

11. Perturbation Theory

11.1 Time-independent perturbation theory

11.1.1 Non-degenerate case

11.1.2 Degenerate case

11.1.3 The Stark effect

11.2 Time-dependent perturbation theory

11.2.1 Review of interaction picture

11.2.2 Dyson series

11.2.3 Fermi's Golden Rule

11.1 Time-independent perturbation theory

Because of the complexity of many physical problems, very few can be solved exactly (unless they involve only small Hilbert spaces). In particular, to analyze the interaction of radiation with matter we will need to develop approximation methods³⁶.

11.1.1 Non-degenerate case

We have an Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \epsilon V$$

where we know the eigenvalue of the unperturbed Hamiltonian \mathcal{H}_0 and we want to solve for the perturbed case $\mathcal{H} = \mathcal{H}_0 + \epsilon V$, in terms of an expansion in ϵ (with ϵ varying between 0 and 1). The solution for $\epsilon \rightarrow 1$ is the desired solution.

We assume that we know exactly the energy eigenkets and eigenvalues of \mathcal{H}_0 :

$$\mathcal{H}_0 |k\rangle = E_k^{(0)} |k\rangle$$

As \mathcal{H}_0 is hermitian, its eigenkets form a complete basis $\sum_k |k\rangle\langle k| = \mathbb{1}$. We assume at first that the energy spectrum is not degenerate (that is, all the $E_k^{(0)}$ are different, in the next section we will study the degenerate case). The eigensystem for the total hamiltonian is then

$$(\mathcal{H}_0 + \epsilon V) |\varphi_k\rangle_\epsilon = E_k(\epsilon) |\varphi_k\rangle_\epsilon$$

where $\epsilon = 1$ is the case we are interested in, but we will solve for a general ϵ as a perturbation in this parameter:

$$|\varphi_k\rangle = \left| \varphi_k^{(0)} \right\rangle + \epsilon \left| \varphi_k^{(1)} \right\rangle + \epsilon^2 \left| \varphi_k^{(2)} \right\rangle + \dots, \quad E_k = E_k^{(0)} + \epsilon E_k^{(1)} + \epsilon^2 E_k^{(2)} + \dots$$

³⁶ A very good treatment of perturbation theory is in Sakurai's book –J.J. Sakurai “Modern Quantum Mechanics”, Addison-Wesley (1994), which we follow here.

where of course $|\varphi_k^{(0)}\rangle = |k\rangle$. When ϵ is small, we can in fact approximate the total energy E_k by $E_k^{(0)}$. The energy shift due to the perturbation is then only $\Delta_k = E_k - E_k^{(0)}$ and we can write:

$$(\mathcal{H}_0 + \epsilon V) |\varphi_k\rangle = (E_k^{(0)} + \Delta_k) |\varphi_k\rangle \rightarrow (E_k^{(0)} - \mathcal{H}_0) |\varphi_k\rangle = (\epsilon V - \Delta_k) |\varphi_k\rangle$$

Then, we project onto $\langle k|$:

$$\langle k| (E_k^{(0)} - \mathcal{H}_0) |\varphi_k\rangle = \langle k| (\epsilon V - \Delta_k) |\varphi_k\rangle$$

The LHS is zero since $\langle k| \mathcal{H}_0 |\varphi_k\rangle = \langle k| E_k^{(0)} |\varphi_k\rangle$, and from the RHS $\langle k| (\epsilon V - \Delta_k) |\varphi_k\rangle = 0$ we obtain:

$$\Delta_k = \epsilon \frac{\langle k| V |\varphi_k\rangle}{\langle k| \varphi_k\rangle} \rightarrow \Delta_k = \epsilon \langle k| V |\varphi_k\rangle$$

$|\varphi_k\rangle$ in the full perturbative expansion

where we set $\langle k| \varphi_k\rangle = 1$ (a non-canonical normalization, although, as we will see, it is approximately valid). Using the expansion above, we can replace Δ_k by $\epsilon E_k^1 + \epsilon^2 E_k^2 + \dots$ and $|\varphi_k\rangle$ by its expansion:

$$\epsilon E_k^1 + \epsilon^2 E_k^2 + \dots = \epsilon \langle k| V (|k\rangle + \epsilon |\varphi_k^{(1)}\rangle + \epsilon^2 |\varphi_k^{(2)}\rangle + \dots)$$

and equating terms of the same order in ϵ we obtain:

$$E_k^n = \langle k| V |\varphi_k^{(n-1)}\rangle$$

we now need $|\varphi_k^{(n-1)}\rangle$

This is a recipe to find the energy at all orders based only on the knowledge of the eigenstates of lower orders. However, the question still remains: how do we find $|\varphi_k^{(n-1)}\rangle$?

We could think of solving the equation:

$$(E_k^{(0)} - \mathcal{H}_0) |\varphi_k\rangle = (\epsilon V - \Delta_k) |\varphi_k\rangle \quad (*)$$

for $|\varphi_k\rangle$, by inverting the operator $(E_k^{(0)} - \mathcal{H}_0)$ and again doing an expansion of $|\varphi_k\rangle$ to equate terms of the same order:

$$|k\rangle + \epsilon |\varphi_k^{(1)}\rangle + \dots = (E_k^{(0)} - \mathcal{H}_0)^{-1} (\epsilon V - \Delta_k) (|k\rangle + \epsilon |\varphi_k^{(1)}\rangle + \dots)$$

Unfortunately this promising approach is not correct, since the operator $(E_k^{(0)} - \mathcal{H}_0)^{-1}$ is not always well defined. Specifically, there is a singularity for $(E_k^{(0)} - \mathcal{H}_0)^{-1} |k\rangle$. What we need is to make sure that $(E_k^{(0)} - \mathcal{H}_0)^{-1}$ is never applied to eigenstates of the unperturbed Hamiltonian, that is, we need $|\psi_k\rangle = (\epsilon V - \Delta_k) |\varphi_k\rangle \neq |k\rangle$ for any $|\varphi_k\rangle$. We thus define the projector $P_k = \mathbb{1} - |k\rangle \langle k| = \sum_{h \neq k} |h\rangle \langle h|$. Then we can ensure that $\forall |\psi\rangle$ the projected state $|\psi'\rangle = P_k |\psi\rangle$ is such that $\langle k| \psi'\rangle = 0$ since this is equal to $\langle k| \psi\rangle - \langle k| k\rangle \langle k| \psi\rangle = 0$ *$|h\rangle$ are all eigenstates $\neq |k\rangle$*

$$\langle k| P_k |\psi\rangle = \langle k| \psi\rangle - \langle k| k\rangle \langle k| \psi\rangle = 0$$

Now, using the projector, $(E_k^{(0)} - \mathcal{H}_0)^{-1} P_k |\psi\rangle$ is well defined. We then take the equation $(*)$ and multiply it by P_k from the left:

$$P_k (E_k^{(0)} - \mathcal{H}_0) |\varphi_k\rangle = P_k (\epsilon V - \Delta_k) |\varphi_k\rangle.$$

Since P_k commutes with \mathcal{H}_0 (as $|k\rangle$ is an eigenstate of \mathcal{H}_0) we have $P_k (E_k^{(0)} - \mathcal{H}_0) |\varphi_k\rangle = (E_k^{(0)} - \mathcal{H}_0) P_k |\varphi_k\rangle$ and we can rewrite the equation as

$$P_k |\varphi_k\rangle = (E_k^{(0)} - \mathcal{H}_0)^{-1} P_k (\epsilon V - \Delta_k) |\varphi_k\rangle$$

