Physics 472 Lecture 10

Time-independent perturbation theory

1) Nondegenerate perturbation theory

Believe it or not, we have already solved a large fraction of the problems in quantum mechanics that admit exact solutions: the particle in a rectangular well or box, the harmonic oscillator, the rigid rotor, the hydrogen atom. Even here, we have begun to detect discrepancies due to additional interactions, such as the spin-orbit interaction. A further difficulty arises when additional particles are added to the system. Here

we have obtained the exact solution only for the unrealistic case of noninteracting particles.

In order to make progress in the application of QM to realistic systems, we need to develop techniques for arriving at approximate solutions. The most widely used approximation technique for bound systems is perturbation theory, in which a real physical system is regarded as a modification of one of the model systems whose solutions we already know. In particular, we assume

$$H = H_0 + \lambda H_1 ,$$

where the solutions of H_0 are known, and H_1 contains additional

interactions. λ, which takes values in the range $[0, 1]$, is a parameter that allows us to "turn on" the perturbation. For small λ, the corrections to both the eigenvalues and eigenfunctions resulting from H_1 will be small. In such cases, it is possible to use perturbation theory.

The known eigenfunctions and eigenvalues are given by

$$H_0 \psi_i^{(0)} = E_i^{(0)} \psi_i^{(0)},$$

where the $\psi_i^{(0)}$ form a complete orthonormal basis so that

$$\langle i | j \rangle = \delta_{ij}.$$

The equation we wish to solve is

$$(H_0 + \lambda H_1)\,\psi_n = E_n\,\psi_n .$$

For now, we assume that both the $\psi_i^{(0)}$ and the ψ_n are discrete, nondegenerate sets of time-independent functions. We further assume a one-to-one correspondence between the members of each set:

$$\lim_{\lambda \to 0} \psi_n = \psi_n^{(0)}, \qquad \lim_{\lambda \to 0} E_n = E_n^{(0)}.$$

We represent the new eigenfunctions and eigenvalues by power series in λ:

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

It is assumed that successive terms of these series get smaller, so that the series converge.

We may assume the corrections to each eigenfunction are orthogonal to it:

$$\langle \psi_n^{(0)} | \psi_n^{(k)} \rangle = 0 \quad , \quad k = 1, 2, 3, \ldots .$$

Otherwise, they would just add to the zeroth-order term, which would merely change the normalization of the wavefunction.

Our task is to find the corrections to the eigenenergies and eigenfunctions to any desired order in λ. Inserting the power series for ψ_n and E_n into the Schrödinger equation, we obtain:

$$(H_0+\lambda H_1)(\psi_n^{(0)} + \lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)}+\cdots)$$

$$= (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)}+\cdots)(\psi_n^{(0)}+\lambda\psi_n^{(1)}+\cdots)$$

Equating the coefficients of powers of λ on each side of the equation yields the following equations:

λ^0. $\quad H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$

λ^1. $\quad H_1\psi_n^{(0)} + H_0\psi_n^{(1)} = E_n^{(1)}\psi_n^{(0)} + E_n^{(0)}\psi_n^{(1)}$

λ^2. $\quad H_1\psi_n^{(1)} + H_0\psi_n^{(2)} = E_n^{(2)}\psi_n^{(0)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(0)}\psi_n^{(2)}$

$\vdots$

λ^k. $\quad H_1\psi_n^{(k-1)} + H_0\psi_n^{(k)} = E_n^{(k)}\psi_n^{(0)} + \cdots + E_n^{(0)}\psi_n^{(k)}$

The equation for λ^0 we already knew. The second equation may be solved by expanding $\psi_n^{(1)}$ in terms of the unperturbed eigenfunctions:

$$\psi_n^{(1)} = \sum_{m \neq n} C_{nm}^{(1)} \psi_m^{(0)}.$$

The first-order equation then becomes:

$$H_1 \psi_n^{(0)} + H_0 \sum_{m \neq n} C_{nm}^{(1)} \psi_m^{(0)} = E_n^{(1)} \psi_n^{(0)} + E_n^{(0)} \sum_{m \neq n} C_{nm}^{(1)} \psi_m^{(0)}.$$

Taking the inner product with the state $\psi_{n'}^{(0)}$ gives

$$\langle n' | H_1 | n \rangle + \sum_{m \neq n} C_{nm}^{(1)} \langle n' | H_0 | m \rangle = E_n^{(1)} \langle n' | n \rangle + E_n^{(0)} \sum_{m \neq n} C_{nm}^{(1)} \langle n' | m \rangle$$

But $\langle n'|n\rangle = \delta_{nn'}$, $\langle n'|m\rangle = \delta_{mn'}$,

and $\langle n'|H_0|m\rangle = E_m^{(0)}\langle n'|m\rangle = E_m^{(0)}\delta_{mn'}$.

$$\Rightarrow \langle n'|H_1|n\rangle + C_{nn'}^{(1)} E_{n'}^{(0)} = E_n^{(1)}\delta_{nn'} + E_n^{(0)} C_{nn'}^{(1)}$$

or $$E_n^{(1)}\delta_{nn'} = \langle n'|H_1|n\rangle + C_{nn'}^{(1)}\left(E_{n'}^{(0)} - E_n^{(0)}\right)$$

For $n = n'$, this gives

$$\boxed{E_n^{(1)} = \langle n|H_1|n\rangle .}$$

For $n \neq n'$, this gives

$$C_{nn'}^{(1)} = \frac{\langle n'|H_1|n\rangle}{E_n^{(0)} - E_{n'}^{(0)}} .$$

The first-order correction to the energy of the nth eigenstate is just the expectation value of the perturbation H_1 in the unperturbed state $\psi_n^{(0)}$. This simple result is one of the most widely used results in quantum mechanics!

