

Lecture 11

11 Perturbation Theory

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11.1 Variational Principle

If we need to compute the ground state energy of a system, it may be easier to use the variational principle rather than a perturbation theory. The variational method defines the upper boundary for the ground state energy as

$$E_0 \leq \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle}, \quad (1)$$

where $|\phi\rangle$ is a variational wavefunction. The ratio at the right hand side of inequality (1) is also called *Rayleigh ratio*.

Equation (1) can be proven as follows. Let us assume that the eigenenergies and the eigenstates of the Hamiltonian H are defined by

$$H|\psi_n\rangle = E_n|\psi_n\rangle. \quad (2)$$

Any arbitrary wavefunction $|\phi\rangle$ may be written as

$$|\phi\rangle = \sum_n a_n |\psi_n\rangle. \quad (3)$$

If we substitute Eq. (3) into Eq. (1) we get that

$$\sum_n |a_n|^2 E_n \geq E_0 \sum_n |a_n|^2, \quad (4)$$

which is correct because E_0 is the smallest eigenvalue.

To get the upper boundary close enough to the real value we need to make a correct choice of the wavefunction. The wavefunction should satisfy the symmetry of the problem. If the variational wavefunction has an improper symmetry it will give a worse estimation of the energy. We may introduce a class of wavefunctions $|\phi(\lambda)\rangle$ that depends on the parameter λ . Then, varying λ we can

minimize the value at the right hand side of Eq. (1), which will define the upper boundary for the ground state energy. It should be noticed that while the eigenenergy has quadratic dependence on λ , in a general case, the wavefunction depends linearly on the variational parameter. This means that for the energy we always get better estimations rather than for the wavefunctions.

Example: Harmonic Oscillator.

The Hamiltonian of a one-dimensional harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2. \quad (5)$$

We use a trial function

$$\langle x|\psi\rangle = e^{-\lambda x^2}, \quad (6)$$

to estimate the ground state energy. We get that

$$\langle \psi|\psi\rangle = \sqrt{\frac{\pi}{2\lambda}}, \quad (7)$$

$$\langle \psi|x^2|\psi\rangle = \frac{\sqrt{\pi}}{2(2\lambda)^{3/2}}, \quad (8)$$

and

$$\langle \psi|p^2|\psi\rangle = \hbar^2 \sqrt{\frac{\pi\lambda}{2}}. \quad (9)$$

The Rayleigh ration is

$$\varepsilon(\lambda) = \frac{\hbar^2 \lambda}{2m} + \frac{m\omega^2}{8\lambda}. \quad (10)$$

It has a minimum if

$$\frac{\partial \varepsilon}{\partial \lambda} = 0, \quad (11)$$

and

$$\frac{\partial^2 \varepsilon}{\partial \lambda^2} > 0. \quad (12)$$

In the result we get that

$$\lambda = \frac{m\omega}{2\hbar}, \quad (13)$$

and the upper boundary of the ground state energy coincides with its exact value

$$E_0 = \frac{\hbar\omega}{2}. \quad (14)$$

The Rayleigh-Ritz method: In this method we choose a trial wavefunction as a superposition of some basis functions

$$|\phi\rangle = \sum_i c_i |\psi_i\rangle. \quad (15)$$

In this case the variational parameters are the coefficients c_i .

Self-reading: For the details of the Rayleigh-Ritz method see Ref. [1], section 6.10.

11.2 Time-dependent perturbation theory

We solve a problem similar to that is defined in section Time-independent perturbation theory. The difference is that the perturbation V can be time dependent. Though, we do not write it explicitly to simplify the notation. The Hamiltonian is

$$H = H_0 + V. \quad (16)$$

Eigenenergies and eigenstates of the unperturbed Hamiltonian are defined by

$$H_0|n\rangle = E_n|n\rangle. \quad (17)$$

The time-dependent Schrödinger equation is

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H|\psi(t)\rangle. \quad (18)$$

Firstly, we rewrite the Schrödinger equation (18) in *Interaction Picture*. This allows us to eliminate wavefunction dynamics associated with the unperturbed Hamiltonian. The wavefunction in interaction picture is related to the wavefunction in Schrödinger picture as

$$|\psi_I(t)\rangle = e^{iH_0t/\hbar}|\psi_S(t)\rangle. \quad (19)$$

The Hamiltonian is also transformed as

$$H_I = e^{iH_0t/\hbar}He^{-iH_0t/\hbar}. \quad (20)$$

If we substitute Eqs. (19) and (20) into the Schrödinger equation (18) we get that in interaction picture it may be written as