We can further simplify this expression, noting that $P_k |\varphi_k\rangle = |\varphi_k\rangle - |k\rangle \langle k| \varphi_k\rangle = |\varphi_k\rangle - |k\rangle$ (since we adopted the normalization $\langle k| \varphi_k\rangle = 1$). Finally we obtain:

$$|\varphi_k\rangle = |k\rangle + (E_k^{(0)} - \mathcal{H}_0)^{-1} P_k (\epsilon V - \Delta_k) |\varphi_k\rangle \quad (**)$$

This equation is now ready to be solved by using the perturbation expansion. To simplify the expression, we define the operator R_k

$$R_k = (E_k^{(0)} - \mathcal{H}_0)^{-1} P_k = \sum_{h \neq k} \frac{|h\rangle \langle h|}{E_k^0 - E_h^0}$$

Now using the expansion

$$|k\rangle + \epsilon |\varphi_k^{(1)}\rangle + \dots = |k\rangle + R_k \epsilon (V - E_k^1 - \epsilon E_k^2 - \dots) (|k\rangle + \epsilon |\varphi_k^{(1)}\rangle + \dots)$$

we can solve term by term to obtain:

$$1^{st} \text{ order: } |\varphi_k^{(1)}\rangle = R_k (V - E_k^1) |k\rangle = R_k (V - \langle k| V |k\rangle) |k\rangle = R_k V |k\rangle$$

(where we used the expression for the first order energy and the fact that $R_k |k\rangle = 0$ by definition).

We can now calculate the second order energy, since we know the first order eigenstate:

$$E_k^2 = \langle k| V |\varphi_k^{(1)}\rangle = \langle k| V R_k V |k\rangle = \langle k| V \left(\sum_{h \neq k} \frac{|h\rangle \langle h|}{E_k^0 - E_h^0} \right) V |k\rangle$$

or explicitly

$$E_k^2 = \sum_{h \neq k} \frac{|V_{kh}|^2}{E_k^0 - E_h^0}$$

Then the second order eigenstate is

$$2^{nd} \text{ order: } |\varphi_k^{(2)}\rangle = R_k V R_k V |k\rangle$$

A. Formal Solution

We can also find a more formal expression that can yield the solution to all orders. We rewrite Eq. (**) using R_k and obtain

$$|\varphi_k\rangle = |k\rangle + R_k (\epsilon V - \Delta_k) |\varphi_k\rangle = R_k H_1 |\varphi_k\rangle$$

where we defined $H_1 = (\epsilon V - \Delta_k)$. Then by iteration we can write:

$$|\varphi_k\rangle = |k\rangle + R_k H_1 (|k\rangle + R_k H_1 |\varphi_k\rangle) = |k\rangle + R_k H_1 |k\rangle + R_k H_1 R_k H_1 |\varphi_k\rangle$$

and in general:

$$|\varphi_k\rangle = |k\rangle + R_k H_1 |k\rangle + R_k H_1 R_k H_1 |k\rangle + \dots + (R_k H_1)^n |k\rangle + \dots$$

This is just a geometric series, with formal solution:

$$|\varphi_k\rangle = (\mathbb{1} - R_k H_1)^{-1} |k\rangle$$

B. Normalization

In deriving the TIPT we introduced a non-canonical normalization $\langle k|\varphi_k\rangle = 1$, which implies that the perturbed state $|\varphi_k\rangle$ is not normalized. We can then define a properly normalized state as

$$|\psi_k\rangle = \frac{|\varphi_k\rangle}{\sqrt{\langle \varphi_k|\varphi_k\rangle}}$$

so that $\langle k|\psi_k\rangle = 1/\sqrt{\langle \varphi_k|\varphi_k\rangle}$. We can calculate perturbatively the normalization factor $\langle \varphi_k|\varphi_k\rangle$:

$$\langle \varphi_k|\varphi_k\rangle = \langle k + \epsilon \varphi_k^1 + \dots | k + \epsilon \varphi_k^1 + \dots \rangle = 1 + \cancel{\epsilon \langle k|\varphi_k^1\rangle} + \dots + \epsilon^2 \langle \varphi_k^1|\varphi_k^1\rangle + \dots = 1 + \epsilon^2 \sum_{h \neq k} \frac{|V_{kh}|^2}{(E_h^0 - E_k^0)^2}$$

Notice that the state is correctly normalized up to the second order in ϵ .

C. Anti-crossing

Consider two levels, h and k with energies E_k^0 and E_h^0 and assume that we apply a perturbation V which connects only these two states (that is, V is such that $\langle l|V|j\rangle = 0$ and it is different than zero only for the transition from h to k : $\langle h|V|k\rangle \neq 0$.)

If the perturbation is small, we can ask what are the perturbed state energies.

The first order is zero by the choice of V , then we can calculate the second order:

$$E_k^{(2)} = \sum_{j \neq k} \frac{|V_{kj}|^2}{E_k^0 - E_j^0} = \frac{|V_{kh}|^2}{E_k^0 - E_h^0}$$

and similarly

$$E_h^{(2)} = \sum_{j \neq h} \frac{|V_{hj}|^2}{E_h^0 - E_j^0} = \frac{|V_{kh}|^2}{E_h^0 - E_k^0} = -E_k^{(2)}.$$

This opposite energy shift will be more important (more noticeable) when the energies of the two levels E_k^0 and E_h^0 are close to each other. Indeed, in the absence of the perturbation, the two energy levels would “cross” when $E_k^0 = E_h^0$. If we add the perturbation, however, the two levels are repelled with opposite energy shifts. We describe what is happening as an “anti-crossing” of the levels: even as the levels become connected by an interaction, the levels never meet (never have the same energy) since each level gets shifted by the same amount in opposite directions.

D. Example: TLS energy splitting from perturbation

Consider the Hamiltonian $\mathcal{H} = \omega\sigma_z + \epsilon\Omega\sigma_x$. For $\epsilon = 0$ the eigenstates are $|k\rangle = \{|0\rangle, |1\rangle\}$ and eigenvalues $E_k^0 = \pm\omega$. We also know how to solve exactly this simple problem by diagonalizing the entire matrix:

$$E_{1,2} = \pm\sqrt{\omega^2 + \epsilon^2\Omega^2},$$

$$|\varphi_1\rangle = \cos(\vartheta/2)|0\rangle + \sin(\vartheta/2)|1\rangle, \quad |\varphi_2\rangle = \cos(\vartheta/2)|1\rangle - \sin(\vartheta/2)|0\rangle \quad \text{with} \quad \vartheta = \arctan(\epsilon\Omega/\omega)$$

For $\epsilon \ll 1$ we can expand in series these results to find:

$$E_{1,2} \approx \pm(\omega + \frac{\epsilon^2\Omega^2}{2\omega} + \dots)$$

$$|\varphi_1\rangle \approx |0\rangle + \frac{\vartheta}{2}|1\rangle = |0\rangle + \frac{\epsilon\Omega}{2\omega}|1\rangle \quad |\varphi_2\rangle \approx |1\rangle - \frac{\vartheta}{2}|0\rangle = |1\rangle - \frac{\epsilon\Omega}{2\omega}|0\rangle$$

As an exercise, we can find as well the results of TIPT. First we find that the first order energy shift is zero, since $E_k^1 = \langle k|V|k\rangle = \langle 0|(\Omega\sigma_x)|0\rangle = 0$ (and same for $\langle 1|(\Omega\sigma_x)|1\rangle$). Then we can calculate the first order eigenstate:

$$\varphi_1^1 = |0\rangle + (E_1^0 - \mathcal{H}_0)^{-1}P_1V|0\rangle = |0\rangle + [\omega(\mathbb{1} - \sigma_z)]^{-1}|1\rangle\langle 1|\epsilon\Omega\sigma_x|0\rangle = |0\rangle + \frac{1}{2\omega}\epsilon\Omega|1\rangle\langle 1|\sigma_x|0\rangle = |0\rangle + \epsilon\frac{\Omega}{2\omega}|1\rangle$$

similarly, we find $\varphi_2^1 = |1\rangle - \epsilon\frac{\Omega}{2\omega}|0\rangle$. Finally, the second order energy shift is $E_1^2 = \frac{|V_{12}|^2}{E_1^0 - E_2^0} = \frac{(\epsilon\Omega)^2}{2\omega}$ in agreement with the result from the series expansion.

