \right),$$

where $V_{ni} = \langle n | V | i \rangle$ is a matrix element of V in the $| n \rangle$ basis. Therefore, we have

$$c_n^{(1)}(t) = -\frac{V_{ni}}{2\hbar} \int_{t_0=0}^t dt' \ e^{i\omega_{ni}t'} \left[e^{i\omega t'} - e^{-i\omega t'} \right]$$
$$= -\frac{V_{ni}}{2\hbar} \left[\frac{e^{i(\omega_{ni}+\omega)t} - 1}{i(\omega_{ni}+\omega)} - \frac{e^{i(\omega_{ni}-\omega)t} - 1}{i(\omega_{ni}-\omega)} \right]$$
$$\Rightarrow c_n^{(1)}(t) = \frac{1}{i} \frac{V_{ni}}{2\hbar} \left[\frac{1 - e^{i(\omega_{ni}+\omega)t}}{\omega_{ni}+\omega} - \frac{1 - e^{i(\omega_{ni}-\omega)t}}{\omega_{ni}-\omega} \right]$$

Similarly, for $V(t) = V \cos \omega t$, we obtain

=

$$c_n^{(1)}(t) = \frac{V_{ni}}{2\hbar} \left[\frac{1 - e^{i(\omega_{ni} + \omega)t}}{\omega_{ni} + \omega} + \frac{1 - e^{i(\omega_{ni} - \omega)t}}{\omega_{ni} - \omega} \right].$$

Constant Perturbation

If $\omega = 0$ for the case of $V(t) = V \cos \omega t$, we have a constant perturbation V(t) = V and the transition amplitude becomes

$$\Rightarrow \quad c_n^{(1)}(t) = \frac{V_{ni}}{\hbar\omega_{ni}} \left(1 - e^{i\omega_{ni}t}\right),$$

and the transition probability is equal to

$$P^{(1)}(i \to n) = \left| c_n^{(1)}(t) \right| = \frac{4 \left| V_{ni} \right|^2}{\left(E_n - E_i \right)^2} \sin^2 \left(\frac{E_n - E_i}{2\hbar} t \right)$$

We can plot this transition probability as a function of $\omega_{ni} = \frac{E_n - E_i}{\hbar}$.



The width of the main peak at $\omega_{ni} = 0$ is proportional to 1/t and the probability grows proportionally to t^2 . Therefore, after time t, the transition probability becomes taller but skinnier. The uncertainty of ω is equal to

$$\Delta\omega\approx\frac{2\pi}{t}\quad\Rightarrow\quad \Delta E\approx\frac{2\pi\hbar}{t}\quad\Rightarrow\quad \Delta E\Delta t\sim\hbar.$$

Therefore, the energy conservation only happen where $\Delta E = 0$ as $t \to \infty$ in a semi-classical picture.

Fermi's Golden Rule

As you can see from the graph above, the transition probability peaks around $\omega_{ni} = 0$, that is, $E_n \sim E_i$. If the states around E_i is closely spaced, then the total transition probability is approximately equal to

$$P^{(1)}(i \to [n]) = \sum_{n \neq i} \left| c_n^{(1)} \right|^2,$$

where [n] denotes the states around E_i . When the spectrum of E_n is continuous, we can write the density of states as

$$\rho(E) = \lim_{\Delta E \to 0} \frac{\text{numbers of states with } E - \Delta E/2 \leqslant E \leqslant E + \Delta E/2}{\Delta E},$$

and the sum changes to an integral,

$$P^{(1)}(i \to [n]) = \int dE_n \ \rho(E_n) \left| c_n^{(1)} \right|^2$$

= $4 \int dE_n \ \sin^2 \left[\frac{(E_n - E_i) t}{2\hbar} \right] \frac{|V_{ni}|^2}{(E_n - E_i)^2} \rho(E_n)$

Since the area under the main peak grows linearly with t, the transition probability also grows linearly with t. For large t (but small enough that the first order calculation is still valid), we can use the following identity

$$\lim_{\alpha \to \infty} \frac{\sin^2 \alpha x}{\alpha x^2} = \pi \delta(x),$$

to calculate

$$\lim_{t \to \infty} \frac{1}{\left(E_n - E_i\right)^2} \sin^2 \left[\frac{\left(E_n - E_i\right)t}{2\hbar}\right] = \frac{\pi t}{2\hbar} \delta\left(E_n - E_i\right)$$

