10 Time-Independent Perturbation Theory

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Only a few quantum mechanical problems can be solved exactly. However, if the system Hamiltonian can be separated into two parts: an unperturbed part (we know how to solve it) and a perturbation (it is small as compared to the first term) we may get an approximate solution using a perturbation approach.

Suppose that we search for eigenenergies and eigenstates of a Hamiltonian \( H \),

\[
H|k\rangle = E_k|k\rangle,
\]

and the Hamiltonian can be written in a form

\[
H = H_0 + V,
\]

where \( H_0 \) is an unperturbed part and \( V \) is a perturbation. Let us also assume that the unperturbed Hamiltonian is rather simple and its eigenvalues and eigenstates are known

\[
H_0|n_0\rangle = E_n^{(0)}|n_0\rangle.
\]

Below we discuss two distinct situations: a) all the eigenvalues of the Hamiltonian \( H_0 \) are different (it is a non-degenerate case) and b) some of the states of the unperturbed Hamiltonian have the same energy (degenerate case).

### 10.1 Non-degenerate case

We consider a non-degenerate case, assuming that the perturbation term, \( V \) is much smaller than the splitting between any two energy levels of the unperturbed Hamiltonian

\[
E_i^{(0)} - E_m^{(0)} \gg ||V||,
\]

where \(||V||\) may be defined as a maximal eigenvalue of the perturbation term.

Firstly, we rewrite the Hamiltonian (2) introducing explicitly a parameter \( \lambda \) that determines how small is a particular term

\[
H = H_0 + \lambda V.
\]
\( \lambda \) is a fictitious parameter, its actual value is not important.

The eigenstates \(|k\rangle\) and the eigenenergies \(E_k\) of the total Hamiltonian (5) can be expanded in series of \(\lambda\) as

\[ |k\rangle = \sum_{\nu=0}^{\infty} \lambda^\nu |k^{(\nu)}\rangle, \]  
\[ E_k = \sum_{\nu=0}^{\infty} \lambda^\nu E_k^{(\nu)}. \]  

We also can formally write the Hamiltonian (5) as

\[ H = \sum_{\nu=0}^{\infty} \lambda^\nu H^{(\nu)}. \]  

Substituting Eqs. (6-8) into Eq. (1) and collecting terms with the same power of \(\lambda\) we get

\[ \sum_{\nu=0}^{\infty} \lambda^\nu \sum_{\mu} \left( H^{(\mu)} - E_k^{(\mu)} \right) |k^{(\nu-\mu)}\rangle = 0. \]  

Because \(\lambda\) may be an arbitrary number each term with a given power of \(\lambda\) in Eq. (9) should be zero.

In the result, for the correction of the order \(\nu\) we have an equation

\[ (H_0 - E_k^{(0)})|k^{(\nu)}\rangle + (V - E_k^{(1)})|k^{(\nu-1)}\rangle + \sum_{\mu=2}^{\nu} E_k^{(\mu)}|k^{(\nu-\mu)}\rangle = 0, \]  

where we substitute explicitly the terms of the Hamiltonian \(H\) with \(H^{(0)} = H_0\), \(H^{(1)} = V\), and \(H^{(\mu)} = 0\) for \(\mu > 1\).

In a general case, we write corrections to the eigenstates, \(|k^{(\nu)}\rangle\), in the terms of unperturbed orthonormal states as

\[ |k^{(\nu)}\rangle = \sum_{n} a_{nk}^{(\nu)} |n_0\rangle. \]  

We also choose the perturbed state to be unnormalized and satisfying the condition

\[ \langle k^{(0)} | k \rangle = 1. \]  

For the zero-order perturbation \(|k^{(0)}\rangle = |n_0\rangle\). For any order \(\nu > 0\) the correction to the eigenvector, \(|k^{(\nu)}\rangle\), is orthogonal to the initial state, \(|k^{(0)}\rangle\). The normalization of the state can be done at the last stage, after the eigenstate is calculated up to the required order.
The inner product of $\langle k^{(0)} |$ and Eq. 10 gives us that a $\nu$-th order correction to the eigenenergy of a state $k$, which can be calculated using wave functions of the $\nu - 1$ order

$$E_k^{(\nu)} = \langle k^{(0)} | V | k^{(\nu-1)} \rangle.$$  \h  (13)

If we take the inner product of a state $\langle m^{(0)} |$ with Eq. 10, where $m \neq k$ we obtain the expansion coefficients of Eq. 11 as

$$a_{mk}^{(\nu)} = \frac{1}{E_k^{(0)} - E_m^{(0)}} \left( \langle m^{(0)} | V - E_k^{(1)} | k^{(\nu-1)} \rangle - \sum_{\mu=2}^{\nu} E_k^{(\mu)} a_{mk}^{(\nu-\mu)} \right).$$  \h  (14)

As an exercise, it is straightforward to get first and second order perturbations of the eigenenergies and eigenstates. Using Eqs. (13) and (14), and evaluating matrix elements of $V$ in the unperturbed basis $\{ n_0 \}$, we obtain

First order:

$$E_k^{(1)} = V_{kk},$$  \h  (15)

$$a_{mk}^{(1)} = \frac{V_{mk}}{E_k^{(0)} - E_m^{(0)}}.$$  \h  (16)

Second order:

$$E_k^{(2)} = \sum_m \frac{V_{km} V_{mk}}{E_k^{(0)} - E_m^{(0)}}.$$  \h  (17)

Exercise: derive second order corrections to the eigenstate.