We can also look at the level anti-crossing: If we vary the energy ω around zero, the two energy levels cross each other.

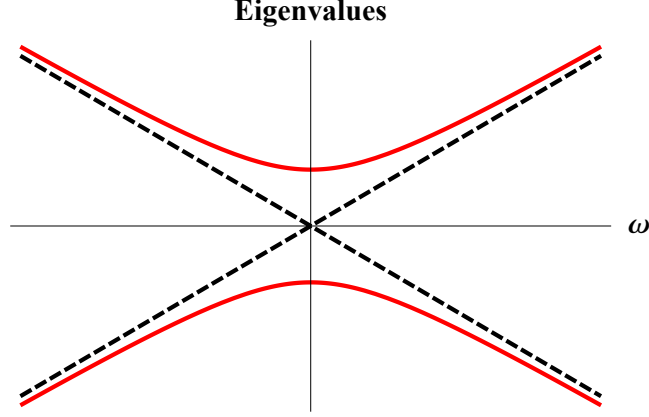


Fig. 18: Level anticrossing: Eigenvalues of the Hamiltonian $\mathcal{H} = \omega\sigma_z + \epsilon\Omega\sigma_x$ as a function of ω . Dashed lines: $\Omega = 0$. Red lines: $\Omega \neq 0$ showing the anticrossing.

11.1.2 Degenerate case

If there are degenerate (or quasi-degenerate) eigenvalues of the unperturbed Hamiltonian \mathcal{H}_0 , the expansion used above is no longer valid. There are two problems:

1. If $|k'\rangle, |k''\rangle, \dots$ have the same eigenvalue, we can choose any combination of them as the unperturbed eigenket. But then, if we were to find the perturbed eigenket $|\psi_k\rangle$, to which state would this go to when $\epsilon \rightarrow 0$?
2. The term $R_k = \frac{P_k}{E_k^{(0)} - \mathcal{H}_0}$ can be singular for the degenerate eigenvalues.

Assume there is a d -fold degeneracy of the eigenvalue E_d , with the unperturbed eigenkets $\{|k_i\rangle\}$ forming a subspace \mathbb{H}_d . We can then define the projectors $Q_d = \sum_{k_i \in \mathbb{H}_d} |k_i\rangle\langle k_i|$ and $P_d = \mathbb{1} - Q_d$. These projectors also define subspaces of the total Hilbert space \mathbb{H} that we will call \mathbb{H}_d (spanned by Q_d) and $\mathbb{H}_{\bar{d}}$ (spanned by P_d).

Notice that because of their nature of projectors, we have the following identities:

$$P_d^2 = P_d, \quad Q_d^2 = Q_d, \quad P_d Q_d = Q_d P_d = 0 \quad \text{and} \quad P_d + Q_d = \mathbb{1}.$$

We then rewrite the eigenvalue equation as:

$$\begin{aligned} (\mathcal{H}_0 + \epsilon V) |\varphi_k\rangle = E_k |\varphi_k\rangle &\rightarrow \mathcal{H}_0(Q_d + P_d) |\varphi_k\rangle + \epsilon V(Q_d + P_d) |\varphi_k\rangle = E_k(Q_d + P_d) |\varphi_k\rangle \\ &\rightarrow (Q_d + P_d)\mathcal{H}_0 |\varphi_k\rangle + \epsilon V(Q_d + P_d) |\varphi_k\rangle = E_k(Q_d + P_d) |\varphi_k\rangle \end{aligned}$$

where we used the fact that $[\mathcal{H}_0, Q_d] = [\mathcal{H}_0, P_d] = 0$ since the projectors are diagonal in the Hamiltonian basis. We then multiply from the left by Q_d and P_d , obtaining 2 equations:

$$\begin{aligned} 1. \quad P_d \times [(Q_d + P_d)\mathcal{H}_0 |\varphi_k\rangle + \epsilon V(Q_d + P_d) |\varphi_k\rangle] &= P_d \times (E_k(Q_d + P_d) |\varphi_k\rangle) \\ &\rightarrow \mathcal{H}_0 P_d |\varphi_k\rangle + \epsilon P_d V(Q_d + P_d) |\varphi_k\rangle = E_k P_d |\varphi_k\rangle \\ 2. \quad Q_d \times [(Q_d + P_d)\mathcal{H}_0 |\varphi_k\rangle + \epsilon V(Q_d + P_d) |\varphi_k\rangle] &= Q_d \times (E_k(Q_d + P_d) |\varphi_k\rangle) \\ &\rightarrow \mathcal{H}_0 Q_d |\varphi_k\rangle + \epsilon Q_d V(Q_d + P_d) |\varphi_k\rangle = E_k Q_d |\varphi_k\rangle \end{aligned}$$

and we simplify the notation by setting $|\psi_k\rangle = P_d |\varphi_k\rangle$ and $|\chi_k\rangle = Q_d |\varphi_k\rangle$

$$\mathcal{H}_0 |\psi_k\rangle + \epsilon P_d V(|\chi_k\rangle + |\psi_k\rangle) = E_k |\psi_k\rangle$$

$$\mathcal{H}_0 |\chi_k\rangle + \epsilon Q_d V(|\chi_k\rangle + |\psi_k\rangle) = E_k |\chi_k\rangle$$

which gives a set of coupled equations in $|\psi_k\rangle$ and $|\chi_k\rangle$:

1. $\epsilon P_d V |\chi_k\rangle = (E_k - \mathcal{H}_0 - \epsilon P_d V P_d) |\psi_k\rangle$
2. $\epsilon Q_d V |\psi_k\rangle = (E_k - \mathcal{H}_0 - \epsilon Q_d V Q_d) |\chi_k\rangle$

Now $(E_k - \mathcal{H}_0 - \epsilon P_d V P_d)^{-1}$ is finally well defined in the P_d subspace, so that we can solve for $|\psi_k\rangle$ from (1.):

$$|\psi_k\rangle = \epsilon P_d (E_k - \mathcal{H}_0 - \epsilon P_d V P_d)^{-1} P_d V |\chi_k\rangle$$

and by inserting this in (2.) we find

$$(E_k - \mathcal{H}_0 - \epsilon Q_d V Q_d) |\chi_k\rangle = \epsilon^2 Q_d V P_d (E_k - \mathcal{H}_0 - \epsilon P_d V P_d)^{-1} P_d V |\chi_k\rangle.$$

If we keep only the first order in ϵ in this equation we have:

$$[(E_k - E_d) - \epsilon Q_d V Q_d] |\chi_k\rangle = 0$$

which is an equation defined on the subspace \mathbb{H}_d only.