Therefore, we have

$$\lim_{t \to \infty} P^{(1)}(i \to [n]) = 4 \overline{|V_{ni}|^2} \lim_{t \to \infty} \int dE_n \sin^2 \left[\frac{(E_n - E_i)t}{2\hbar} \right] \frac{1}{(E_n - E_i)^2} \rho(E_n)$$
$$= 4 \overline{|V_{ni}|^2} \frac{\pi t}{2\hbar} \int dE_n \rho(E_n) \delta(E_n - E_i)$$
$$= \frac{2\pi}{\hbar} \overline{|V_{ni}|^2} \rho(E_n) t \Big|_{E_n \simeq E_i},$$

where $\overline{|V_{ni}|^2} = \lim_{\Delta E \to 0} \int_{-\Delta E/2}^{\Delta E/2} dE_n |V_{ni}|^2$, which is well defined given that V_{ni} varies smoothly with E_n . We can also calculate the transition rate ω .

$$\omega_{i \to [n]} = \frac{d}{dt} \left[P^{(1)} \left(i \to [n] \right) \right] = \left. \frac{2\pi}{\hbar} \overline{\left| V_{ni} \right|^2} \rho \left(E_n \right) \right|_{E_n \simeq E_i},$$

which does not depend on t. This equation is called "Fermi Golden Rule", and we can rewrite it as

$$\omega_{i \to [n]} = \frac{2\pi}{\hbar} \overline{\left| V_{ni} \right|^2} \delta \left(E_n - E_i \right),$$

where $\int dE_n \rho(E_n)$ is replaced by $\delta(E_n - E_i)$, which is valid for $t \to \infty$.

Harmonic Perturbation

Consider a harmonic perturbation of the following form,

$$V(t) = \nu e^{i\omega t} + \nu^{\dagger} e^{-i\omega t}.$$

Using the same calculation we have done previously, we find that to first order the probability amplitude is equal to

$$c_n^{(1)}(t) = \frac{1}{\hbar} \left[\underbrace{\frac{1 - e^{i(\omega_{ni} + \omega)t}}{\omega_{ni} + \omega} \nu_{ni}}_{\text{emission near } \omega_{ni} \simeq -\omega} + \underbrace{\frac{1 - e^{i(\omega_{ni} - \omega)t}}{\omega_{ni} - \omega} \nu_{ni}^{\dagger}}_{\text{absorbtion near } \omega_{ni} \simeq \omega} \right].$$

For the stimulated emission where $\omega \simeq -\omega_{ni}$, the transition probability is equal to

$$\left| c_{n}^{(1)}(t) \right|^{2} = \frac{4 \left| \nu_{ni} \right|^{2}}{\hbar^{2} \left(\omega + \omega_{ni} \right)^{2}} \sin^{2} \left[\frac{\left(\omega + \omega_{ni} \right) t}{2} \right].$$

The transition rate to the state $|n\rangle$ with energy $E_n = E_i - \hbar\omega$ at large t is equal to

$$\omega_{i \to n} = \frac{2\pi}{\hbar} \left| \nu_{ni} \right|^2 \delta \left(E_n - E_i + \hbar \omega \right)$$

and if the spectrum of E_n is continuous or closely spaced, then

$$\omega_{i\to[n]} = \left. \frac{2\pi}{\hbar} \left| \nu_{ni} \right|^2 \rho\left(E_n \right) \right|_{E_n \simeq E_i - \hbar \omega}.$$

Similarly for the absorption at $\omega \simeq \omega_{ni}$, the transition probability is

$$\left|c_{n}^{(1)}(t)\right|^{2} = \frac{4\left|\nu_{ni}^{\dagger}\right|^{2}}{\hbar^{2}\left(\omega - \omega_{ni}\right)^{2}}\sin^{2}\left[\frac{\left(\omega - \omega_{ni}\right)t}{2}\right].$$

