FY2045 Quantum Mechanics I

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Week 11

Time-independent perturbation theory

General formulation

In most situations, a system is defined by a Hamiltonian H for which the Schrödinger equation cannot be solved exactly. However, if $H = H_0 + V$, where V is a small, time-independent term — a **perturbation** — and we know the solutions to

$$H_0|n\rangle = E_n^0|n\rangle, \tag{1}$$

we can find **approximate** solutions of

$$H|\psi_n\rangle = E_n|\psi_n\rangle, \tag{2}$$

using **time-independent perturbation theory**.

Ø15, H7.1, G7

Non-degenerate perturbation theory

We write $H = H_0 + \lambda V$, where $\lambda \in [0,1]$. When $\lambda \to 0$, we should have

$$E_n \to E_n^0 \text{ and } |\psi_n\rangle \to |n\rangle.$$

We therefore write

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots, \tag{3}$$

$$|\psi_n\rangle = |n\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \dots, \tag{4}$$

where we have assumed **non-degenerate** states. Inserting into the SE, eq. (2), and collecting like powers of λ, we get

$$\lambda^0 : \quad H_0|n\rangle = E_n^0|n\rangle,$$

$$\lambda^1 : \quad H_0|n^{(1)}\rangle + V|n\rangle = E_n^0|n^{(1)}\rangle + E_n^{(1)}|n\rangle, \tag{5}$$

$$\lambda^2 : \quad H_0|n^{(2)}\rangle + V|n^{(1)}\rangle = E_n^0|n^{(2)}\rangle + E_n^{(1)}|n^{(1)}\rangle + E_n^{(2)}|n\rangle. \tag{6}$$

Non-degenerate perturbation theory

First-order corrections

$$E_n^{(1)} = \langle n|V|n\rangle$$
$$|n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle m|V|n\rangle}{E_n^0 - E_m^0}|m\rangle$$

Second-order energies

$$E_n^{(2)} = \sum_{m\neq n} \frac{|\langle m|V|n\rangle|^2}{E_n^0 - E_m^0}$$

Summary

The solution to the eigenvalue problem

$$(H_0 + \lambda V)|\psi_n\rangle = E_n|\psi_n\rangle$$

is

$$|\psi_n\rangle = |n\rangle + \sum_{m\neq n} \frac{\langle m|\lambda V|n\rangle}{E_n^0 - E_m^0}|m\rangle + \mathcal{O}(\lambda^2),$$
$$E_n = E_n^0 + \langle n|\lambda V|n\rangle + \sum_{m\neq n} \frac{|\langle m|\lambda V|n\rangle|^2}{E_n^0 - E_m^0} + \mathcal{O}(\lambda^3).$$

Example — Perturbed harmonic oscillator

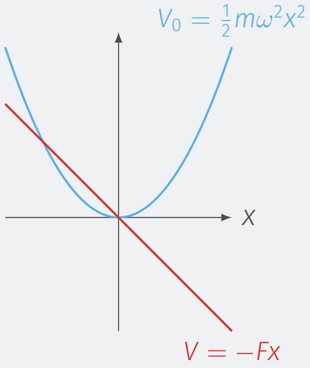
A harmonic oscillator is perturbed by force F in positive x-direction:

$$V = -Fx.$$

The perturbed Hamiltonian is

$$H = H_0 + V = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 - Fx.$$

What are the corrections to the energies and eigenstates?



Example — Perturbed harmonic oscillator

To second order in F we find the energies

$$\begin{aligned} E_n &= E_n^0 + E_n^{(1)} + E_n^{(2)} \\ &= \hbar\omega\left[n + \frac{1}{2}\right] - \frac{F^2}{2m\omega^2}, \end{aligned}$$

and to first order the state vectors

$$\begin{aligned} |\psi_n\rangle &= \left(1 - \frac{i x_0 \hat{p}_x}{\hbar}\right)|n\rangle, \\ \Rightarrow \psi_n(x) &= \left(1 - x_0 \frac{d}{dx}\right)\psi_n^{(0)}(x), \end{aligned}$$

with $x_0 = \frac{F}{m\omega^2}$.