We now call $U_d = Q_d V Q_d$ the perturbation Hamiltonian in the \mathbb{H}_d space and $\Delta_k = (E_k - E_d)\mathbb{1}_d$, to get:

$$(\Delta_k - \epsilon U_d) |\chi_k\rangle = 0$$

Often it is possible to just diagonalize U_d (if the degenerate subspace is small enough, for example for a simple double degeneracy) and notice that of course Δ_k is already diagonal. Otherwise one can apply perturbation theory to this subspace. Then we will have found some (exact or approximate) eigenstates of U_d , $|k_i^{(0)}\rangle$, s.t. $U_d |k_i^{(0)}\rangle = u_i |k_i^{(0)}\rangle$ and $\mathcal{H}_0 |k_i^{(0)}\rangle = E_d |k_i^{(0)}\rangle$, $\forall i$. Thus, this step sets what unperturbed eigenstates we should choose in the degenerate subspace, hence solving the first issue of degenerate perturbation theory.

We now want to look at terms $\propto \epsilon^2$ in

$$(E_k - \mathcal{H}_0 - \epsilon U_d) |\chi_k\rangle = \epsilon^2 Q_d V P_d (E_k - \mathcal{H}_0 - \epsilon P_d V P_d)^{-1} P_d V |\chi_k\rangle$$

where we neglected terms higher than second order. Rearranging the terms, we have:

$$E_k |\chi_k\rangle = [\mathcal{H}_0 + \epsilon U_d + \epsilon^2 Q_d V P_d (E_k - \mathcal{H}_0)^{-1} P_d V] |\chi_k\rangle \rightarrow (\tilde{\mathcal{H}}_0 + \tilde{V}) |\chi_k\rangle = E_k |\chi_k\rangle$$

with

$$\tilde{\mathcal{H}}_0 = \mathcal{H}_0 + \epsilon U_d \quad \tilde{V} = \epsilon Q_d V P_d (E_k - \mathcal{H}_0)^{-1} P_d V Q_d$$

If there are no degeneracies left in $\tilde{\mathcal{H}}_0$, we can solve this problem by TIPT and find $|\chi_k^{(n)}\rangle$.

For example, to first order, we have

$$|\chi_{k,i}^{(1)}\rangle = \sum_{j \neq i} \frac{\langle k_j^{(0)} | \tilde{V} | k_i^{(0)} \rangle}{\epsilon(u_i - u_j)} |k_j^{(0)}\rangle$$

and using the explicit form of the matrix element $\tilde{V}_{ij} = \langle k_j^{(0)} | \tilde{V} | k_i^{(0)} \rangle$,

$$\tilde{V}_{ij} = \left\langle k_j^{(0)} \left| \epsilon^2 V P_d (E_d^0 - \mathcal{H}_0)^{-1} P_d V \right| k_i^{(0)} \right\rangle = \epsilon^2 \sum_{h \notin \mathcal{H}_d} \frac{\langle k_j^{(0)} | V | h \rangle \langle h | V | k_i^{(0)} \rangle}{E_d^{(0)} - E_h^{(0)}}$$

we obtain:

$$|\chi_{k,i}^{(1)}\rangle = \epsilon \sum_{j \neq i} \frac{\langle k_j^{(0)} | V | h \rangle}{(u_i - u_j)} \frac{\langle h | V | k_i^{(0)} \rangle}{E_d^{(0)} - E_h^{(0)}} |k_j^{(0)}\rangle$$

Finally, we need to add $|\chi\rangle$ and $|\psi\rangle$ to find the total vector:

$$\begin{aligned} |\varphi_k^{(1)}\rangle &= \sum_{h \notin \mathcal{H}_d} \left(\frac{\langle h|V|k_i\rangle}{E_d^0 - E_h^{(0)}} |h\rangle + \epsilon \sum_{j \neq i} \frac{\langle k_j^{(0)}|V|h\rangle}{(u_i - u_j)} |k_j^{(0)}\rangle \frac{\langle h|V|k_i^{(0)}\rangle}{E_d^{(0)} - E_h^{(0)}} \right) \\ |\varphi_k^{(1)}\rangle &= \sum_{h \notin \mathcal{H}_d} \frac{\langle h|V|k_i\rangle}{E_d^0 - E_h^{(0)}} \left(|h\rangle + \epsilon \sum_{j \neq i} \frac{\langle k_j^{(0)}|V|h\rangle}{(u_i - u_j)} |k_j^{(0)}\rangle \right) \end{aligned}$$

Example: Degenerate TLS

Consider the Hamiltonian $\mathcal{H} = \omega\sigma_z + \epsilon\Omega\sigma_x$. We already solved this Hamiltonian, both directly and with TIPT. Now consider the case $\omega \approx 0$ and a slightly modified Hamiltonian:

$$\mathcal{H} = (\omega_0 + \omega)|0\rangle\langle 0| + (\omega_0 - \omega)|1\rangle\langle 1| + \epsilon\Omega\sigma_x = \omega_0\mathbb{1} + \omega\sigma_z + \epsilon\Omega\sigma_x.$$

We could solve exactly the system for $\omega = 0$, simply finding $E_{0,1} = \omega_0 \pm \epsilon\Omega$ and $|\varphi\rangle_{0,1} = |\pm\rangle = \frac{1}{\sqrt{2}}(|0\rangle \pm |1\rangle)$. We can also apply TIPT.

However the two eigenstates $|0\rangle, |1\rangle$ are (quasi-)degenerate thus we need to apply degenerate perturbation theory. In particular, any basis arising from a rotation of these two basis states could be a priori a good basis, so we need first to obtain the *correct* zeroth order eigenvectors. In this very simple case we have $\mathbb{H}_d = \mathbb{H}$ (the total Hilbert space) and $\mathbb{H}_{\bar{d}} = 0$, or in other words, $Q_d = \mathbb{1}$, $P_d = 0$. We first need to define an equation in the degenerate subspace only:

$$(\Delta_k - \epsilon U_d) |\chi_k\rangle = 0$$

where $U_d = Q_d V Q_d$. Here we have: $U_d = V = \Omega\sigma_x$. Thus we obtain the *correct* zeroth order eigenvectors from diagonalizing this Hamiltonian. Not surprisingly, they are:

$$|\varphi_{0,1}^{(0)}\rangle = |\pm\rangle = \frac{1}{\sqrt{2}}(|0\rangle \pm |1\rangle).$$

with eigenvalues: $E_{0,1} = \omega_0 \pm \epsilon\Omega$. We can now consider higher orders, from the equation:

$$(\tilde{\mathcal{H}}_0 + \tilde{V}) |\chi_k\rangle = E_k |\chi_k\rangle$$

with $\tilde{\mathcal{H}}_0 = \omega_0\mathbb{1} + \epsilon\Omega\sigma_x$ and $\tilde{V} = 0$. Thus in this case, there are no higher orders and we solved the problem.

Example: Spin-1 system

We consider a spin-1 system (that is, a spin system with $S=1$ defined in a 3-dimensional Hilbert space). The matrix representation for the angular momentum operators S_x and S_z in this Hilbert space are:

$$S_x = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad S_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The Hamiltonian of the system is $\mathcal{H} = \mathcal{H}_0 + \epsilon V$ with

$$\mathcal{H}_0 = \Delta S_z^2; \quad V = S_x + S_z$$

Given that

$$S_z^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The matrix representation of the total Hamiltonian is :

$$\mathcal{H} = \begin{pmatrix} \Delta + \epsilon & \frac{\epsilon}{\sqrt{2}} & 0 \\ \frac{\epsilon}{\sqrt{2}} & 0 & \frac{\epsilon}{\sqrt{2}} \\ 0 & \frac{\epsilon}{\sqrt{2}} & \Delta - \epsilon \end{pmatrix}$$

Possible eigenstates of the unperturbed Hamiltonian are $|+1\rangle, |0\rangle, |-1\rangle$:

$$|+1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad |0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |-1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix},$$

with energies $+\Delta, 0, +\Delta$ respectively. However, any combination of $|+1\rangle$ and $|-1\rangle$ is a valid eigenstate, for example we could have chosen:

$$|+1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}, \quad |-1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

This is the case because the two eigenstates are degenerate. So how do we choose which are the correct eigenstates to zeroth order³⁷? We need to first consider the total Hamiltonian in the degenerate subspace.