The transition rate as $t \to \infty$ is

$$\omega_{i \to n} = \frac{2\pi}{\hbar} \left| \nu_{ni}^{\dagger} \right|^2 \delta \left(E_n - E_i - \hbar \omega \right)$$

and if the spectrum of E_n is continuous or closely spaced, then

$$\omega_{i \to [n]} = \left. \frac{2\pi}{\hbar} \left| \nu_{ni}^{\dagger} \right|^2 \rho\left(E_n \right) \right|_{E_n \simeq E_i + \hbar \omega}$$

We note that the harmonic perturbation can give rise to both stimulated emission and absorption of $\Delta E = \hbar \omega$ or the final states over a continuous spectrum of energy. For the latter, the radiation does not have a single well defined wavelength. For the discrete states as $t \to \infty$, we have the following relationship between the absorption and stimulated emission rate,

$$\omega_{i \to n}^{(absorption)} = \omega_{n \to i}^{(emission)} \quad \Rightarrow \quad \left|\nu_{ni}\right|^2 = \left|\nu_{in}^{\dagger}\right|^2,$$

which is called "detailed balancing".

9.3.2 Applications to interactions with classical radiation field

We will use the results of the time-dependent perturbation theory to study the interactions of atomic electrons with classical electromagnetic field. Fermi showed that the Hamiltonian for a charged particle in the electromagnetic field can be described by

$$\mathcal{H} = \underbrace{\left(\frac{P^2}{2m} + V\right)}_{\mathcal{H}_0} \underbrace{-\frac{e}{mc} \vec{P} \cdot \vec{A_\perp}(t)}_{V(t)} + \underbrace{\frac{e^2}{2mc^2} A_\perp^2 - \frac{g\mu_B}{\hbar} \vec{S} \cdot \vec{B} + \mathcal{H}_{rad}}_{\text{ignored}},$$

where \vec{A}_{\perp} is a purely transverse field. Since we choose the Coulomb gauge or the radiation gauge, that is,

$$\vec{\nabla} \cdot \vec{A} = 0$$

only the transverse field survives. We assume that the vector potential \vec{A} originates from a monochromatic plane wave, where

$$\vec{A}(\vec{x},t) = A_0 \hat{\epsilon} \left[\underbrace{\underbrace{e^{i(\omega/c)\hat{n} \cdot \vec{x} - i\omega t}}_{\text{absorption}} + \underbrace{e^{-i(\omega/c)\hat{n} \cdot \vec{x} + i\omega t}}_{\text{emission}} \right]$$

For absorption, the transition rate is equal to

$$\omega_{i \to n} = \frac{2\pi}{\hbar} \left| \nu_{ni}^{\dagger} \right|^2 \delta \left(E_n - E_i - \hbar \omega \right)$$

where

$$\begin{split} \nu_{ni}^{\dagger} &= \left. \left\langle n \right| - \frac{e}{mc} \vec{P} \cdot \vec{A} \right| i \right\rangle \\ &= \left. - \frac{eA_0}{mc} \left\langle n \right| e^{i(\omega/c)\hat{n} \cdot \vec{x}} \hat{\epsilon} \cdot \vec{P} \right| i \right\rangle. \end{split}$$

We define the absorption cross section as

$$\sigma_{abs} = \frac{\text{energy absorbed per unit time}}{\text{energy flux}}$$

A unit of the cross section is length squared, which is equivalent to an area. Physically, we can think of the cross section as an area that absorbs energy.

$$\Rightarrow \quad \sigma_{abs} = \frac{\hbar\omega \cdot \omega_{i \to n}}{cU},$$

where c is the speed of light and U is the energy density (cU is the energy flux). For the electromagnetic radiation, the energy density is equal to

$$U = \frac{1}{2} \left(\frac{E_{max}^2}{8\pi} + \frac{B_{max}^2}{8\pi} \right) = \frac{1}{2\pi} \frac{\omega^2}{c^2} \left| A_0 \right|^2.$$

Therefore, the absorption cross section is equal to

$$\sigma_{abs} = \frac{4\pi^2 \hbar}{m^2 \omega} \underbrace{\left(\frac{e^2}{\hbar c}\right)}_{\alpha = \frac{1}{137}} \left| \left\langle n \right| e^{i(\omega/c)\hat{n}\cdot\vec{x}} \hat{\epsilon} \cdot \vec{P} \left| i \right\rangle \right|^2 \delta\left(E_n - E_i - \hbar \omega \right).$$