The first-order correction to the wavefunction is

$$\psi_n^{(1)} = \sum_{n' \neq n} \frac{\langle n' | H_1 | n \rangle}{E_n^{(0)} - E_{n'}^{(0)}} \psi_{n'}^{(0)}.$$

Thus, if the perturbation couples states $\psi_n^{(0)}$ and $\psi_{n'}^{(0)}$ (i.e., $\langle n' | H_1 | n \rangle \neq 0$),

then the wavefunction ψ_n contains admixtures of these states in first order. However, their contribution is reduced if the energy denominator is large; their is little mixing of states with very different energies. Here we see the importance of the assumption of nondegenerate states: the coefficient $C_{nn'}^{(1)}$ blows up if $E_n^{(0)} = E_{n'}^{(0)}$. This case necessitates a more careful treatment, discussed later under degenerate perturbation theory.

In bra-ket notation, the first-order correction to the eigenstate is

$$|\psi_n^{(1)}\rangle = \sum_{n' \neq n} \frac{|n'\rangle\langle n'|H|n\rangle}{E_n^{(0)} - E_{n'}^{(0)}},$$

where $|n\rangle \equiv |\psi_n^{(0)}\rangle$.

Higher-order corrections

Taking the inner product of the k-th order Schrödinger equation with $\psi_n^{(0)}$, and using $\langle n|\psi_n^{(k)}\rangle = 0$, gives

$$\langle n|H_1|\psi_n^{(k-1)}\rangle = E_n^{(k)}.$$

Thus, we can find $E_n^{(2)}$ using $\psi_n^{(1)}$.

$$E_n^{(2)} = \sum_{n' \neq n} \frac{\langle n|H_1|n'\rangle\langle n'|H_1|n\rangle}{E_n^{(0)} - E_{n'}^{(0)}}$$

$$\boxed{E_n^{(2)} = \sum_{n' \neq n} \frac{|\langle n'|H_1|n\rangle|^2}{E_n^{(0)} - E_{n'}^{(0)}}}$$

Note that the second-order correction to the ground state energy is always negative!

The higher-order corrections to the eigenenergies and eigenfunctions can also be obtained, but the expressions become rather complicated, especially for the eigenfunctions.

For the higher-order terms,

an alternative formulation of perturbation theory due to Brillouin and Wigner is more useful than the standard Rayleigh-Schrödinger perturbation theory we have developed.

Wave function renormalization constant

Since $\psi_n = \psi_n^{(0)} + \sum_{k=1}^{\infty} \lambda^k \psi_n^{(k)}$,

with $\langle \psi_n^{(0)} | \psi_n^{(k)} \rangle = 0$ if $k > 0$,

ψ_n is normalized according to

$$\langle \psi_n^{(0)} | \psi_n \rangle = 1.$$

If we want the perturbed state to be normalized to one, we must

multiply ψ_n by

$$(\langle \psi_n | \psi_n \rangle)^{-1/2} \equiv Z^{1/2}.$$

The state $\bar{\psi}_n = Z^{1/2} \psi_n$ obeys

$$\langle \bar{\psi}_n | \bar{\psi}_n \rangle = 1.$$

The quantity Z is known as the wavefunction renormalization constant.

Let us calculate Z up to second order:

$$\langle \psi_n | \psi_n \rangle = \langle \psi_n^{(0)} + \lambda \psi_n^{(1)} + \cdots \mid \psi_n^{(0)} + \lambda \psi_n^{(1)} + \cdots \rangle$$

$$= 1 + \lambda^2 \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \cdots$$

$$= 1 + \lambda^2 \sum_{n' \neq n} \frac{|\langle n' | H_1 | n \rangle|^2}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)^2} + \cdots$$

Thus ψ_n is properly normalized to first order, with the first correction occuring in second order.

To second order, we have

$$Z = 1 - \lambda^2 \sum_{n' \neq n} \frac{|\langle n'|H_1|n\rangle|^2}{\left(E_n^{(0)} - E_{n'}^{(0)}\right)^2}$$

$$= \frac{\partial}{\partial E_n^{(0)}} \left(E_n^{(0)} + \lambda \langle n|H_1|n\rangle + \lambda^2 \sum_{n' \neq n} \frac{|\langle n'|H_1|n\rangle|^2}{E_n^{(0)} - E_{n'}^{(0)}} \right)$$

$$= \frac{\partial E_n}{\partial E_n^{(0)}} .$$

This result is actually correct to all orders in perturbation theory.