The degenerate subspace is the subspace of the total Hilbert space H spanned by the basis $|+1\rangle, |-1\rangle$; we can call this subspace H_Q . We can obtain the Hamiltonian in this subspace by using the projector operator Q : $\mathcal{H}_Q = Q\mathcal{H}Q$, with $Q = |+1\rangle\langle+1| + |-1\rangle\langle-1| = S_z^2$. Then:

$$\mathcal{H}_Q = Q(\Delta S_z^2 + \epsilon(S_z + S_x))Q = \Delta S_z^2 + \epsilon S_z$$

(Notice this can be obtained by direct matrix multiplication or multiplying the operators). In matrix form:

$$\mathcal{H}_Q = \begin{pmatrix} \Delta + \epsilon & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \Delta - \epsilon \end{pmatrix} \rightarrow \mathcal{H}_Q = \begin{pmatrix} \Delta + \epsilon & 0 \\ 0 & \Delta - \epsilon \end{pmatrix}$$

where in the last line I represented the matrix in the 2-dimensional subspace H_Q . We can now easily see that the correct eigenvectors for the unperturbed Hamiltonian were the original $|+1\rangle$ and $|-1\rangle$ after all. From the Hamiltonian in the H_Q subspace we can also calculate the first order correction to the energy for the states in the degenerate subspace. These are just $E_{+1}^{(1)} - E_{+1}^{(0)} = +\epsilon$ and $E_{-1}^{(1)} - E_{-1}^{(0)} = -\epsilon$.

Now we want to calculate the first order correction to the eigenstates $|\pm 1\rangle$. This will have two contributions: $|\psi\rangle_{\pm 1}^{(1)} = Q|\psi\rangle_{\pm 1}^{(1)} + P|\psi\rangle_{\pm 1}^{(1)}$ where $P = \mathbb{1} - Q = |0\rangle\langle 0|$ is the complementary projector to Q . We first calculate the first term in the following way. We redefine an unperturbed Hamiltonian in the subspace H_Q :

$$\tilde{\mathcal{H}}_0 = \mathcal{H}_Q = Q\mathcal{H}Q = \Delta S_z^2 + \epsilon S_z$$

and the perturbation in the same subspace is (following Sakurai):

$$\tilde{V} = V_Q = \epsilon Q(VP(\Delta - \mathcal{H}_0)^{-1}PV)Q = \epsilon Q((S_z + S_x)|0\rangle\langle 0|(\Delta|0\rangle\langle 0|)^{-1}|0\rangle\langle 0|(S_z + S_x))Q = \frac{\epsilon}{\Delta}QS_xPS_xQ$$

In matrix form:

$$V_Q = \frac{\epsilon}{2\Delta} \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix} \rightarrow V_Q = \frac{\epsilon}{2\Delta} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = \frac{\epsilon}{2\Delta}(\mathbb{1} + \sigma_x)$$

Now the perturbed eigenstates can be calculated as:

$$Q|\psi\rangle_k^{(1)} = |k\rangle + \epsilon \sum_{h \in H_Q=k} \frac{\langle h|V_Q|k\rangle}{E_k^{(1)} - E_h^{(1)}} |h\rangle$$

³⁷ Here by correct eigenstates I means the eigenstates to which the eigenstates of the total Hamiltonian will tend to when $\epsilon \rightarrow 0$

In our case:

$$Q|\psi\rangle_{+1}^{(1)} = | +1 \rangle + \epsilon \frac{\langle -1 | V_Q | +1 \rangle}{E_{+1}^{(1)} - E_{-1}^{(1)}} | -1 \rangle = | +1 \rangle + \epsilon \frac{\epsilon}{2\Delta} \frac{\langle -1 | (\mathbb{1} + \sigma_x) | +1 \rangle}{2\epsilon} | -1 \rangle = | +1 \rangle + \frac{\epsilon}{4\Delta} | -1 \rangle,$$

$$Q\psi_{-1}^{(1)} = | -1 \rangle - \frac{\epsilon}{4\Delta} | 1 \rangle$$

In order to calculate $P\psi_{\pm 1}^{(1)}$ we can just use the usual formula for non-degenerate perturbation theory, but summing only over the states outside H_Q . Here there's only one of them $|0\rangle$, so :

$$P|\psi\rangle_{\pm 1}^{(1)} = \epsilon \frac{\langle 0 | V | \pm 1 \rangle}{E_{\pm 1} - E_0} | 0 \rangle = \frac{\epsilon}{\sqrt{2}\Delta} | 0 \rangle$$

Finally, the eigenstates to first order are:

$$|\psi_{+1}\rangle^{(1)} = | +1 \rangle + \frac{\epsilon}{4\Delta} | -1 \rangle + \frac{\epsilon}{\sqrt{2}\Delta} | 0 \rangle$$

and

$$|\psi_{-1}\rangle^{(1)} = | -1 \rangle - \frac{\epsilon}{4\Delta} | 1 \rangle + \frac{\epsilon}{\sqrt{2}\Delta} | 0 \rangle$$

The energy shift to second order is calculated from $\Delta_{\pm}^{(2)} = \sum_{h \notin H_Q} \frac{|\langle h | V | \pm 1 \rangle|^2}{\Delta - E_h^{(0)}}$:

$$\Delta_{+1}^{(2)} = \frac{|\langle 0 | V | +1 \rangle|^2}{\Delta} = \frac{\epsilon^2}{2\Delta}$$

and

$$\Delta_{-1}^{(2)} = \frac{|\langle 0 | V | -1 \rangle|^2}{\Delta} = \frac{\epsilon^2}{2\Delta}$$

To calculate the perturbation expansion for $|0\rangle$ and its energy, we use non-degenerate perturbation theory, to find:

$$\Delta_{+1}^{(1)} = \langle 0 | V | 0 \rangle = 0$$

$$|\psi_{+1}\rangle^{(1)} = | 0 \rangle + \epsilon \left(\frac{\langle +1 | V | 0 \rangle}{-\Delta} | +1 \rangle + \frac{\langle -1 | V | 0 \rangle}{-\Delta} | -1 \rangle \right) = -\frac{\epsilon}{\Delta} \frac{| +1 \rangle + | -1 \rangle}{\sqrt{2}}$$

and $\Delta_0^{(2)} = -\frac{\epsilon^2}{\Delta}$.

11.1.3 The Stark effect

We analyze the interaction of a hydrogen atom with a (classical) electric field, treated as a perturbation³⁸. Depending on the hydrogen's state, we will need to use TIPT or degenerate TIPT, to find either a quadratic or linear (in the field) shift of the energy. The shift in energy is usually called Stark shift or Stark effect and it is the electric analogue of the Zeeman effect, where the energy level is split into several components due to the presence of a magnetic field. Measurements of the Stark effect under high field strengths confirmed the correctness of the quantum theory over the Bohr model.

