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Lecture 10

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,

$$H|k\rangle = E_k|k\rangle, \tag{1}$$

and the Hamiltonian can be written in a form

$$H = H_0 + V, \tag{2}$$

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

$$H_0|n_0\rangle = E_n^{(0)}|n_0\rangle. \tag{3}$$

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

$$E_l^{(0)} - E_m^{(0)} \gg ||V||, \tag{4}$$

where $||V||$ may be defined as a maximal eigenvalue of the perturbation term.
Firstly, we rewrite the Hamiltonian (2) introducing explicitly a parameter λ that determines how small is a particular term

$$H = H_0 + \lambda V. \tag{5}$$

λ 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 λ as

$$|k\rangle = \sum_{\nu=0}^{\infty} \lambda^{\nu} |k^{(\nu)}\rangle, \tag{6}$$

$$E_k = \sum_{\nu=0}^{\infty} \lambda^{\nu} E_k^{(\nu)}. \tag{7}$$

We also can formally write the Hamiltonian (5) as

$$H = \sum_{\nu=0}^{\infty} \lambda^{\nu} H^{(\nu)}. \tag{8}$$

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

$$\sum_{\nu=0}^{\infty} \lambda^{\nu} \sum_{\mu}^{\nu} \left(H^{(\mu)} - E_k^{(\mu)} \right) |k^{(\nu-\mu)}\rangle = 0. \tag{9}$$

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

In the result, for the correction of the order ν we have an equation

$$(H_0 - E_k^{(0)})|k^{(\nu)}\rangle + (V - E_k^{(1)})|k^{(\nu-1)}\rangle + \sum_{\mu=2}^{\nu} E_k^{(\mu)} |k^{(\nu-\mu)}\rangle = 0, \tag{10}$$

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

$$|k^{(\nu)}\rangle = \sum_{n} a_{nk}^{(\nu)} \cdot |n_0\rangle. \tag{11}$$

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

$$\langle k^{(0)}|k\rangle = 1. \tag{12}$$

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 ν-th order correction to the eigenenergy of a state k, which can be calculated using wave functions of the $\nu-1$ order

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

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

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

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:

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

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

Second order:

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

Exercise: derive second order corrections to the eigenstate.

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

$$H_0 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & E_1 & 0 \\ 0 & 0 & E_2 \end{pmatrix}, \tag{18}$$

and the perturbation term

$$V = \begin{pmatrix} 0 & 0 & V_{02} \\ 0 & V_{11} & V_{12} \\ V_{20} & V_{21} & 0 \end{pmatrix}. \tag{19}$$

The first order corrections to the eigenenergies are

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

$$E_1^{(1)} = V_{11}, \tag{21}$$

$$E_2^{(1)} = 0. \tag{22}$$

The second order corrections to the energies of the states are

$$E_0^{(2)} = -\frac{V_{02}V_{20}}{E_2}, \tag{23}$$

$$E_1^{(2)} = \frac{V_{12}V_{21}}{E_1 - E_2}, \tag{24}$$

$$E_2^{(2)} = \frac{V_{20}V_{02}}{E_2} + \frac{V_{21}V_{12}}{E_2 - E_1}. \tag{25}$$

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

$$H_0 = E(|1\rangle\langle 1| + |2\rangle\langle 2|). \tag{26}$$

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, λV. The Hamiltonian of the system is

$$H = H_0 + \lambda V. \tag{27}$$

Similarly to the previous section, we use the parameter λ 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

$$\begin{aligned} |1'\rangle &= a_1^{(0)}|1\rangle + a_2^{(0)}|2\rangle, \\ |2'\rangle &= b_1^{(0)}|1\rangle + b_2^{(0)}|2\rangle. \end{aligned} \tag{28}$$

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

$$|\psi\rangle = |1'\rangle + \lambda|\psi^{(1)}\rangle + O(V^2). \tag{29}$$

The eigenenergy can be written in a similar form as

$$E = E^{(0)} + \lambda E^{(1)} + O(V^2). \tag{30}$$

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

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

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

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

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

$$\det |V - E^{(1)}| = 0 \tag{33}$$

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

[1] P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics* (Third Ed. Oxford University Press, New York, 1997), Chapters 6.0–6.8