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = V_I|\psi_I(t)\rangle, \quad (21)$$

with a formal solution

$$|\psi_I(t)\rangle = T\{e^{-\int_0^t V_I d\tau}\}|\psi_I(0)\rangle. \quad (22)$$

Let us write the wavefunction $|\psi_I(t)\rangle$ in terms of eigenstates of the unperturbed Hamiltonian

$$|\psi_I(t)\rangle = \sum_m a_m(t)|m\rangle. \quad (23)$$

If we substitute this expansion into Eq. (21) and take an inner product with a state $\langle n|$ we get an equation for the coefficients

$$i\hbar \frac{da_n}{dt} = \sum_m V_{nm} e^{i\omega_{nm}t} a_m, \quad (24)$$

where $\omega_{nm} = (E_n - E_m)/\hbar$ and $V_{nm} = \langle n|V|m\rangle$. If at initial moment of time the system was in a single state

$$a_n(0) = \delta_{nk} \quad (25)$$

then the probability amplitude to find the system in the same state at time t is equal to

$$a_k(t) = e^{-\frac{i}{\hbar} \int_0^t V_{kk} d\tau}, \quad (26)$$

and the probability amplitude to find the system in another state $|n\rangle$ is

$$a_n = -\frac{i}{\hbar} \int_0^t V_{nk} e^{i\omega_{nk}\tau} d\tau. \quad (27)$$

Deriving Eqs. (26) and (27) we assume that the perturbation is weak. The probability of transition from the state $|k\rangle$ to the state $|n\rangle$ is

$$P_{kn}(t) = |a_n|^2 = \left| \frac{1}{\hbar} \int_0^t V_{nk} e^{i\omega_{nk}\tau} d\tau \right|^2. \quad (28)$$

Example: Let us assume that

$$V = \begin{cases} 0, & t < 0 \\ Ae^{i\omega t} + A^\dagger e^{-i\omega t}, & t \geq 0 \end{cases} \quad (29)$$

Using Eq. (27) the probability amplitude for a transition to a state n is

$$a_n = -\frac{1}{\hbar} \left(A_{nk} \frac{e^{i(\omega_{nk}+\omega)t} - 1}{\omega_{nk} + \omega} + A_{nk}^* \frac{e^{i(\omega_{nk}-\omega)t} - 1}{\omega_{nk} - \omega} \right). \quad (30)$$

The first term in Eq. (30) described stimulated emission. It dominates the transition if $\omega \approx -\omega_{nk}$. The second term corresponds to absorption and it is important if $\omega \approx \omega_{nk}$. The probability of transition for the emission/absorption process is

$$P_{kn}(t) \approx \left| \frac{At}{\hbar} \right|^2 \text{sinc}^2\left(\frac{1}{2}(\omega_{nk} \pm \omega)t\right). \quad (31)$$

The function

$$\text{sinc}(x) = \frac{\sin(x)}{x}, \quad (32)$$

for large values x may be approximated by δ -function. Therefore, the perturbation excites transitions resonantly between the eigenstates of the unperturbed Hamiltonian.

Let us consider the probability of a transition into a set of states

$$P(t) = \sum_n |a_n|^2. \quad (33)$$

If the states form a continuum we should introduce the number of states in the energy range $(E, E + dE)$ as $\rho(E)dE$, where $\rho(E)$ is a density of states. Then the transition probability is

$$P_{\text{int}} = \int P(t)\rho(E)dE, \quad (34)$$

where $P(t)$ is defined by Eq. (31). If we rewrite the transition frequencies ω_{nk} in terms of energy and integrate Eq. (34) we get that

$$P_{\text{int}} = \frac{2\pi}{\hbar} t |A|^2 \rho(E_0), \quad (35)$$

where $E_0 = \omega/\hbar$. The transition rate is

$$W = \frac{dP}{dt} = \frac{2\pi}{\hbar} |A|^2 \rho(E_0). \quad (36)$$

It is also known as *Fermi's golden rule*.

References

- [1] P. W. Atkins and R. S. Friedman, *Molecular Quantum Mechanics* (Third Ed. Oxford University Press, New York, 1997), Chapters 6.9–6.18