Suppose that a hydrogen atom is subject to a uniform external electric field, of magnitude $|\mathbf{E}|$, directed along the z -axis. The Hamiltonian of the system can be split into two parts. Namely, the unperturbed Hamiltonian,

$$H_0 = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0 r},$$

³⁸ This section follows [Prof. Fitzpatrick](#) online lectures

and the perturbing Hamiltonian

$$H_1 = e |\mathbf{E}| z.$$

Note that the electron spin is irrelevant to this problem (since the spin operators all commute with H_1), so we can ignore the spin degrees of freedom of the system. Hence, the energy eigenstates of the unperturbed Hamiltonian are characterized by three quantum numbers—the radial quantum number n , and the two angular quantum numbers l and m . Let us denote these states as the $|nlm\rangle$, and let their corresponding energy eigenvalues be the E_{nlm} . We use TIPT to calculate the energy shift to first and second order.

A. The quadratic Stark effect

We first want to study the problem using non-degenerate perturbation theory, thus assuming that the unperturbed states are non-degenerate. According to TIPT, the change in energy of the eigenstate characterized by the quantum numbers n, l, m in the presence of a small electric field is given by

$$\Delta E_{nlm} = e |\mathbf{E}| \langle n, l, m | z | n, l, m \rangle + e^2 |\mathbf{E}|^2 \sum_{n', l', m' = n, l, m} \frac{|\langle n, l, m | z | n', l', m' \rangle|^2}{E_{nlm} - E_{n' l' m'}}.$$

This energy-shift is known as the Stark effect. The sum on the right-hand side of the above equation seems very complicated. However, it turns out that most of the terms in this sum are zero. This follows because the matrix elements $\langle n, l, m | z | n', l', m' \rangle$ are zero for virtually all choices of the two sets of quantum number n, l, m and n', l', m' . Let us try to find a set of rules which determine when these matrix elements are non-zero. These rules are usually referred to as the selection rules for the problem in hand.

Now, since $[L_z, z] = 0$, it follows that

$$\langle n, l, m | [L_z, z] | n', l', m' \rangle = \langle n, l, m | L_z z - z L_z | n', l', m' \rangle = \hbar (m - m') \langle n, l, m | z | n', l', m' \rangle = 0.$$

Hence, one of the selection rules is that the matrix element $\langle n, l, m | z | n', l', m' \rangle$ is zero unless

$$m' = m.$$

The selection rule for l can be similarly calculated from properties of the total angular momentum L^2 and its commutator with z . We obtain that the matrix element is zero unless

$$l' = l \pm 1.$$

Application of these selection rules to the perturbation equation shows that the linear (first order) term is zero, while the second order term yields

$$\Delta E_{nlm} = e^2 |\mathbf{E}|^2 \sum_{n', l' = l \pm 1} \frac{|\langle n, l, m | z | n', l', m \rangle|^2}{E_{nlm} - E_{n' l' m}}.$$

Only those terms which vary quadratically with the field-strength have survived. Hence, this type of energy-shift of an atomic state in the presence of a small electric field is known as the **quadratic Stark effect**.

Now, the electric polarizability of an atom is defined in terms of the energy-shift of the atomic state as follows:

$$\Delta E = -\frac{1}{2} \alpha |\mathbf{E}|^2.$$

Hence, we can write

$$\alpha_{nlm} = 2 e^2 \sum_{n', l' = l \pm 1} \frac{|\langle n, l, m | z | n', l', m \rangle|^2}{E_{n' l' m} - E_{nlm}}.$$

Although written for a general state, the equations above assume there is no degeneracy of the unperturbed eigenvalues. However, the unperturbed eigenstates of a hydrogen atom have energies which only depend on the radial quantum number n , thus they have high (and increasing with n) order of degeneracy. We can then only apply the above results to the $n = 1$ eigenstate (since for $n \geq 1$ there will be coupling to degenerate eigenstates with the same

value of n but different values of l). Thus, according to non-degenerate perturbation theory, the polarizability of the ground-state (i.e., $n = 1$) of a hydrogen atom is given by

$$\alpha = 2e^2 \sum_{n>1} \frac{|\langle 1, 0, 0 | z | n, 1, 0 \rangle|^2}{E_n - E_1}.$$

Here, we have made use of the fact that $E_{n10} = E_{n00} = E_n$.

The sum in the above expression can be evaluated approximately by noting that

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2},$$

where $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$ is the Bohr radius. Hence, we can write

$$E_n - E_1 \geq E_2 - E_1 = \frac{3}{4} \frac{e^2}{8\pi\epsilon_0 a_0},$$

which implies that the polarizability is

$$\alpha < \frac{16}{3} 4\pi\epsilon_0 a_0 \sum_{n>1} |\langle 1, 0, 0 | z | n, 1, 0 \rangle|^2.$$

However, thanks to the selection rules we have, $\sum_{n>1} |\langle 1, 0, 0 | z | n, 1, 0 \rangle|^2 = \langle 1, 0, 0 | z^2 | 1, 0, 0 \rangle = \frac{1}{3} \langle 1, 0, 0 | r^2 | 1, 0, 0 \rangle$, where we have made use of the fact that the ground-state of hydrogen is spherically symmetric. Finally, from $\langle 1, 0, 0 | r^2 | 1, 0, 0 \rangle = 3a_0^2$ we conclude that

$$\alpha < \frac{16}{3} 4\pi\epsilon_0 a_0^3 \simeq 5.3 \ 4\pi\epsilon_0 a_0^3.$$

The exact result (which can be obtained by solving Schrödinger's equation in parabolic coordinates) is

$$\alpha = \frac{9}{2} 4\pi\epsilon_0 a_0^3 = 4.5 \ 4\pi\epsilon_0 a_0^3.$$

B. The linear Stark effect

We now examine the effect of an electric field on the excited energy levels $n \geq 1$ of a hydrogen atom. For instance, consider the $n = 2$ states. There is a single $l = 0$ state, usually referred to as 2s, and three $l = 1$ states (with $m = -1, 0, 1$), usually referred to as 2p. All of these states possess the same energy, $E_2 = -e^2/(32\pi\epsilon_0 a_0)$. Because of the degeneracy, the treatment above is no longer valid and in order to apply perturbation theory, we have to recur to degenerate perturbation theory.

We first need to $U_d = Q_d V Q_d$, where Q_d is the projector obtained from the degenerate 2s and 2p states (that is, the operator that project into the degenerate subspace). This operator is,

$$U_d = e |\mathbf{E}| \begin{pmatrix} 0 & \langle 2, 0, 0 | z | 2, 1, 0 \rangle & 0 & 0 \\ \langle 2, 1, 0 | z | 2, 0, 0 \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \rightarrow \begin{pmatrix} 0 & \langle 2, 0, 0 | z | 2, 1, 0 \rangle \\ \langle 2, 1, 0 | z | 2, 0, 0 \rangle & 0 \end{pmatrix},$$

where the rows and columns correspond to the $|2, 0, 0\rangle$, $|2, 1, 0\rangle$, $|2, 1, 1\rangle$ and $|2, 1, -1\rangle$ states, respectively and in the second step we reduce the operator to the degenerate subspace only. To simplify the matrix we used the selection rules, which tell us that the matrix element of between two hydrogen atom states is zero unless the states possess the same n quantum number, and l quantum numbers which differ by unity. It is easily demonstrated, from the exact forms of the 2s and 2p wave-functions, that

$$\langle 2, 0, 0 | z | 2, 1, 0 \rangle = \langle 2, 1, 0 | z | 2, 0, 0 \rangle = 3a_0.$$

It can be seen, by inspection, that the eigenvalues of U_d are $u_1 = 3 e a_0 |\mathbf{E}|$, $u_2 = -3 e a_0 |\mathbf{E}|$, with corresponding eigenvectors

$$\begin{aligned} |k_1^{(0)}\rangle &= \frac{|2, 0, 0\rangle + |2, 1, 0\rangle}{\sqrt{2}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}, \\ |k_2^{(0)}\rangle &= \frac{|2, 0, 0\rangle - |2, 1, 0\rangle}{\sqrt{2}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \end{aligned}$$

In the absence of an electric field, all of these states possess the same energy, E_2 . The first-order energy shifts induced by an electric field are given by

$$\begin{aligned} \Delta E_1 &= +3 e a_0 |\mathbf{E}|, \\ \Delta E_2 &= -3 e a_0 |\mathbf{E}|, \end{aligned}$$

Thus, the energies of states 1 and 2 are shifted upwards and downwards, respectively, by an amount $3 e a_0 |\mathbf{E}|$ in the presence of an electric field. States 1 and 2 are orthogonal linear combinations of the original 2s and 2p(m=0) states. Note that the energy shifts are linear in the electric field-strength, so this is a much larger effect than the quadratic effect described in the previous section.