We note that the cross section does not depend on A_0 , which is the strength of the electromagnetic field. For the emission probability, the calculation is also the same using the detailed balance relation. Our next task is to calculation the matrix element $\left\langle n \left| e^{i(\omega/c)\hat{n}\cdot\vec{x}}\hat{\epsilon}\cdot\vec{P} \right| i \right\rangle$

Electric dipole (E1) approximation

If $\lambda = \frac{2\pi c}{\omega} \gg R_{atom}$, then we can neglect sub-leading terms in

$$e^{i(\omega/c)\hat{n}\cdot\vec{x}} = 1 + i\left(\frac{\omega}{c}\right)\hat{n}\cdot\vec{x} + \cdots$$

and use only the zeroth-order term. For example, for an hydrogen atom the energy required to ionize the atom is $E_{\infty} = 13.6 \text{ meV} = \frac{me^4}{2\hbar^2}$ and a size of the atom is $a_0 = 0.52 \text{ Å} = \frac{\hbar^2}{me^2}$. Therefore,

$$\omega = \frac{me^4}{2\hbar^3} = \alpha \frac{mce^2}{2\hbar^2} = \frac{\alpha}{2} \frac{c}{a_0},$$

while

$$\lambda = \frac{2\pi c}{\omega} = \frac{4\pi}{\alpha} a_0 \gg a_0.$$

So, E1 approximation is valid in this case. We note that

1. For large atoms, E1 approximation might not work, and we need to include higher-order terms.

2. In some case, E1 transition is not possible, and we also need to consider the next non-zero terms.

Applying E1 approximation, we obtain

$$\left\langle n \left| e^{i(\omega/c)\hat{n}\cdot\vec{x}}\hat{\epsilon}\cdot\vec{P} \right| i \right\rangle \longrightarrow \hat{\epsilon}\cdot\left\langle n | \vec{P} | i \right\rangle.$$

We assume that $\hat{\epsilon} = \hat{x}$, which is the direction of the oscillation (polarization), and $\hat{n} = \hat{z}$, which is the direction of the traveling wave.

$$\Rightarrow \quad \hat{\epsilon} \cdot \left\langle n \middle| \vec{P} \middle| i \right\rangle = \left\langle n \middle| P_x \middle| i \right\rangle = \frac{m}{i\hbar} \left\langle n \middle| [x, \mathcal{H}_0] \middle| i \right\rangle = im\omega_{ni} \underbrace{\langle n | x | i \rangle}_{\text{dipole moment}}$$

Therefore, the cross section of E1 approximation is equal to

$$\sigma_{abs}^{E1} = 4\pi^2 \alpha \omega_{ni} \left| \langle n | x | i \rangle \right|^2 \delta \left(\omega - \omega_{ni} \right),$$

which is the equation for the *electric dipole absorption cross section*.

Multipole transition

We can also consider higher multipole transition. For example, the next higher order term in the expansion is $i(\omega/c)\hat{n}\cdot\vec{x} \equiv i\vec{k}\cdot\vec{x}$. Therefore, the contribution due to this term can be written as

$$\left(\vec{k} \cdot \vec{x}\right)(\vec{p} \cdot \hat{\epsilon}) = \frac{1}{2} k_i \epsilon_j \left[\underbrace{(x_i p_j - x_j p_i)}_{\text{magnetic dipole } M1} + \underbrace{(x_i p_j + x_j p_i)}_{\text{electric quadrapole } E2}\right],$$

where $x_i p_j - x_j p_i = L_k$ is the angular momentum along \hat{k} .

The matrix elements for M1 and E2 are

$$\nu_{ni}^{(M1)} \propto \left\langle n \left| \left(\hat{k} \times \hat{\epsilon} \right) \cdot \left(\vec{L} + g \vec{S} \right) \right| i \right\rangle,$$

where $\vec{L} + g\vec{S}$ is the net magnetic moment (we manually insert a spin \vec{S}), and

$$\nu_{ni}^{(E2)} \propto \left\langle n \left| k_i \epsilon_j \underbrace{\left(x_i x_j - \frac{1}{3} \delta_{ij} x^2 \right)}_{\text{quadrapole operator}} \right| i \right\rangle$$