Example: let us consider a 3-level system with the unperturbed Hamiltonian

$$H_0 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix},$$  \h  (18)

and the perturbation term

$$V = \begin{pmatrix} 0 & 0 & \hat{V}_{02} \\ 0 & V_{11} & V_{12} \\ \hat{V}_{20} & V_{21} & 0 \end{pmatrix}.$$  \h  (19)

The first order corrections to the eigenenergies are

$$E_0^{(1)} = 0,$$  \h  (20)

$$E_1^{(1)} = \hat{V}_{11},$$  \h  (21)

$$E_2^{(1)} = 0.$$  \h  (22)
The second order corrections to the energies of the states are

\[ E^{(2)}_0 = -\frac{V_{02}V_{20}}{E_2}, \]  
\[ E^{(2)}_1 = \frac{V_{12}V_{21}}{E_1 - E_2}, \]  
\[ E^{(2)}_2 = \frac{V_{20}V_{02}}{E_2} + \frac{V_{21}V_{12}}{E_2 - E_1}. \]  

(23)  
(24)  
(25)

### 10.2 Degenerate case

If some states of the system are degenerate then the perturbation procedure described above is invalid. For instance, the expansion of Eq. (14) diverges if \( E_k = E_n \). We need to derive another procedure to resolve this.

Let us consider a two-level system \{\( |1\rangle, |2\rangle \}\) and assume that the energy levels are degenerate, \( E_1 = E_2 = E \). The unperturbed Hamiltonian is

\[ H_0 = E(|1\rangle\langle 1| + |2\rangle\langle 2|). \]  

(26)

However, any two orthonormal superpositions of the states \( |1\rangle \) and \( |2\rangle \) also can be used as a basis. For a degenerate Hamiltonian all these bases are equivalent.

Now, let us include a perturbation term, \( \lambda V \). The Hamiltonian of the system is

\[ H = H_0 + \lambda V. \]  

(27)

Similarly to the previous section, we use the parameter \( \lambda \) to show that the perturbation is small. In the case when \( \lambda \to 0 \) the Hamiltonian returns to \( H_0 \), but the eigenstates may be different from the original ones. The perturbation determines a specific basis

\[ |1'\rangle = a_1^{(0)}|1\rangle + a_2^{(0)}|2\rangle, \]  
\[ |2'\rangle = b_1^{(0)}|1\rangle + b_2^{(0)}|2\rangle. \]  

(28)

To define that basis it is enough to find only two coefficients in Eq. (28). Why?

Let us expand the eigenstate of the Hamiltonian (27) as

\[ |\psi\rangle = |1'\rangle + \lambda |\psi^{(1)}\rangle + O(V^2). \]  

(29)

The eigenenergy can be written in a similar form as

\[ E = E^{(0)} + \lambda E^{(1)} + O(V^2). \]  

(30)
If we substitute Eqs. (29) and (30) into Eq. (27), the linear in \( \lambda \) term will be

\[
(H_0 - E^{(0)}) |\psi^{(1)}\rangle + (V - E^{(1)}) |1'\rangle = 0.
\] (31)

This relation determines the energy correction \( E^{(1)} \) and the eigenstate \( |1'\rangle \). Equation (31) can be written in a matrix form. We take inner products of Eq. (31) with the basis states \langle 1 | \) and \langle 2 | to get the secular equation

\[
\begin{pmatrix}
V_{11} & V_{12} \\
V_{21} & V_{22}
\end{pmatrix}
\begin{pmatrix}
a_1^{(0)} \\
a_2^{(0)}
\end{pmatrix}
= E^{(1)}
\begin{pmatrix}
a_1^{(0)} \\
a_2^{(0)}
\end{pmatrix}.
\] (32)

This is a homogeneous equation. It has nontrivial solutions if the determinant is zero. Solving the equation

\[
\det |V - E^{(1)}| = 0
\] (33)

we obtain first order corrections to energies of the states. Then, for each value of \( E^{(1)} \) eigenstates of the secular equation (32) determines the “correct” basis states \( |1'\rangle \) and \( |2'\rangle \). If in Eq. (27) \( \lambda \to 0 \), the eigenstates of the system tend to \( |1'\rangle \) and \( |2'\rangle \). If on some reasons we get that the eigenstates of the system are not splitted in the first order we should do the same procedure up to the second order.

References