The energies of states 2p(m=1) and 2p(m=-1) (which are outside the degenerate subspace) are not affected to first-order (as we already saw above for the non-degenerate case). Of course, to second-order the energies of these states are shifted by an amount which depends on the square of the electric field-strength, the quadratic shift found previously. Note that the linear Stark effect depends crucially on the degeneracy of the 2s and 2p states. This degeneracy is a special property of a pure Coulomb potential, and, therefore, only applies to a hydrogen atom. Thus, alkali metal atoms do not exhibit the linear Stark effect.

11.2 Time-dependent perturbation theory

11.2.1 Review of interaction picture

When first studying the time evolution of QM systems, one approach was to separate the Hamiltonian much in the same way we did above for TIPT. We wrote (see Section 5.2):

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

where \mathcal{H}_0 is a "solvable" Hamiltonian of which we already know the eigen-decomposition,

$$\mathcal{H}_0|k\rangle = E_k^0|k\rangle,$$

(so that it is easy to calculate e.g. $U_0 = e^{-i\mathcal{H}_0 t}$) and $V(t)$ is a perturbation that drives an interesting (although unknown) dynamics. Here we even allow for the possibility that V is time-dependent. For any state $|\psi\rangle = \sum_k c_k(0)|k\rangle$ the evolution can be written as $|\psi\rangle = \sum_k c_k(t)e^{-iE_k^0 t}|k\rangle$. This correspond to explicitly writing down the evolution due to the known Hamiltonian (if $\mathcal{H} = \mathcal{H}_0$ then we would have $c_k(t) = c_k(0)$ and the evolution would be given by only the phase factors). In other words, if we want to compare the state evolution with the initial eigenstates, by calculating the overlap $|\langle k|\psi(t)\rangle|^2$, we would be really interested only in the dynamics driven by V since $|\langle k|\psi(t)\rangle|^2 = |c_k(t)|^2$ (while E_k^0 do not play a role).

We define states in the interaction picture by

$$|\psi\rangle_I = U_0(t)^\dagger |\psi\rangle = e^{i\mathcal{H}_0 t} |\psi\rangle$$

Similarly we define the corresponding interaction picture operators as:

$$A_I(t) = U_0^\dagger A U_0 \rightarrow V_I(t) = U_0^\dagger V U_0$$

We can now derive the differential equation governing the evolution of the state in the interaction picture, starting from Schrödinger equation.

$$i \frac{\partial |\psi\rangle_I}{\partial t} = i \frac{\partial (U_0^\dagger |\psi\rangle)}{\partial t} = i \left(\frac{\partial U_0^\dagger}{\partial t} |\psi\rangle + U_0^\dagger \frac{\partial |\psi\rangle}{\partial t} \right)$$

Inserting $\partial_t U_0 = i\mathcal{H}_0 U_0$ and $i\partial_t |\psi\rangle = \mathcal{H}_0 |\psi\rangle$, we obtain

$$i \frac{\partial |\psi\rangle_I}{\partial t} = U_0^\dagger \mathcal{H}_0 |\psi\rangle - U_0^\dagger (\mathcal{H}_0 + V) |\psi\rangle = U_0^\dagger V |\psi\rangle.$$

Inserting the identity $\mathbb{1} = U_0 U_0^\dagger$, we obtain $= U_0^\dagger V U_0 U_0^\dagger |\psi\rangle = V_I |\psi\rangle_I$:

$$i \frac{\partial |\psi\rangle_I}{\partial t} = V_I(t) |\psi\rangle_I$$

This is a Schrödinger -like equation for the vector in the interaction picture, evolving under the action of the operator $V_I(t)$ only.

11.2.2 Dyson series

Besides expressing the Schrödinger equation in the interaction picture, we can also write the equation for the propagator that describes the evolution of the state:

$$\frac{dU_I}{dt} = -iV_I U_I, \quad |\psi(t)\rangle_I = U_I(t) |\psi(0)\rangle$$

Since $V_I(t)$ is time-dependent, we can only write formal solutions for U_I . One expression is given by the Dyson series. The differential equation is equivalent to the integral equation

$$U_I(t) = \mathbb{1} - i \int_0^t V_I(t') U_I(t') dt'$$

By iterating, we can find a formal solution to this equation :

$$\begin{aligned} U_I(t) = & \mathbb{1} - i \int_0^t dt' V_I(t') + (-i)^2 \int_0^t dt' \int_0^{t'} dt'' V_I(t') V_I(t'') + \dots \\ & + (-i)^n \int_0^t dt' \dots \int_0^{t^{(n-1)}} dt^{(n)} V_I(t') \dots V_I(t^{(n)}) + \dots \end{aligned}$$

This is the Dyson series.

11.2.3 Fermi's Golden Rule

The problem that we try to solve via TDPT is to calculate the **transition probability** from an initial state to a final state. Consider an initial state $|i\rangle$ which is an eigenstate of \mathcal{H}_0 ($\mathcal{H}_0 |i\rangle = E_i |i\rangle$). Then in the interaction picture we have the evolution

$$|i(t)\rangle_I = U_I(t) |i\rangle = \sum_k c_k(t) |k\rangle, \quad \text{with} \quad c_k(t) = \langle k | U_I(t) | i \rangle$$

We can insert the perturbation expansion for $U_I(t)$ to obtain an expansion for $c_k(t)$:

$$c_k(t) = \langle k | \mathbb{1} - i \int_0^t V_I(t') U_I(t') dt' | i \rangle = \langle k | \left[\mathbb{1} - i \int_0^t dt' V_I(t') + (-i)^2 \int_0^t dt' \int_0^{t'} dt'' V_I(t') V_I(t'') + \dots \right] | i \rangle$$

In the expansion we will obtain terms such as $\langle k | V_I(t) | i \rangle$ that we can simplify since:

$$\langle k | V_I(t) | i \rangle = \langle k | (U_0^\dagger V(t) U_0) | i \rangle = \langle U_0 k | V(t) | U_0 i \rangle = \langle k | e^{i\omega_k t} V(t) e^{-i\omega_i t} | i \rangle = \langle k | V | i \rangle e^{i\omega_{ki} t} = V_{ki}(t) e^{i\omega_{ki} t}$$

where we defined $\omega_j = E_j/\hbar$ and $\omega_{ki} = \omega_k - \omega_i$. Using these relationships and the series expansion we obtain:

$$\begin{aligned} c_k^{(0)}(t) &= \langle k | \mathbb{1} | i \rangle = \delta_{ki} \\ c_k^{(1)}(t) &= -i \int_0^t \langle k | V_I(t') | i \rangle dt' = -i \int_0^t V_{ki}(t') e^{i\omega_{ki} t'} dt' \\ c_k^{(2)}(t) &= - \int_0^t dt' \int_0^{t'} dt'' V_{kh}(t') V_{hi}(t'') e^{i\omega_{kh} t'} e^{i\omega_{hi} t''} \end{aligned}$$

From this expansion we can calculate the transition probability as $P(i \rightarrow k) = |c_k(t)|^2$.

We first consider the case where the perturbation V is time-independent and it is turned on at the time $t = 0$. Then we have

$$c_k^{(1)}(t) = -i V_{ki} \int_0^t e^{i\omega_{ki} t'} dt' = \frac{V_{ki}}{\omega_{ki}} (1 - e^{i\omega_{ki} t}) = -2i \frac{V_{ki}}{\omega_{ki}} e^{i\omega_{ki} t/2} \sin\left(\frac{\omega_{ki} t}{2}\right)$$

Then to first order perturbation, the transition probability is

$$P(i \rightarrow k) = \frac{4|V_{ki}|^2}{\omega_{ki}^2} \sin^2\left(\frac{\omega_{ki} t}{2}\right)$$

We can plot this transition probability as a function of the energy separation ω_{ki} between the two states. We would expect that if the separation in energy is smaller, it will be easier to make the transition. This is indeed the case, since P has the shape of a sinc function square.

Notice that the peak height is proportional to t^2 , while the zeros appear at $2k\pi/t$, that is, the peak width is proportional to $1/t$ (the other peaks are quite small). This means that the probability is significantly different than

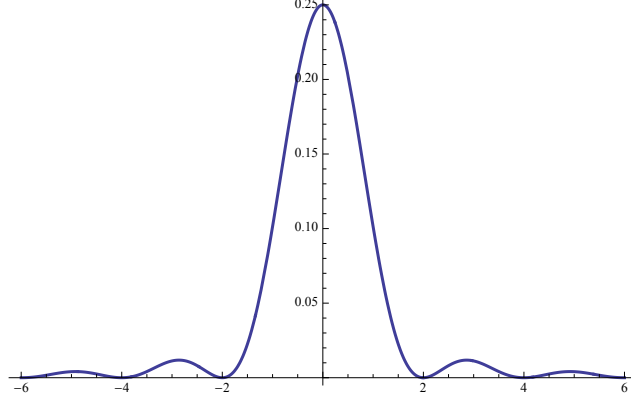


Fig. 19: Transition probability

zero only for $\omega_{ki}t \leq 2\pi$. In terms of energy, we have that $\Delta t \Delta E \sim \hbar$ (where we defined Δt as the duration of the interaction), or in other words, we can have a change of energy in the system only at short times, while at long times we require quasi-conservation of energy. Consider the limit of the sinc function:

$$\lim_{t \rightarrow \infty} \frac{\sin(\omega t/2)}{\omega} = \pi \delta(\omega)$$

Then, from $f(x)\delta(x) = f(0)$ and $\text{sinc}(0) = 1$, we obtain

$$\lim_{t \rightarrow \infty} \left(\frac{\sin(\omega t/2)}{\omega} \right)^2 = \frac{\sin(\omega t/2)}{\omega} \lim_{t \rightarrow \infty} \frac{\sin(\omega t/2)}{\omega} = \frac{\sin(\omega t/2)}{\omega} \pi \delta(\omega) = \left(\frac{\sin(\omega t/2)}{\omega t/2} \right) \frac{t}{2} \pi \delta(\omega) = \frac{\pi t}{2} \delta(\omega)$$

We have then found the transition probability at long time:

$$P(i \rightarrow k) \xrightarrow{t \rightarrow \infty} \frac{\pi t}{2} \delta(\omega) 4|V_{ki}|^2,$$

which confirms the fact that in the long-time limit we need to enforce energy conservation. A better defined quantity is the *rate* of transition:

$$W(i \rightarrow k) = 2\pi |V_{ki}|^2 \delta(\omega).$$

Notice that for $\omega_{ki} = 0$, from $c_k^{(1)}(t) = -iV_{ki} \int_0^t e^{i\omega_{ki}t'} dt'$ we obtain $c_k^{(1)}(t) = -iV_{ki}t$ and thus the probability $|c_k(t)|^2 = |V_{ki}|^2 t^2$. There is a quadratic dependence on time for a single final state.

Now we consider a continuum of final states, all with energy $E_{k_f} \approx E_i$. Then the probability of a transition to this continuum is given by the sum of the probability for each individual state: $P_f = \sum_k |c_k|^2 \rightarrow \int dE_k \rho(E_k) |c_k|^2$, where we defined the density of states $\rho(E_k)$, such that $\rho(E_k)dE_k$ is the number of states with energy between E_k and $E_k + dE_k$. We can then rewrite the probability as

$$P_{i \rightarrow f} = 4 \int dE \rho(E) \sin^2 \left(\frac{(E - E_i)t}{2} \right) \frac{|V_{ki}|^2}{(E - E_i)^2}$$

Using the limit of the sinc function, we find

$$P_{i \rightarrow f} = 4 \int dE \rho(E) \delta(E - E_i) \frac{\pi t}{2} \frac{|V_{ki}|^2}{(E - E_i)^2}$$

Since all the states are in a neighborhood of the energy, we expect $|V_{ki}|^2 \approx |\bar{V}_{ki}|^2$ over the range of energy of interest. Thus by evaluating the integral (with the delta function) we obtain the transition probability:

$$P_{i \rightarrow f} = 2|V_{ki}|^2 \pi t \rho(E_k)|_{E_k \approx E_i}$$

Similarly, we can calculate the transition rate to a continuum of states. From the expression for a single state, $W_{i \rightarrow k} = \frac{2\pi}{\hbar} |V_{ki}|^2 \delta(E_k - E_i)$, we integrate over all final energies, $W_{i \rightarrow f} = \int W_{i \rightarrow k} \rho(E_k) dE_k$, where f is the continuum of states k such that $E_k \approx E_i$. Then we obtain the transition rate:

$$W = \frac{2\pi}{\hbar} |V_{ki}|^2 \rho(E_k)|_{E_k \approx E_i}$$

This is Fermi's Golden Rule.

Virtual Transitions

If the matrix element of the interaction connecting two given state is zero, we have seen from the expression above that no transition is possible, *to first order*.

However, consider $c_k^{(2)}(t)$. This is given by

$$c_k^{(2)}(t) = - \sum_h V_{kh} V_{hi} \int_0^t dt' \int_0^{t'} dt'' e^{i\omega_{kh}t'} e^{i\omega_{hi}t''} = i \sum_h \frac{V_{kh} V_{hi}}{\omega_{ki}} \int_0^t dt' (\underbrace{e^{i\omega_{ki}t'}}_{\text{same as before}} - \underbrace{e^{i\omega_{kh}t'}}_{\approx 0})$$

If $E_h \neq E_k, E_i$, the second term oscillates rapidly and goes to zero. Finally we have:

$$W_{i \rightarrow k} = \frac{2\pi}{\hbar} \left| V_{ki} + \sum_h \frac{V_{kh} V_{hi}}{\omega_{ki}} \right|^2 \delta(E_k - E_i)$$

or for a continuum

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| V_{ki} + \sum_h \frac{V_{kh} V_{hi}}{\omega_{ki}} \right|^2 \rho(E_k)|_{E_k \approx E_i}$$

Notice that even if $V_{ik} = 0$, we can still have a transition to k , via *virtual* transitions to intermediate states, which are connected to the two relevant levels.

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