Example — Perturbed harmonic oscillator

Exact solution

Rewrite perturbed Hamiltonian

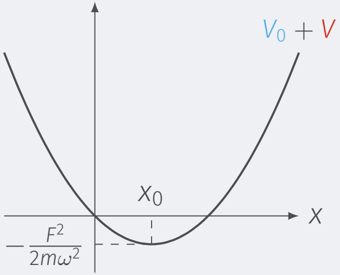
$$H = \frac{\hat{p}_x^2}{2m} + \frac{1}{2}m\omega^2(x - x_0)^2 - \frac{F^2}{2m\omega^2}.$$

Hence, we have exact solution

$$E_n = \hbar\omega\left[n + \frac{1}{2}\right] - \frac{F^2}{2m\omega^2},$$

$$\psi_n(x) = \psi_n^{(0)}(x - x_0) = \psi_n^{(0)}(x) - x_0\frac{d}{dx}\psi_n^{(0)}(x)\ldots,$$

which agrees exactly with the second order energy correction, and to first order with the wavefunction correction.



Degenerate perturbation theory

Non-degenerate perturbation theory

The solution to the eigenvalue problem

$$(H_0 + V)|\psi_n\rangle = E_n|\psi_n\rangle$$

is

$$|\psi_n\rangle = |n\rangle + \sum_{m \neq n} \frac{\langle m|V|n\rangle}{E_n^0 - E_m^0}|m\rangle + \dots,$$

$$E_n = E_n^0 + \langle n|V|n\rangle + \sum_{m \neq n} \frac{|\langle m|V|n\rangle|^2}{E_n^0 - E_m^0} + \dots$$

Ø15.4, H7.2, G7.2

With degenerate unperturbed states, we risk having $E_n^0 - E_m^0 = 0$, giving divergent expressions. Possible way out: $\langle m|V|n\rangle = 0$.

We therefore need a more careful treatment.

Degenerate perturbation theory

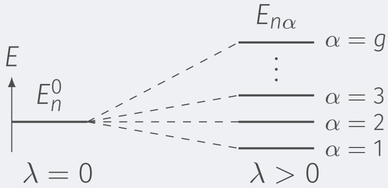
Consider a system where the unperturbed level n is degenerate

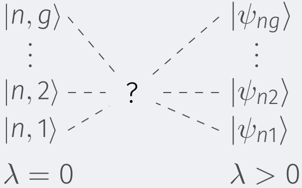
$$H_0|n,r\rangle = E_n^0|n,r\rangle, \quad (r = 1, \dots, g_n),$$

with degree of degeneracy g_n for level n, and we assume orthonormalized states, $\langle n,s|n,r\rangle = \delta_{sr}$. For notational simplicity we drop the subscript n and write $g = g_n$.

Write exact energies and state vectors as power series in λ, with $\alpha = 1, \dots, g$:

$$E_{n\alpha} = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \qquad |\psi_{n\alpha}\rangle = |\psi_{n\alpha}^{(0)}\rangle + \lambda|\psi_{n\alpha}^{(1)}\rangle + \lambda^2|\psi_{n\alpha}^{(2)}\rangle + \dots$$





Degenerate perturbation theory

Inserting the expansions into the eigenvalue equation

$$H|\psi_{n\alpha}\rangle = (H_0 + \lambda V)|\psi_{n\alpha}\rangle = E_{n\alpha}|\psi_{n\alpha}\rangle,$$

and collecting like orders of λ, we get

$$\begin{aligned} \lambda^0 : &\quad H_0|\psi^{(0)}_{n\alpha}\rangle = E^0_n|\psi^{(0)}_{n\alpha}\rangle, \\ \lambda^1 : &\quad (H_0 - E^0_n)|\psi^{(1)}_{n\alpha}\rangle + (V - E^{(1)}_{n\alpha})|\psi^{(0)}_{n\alpha}\rangle = 0, \end{aligned}$$

etc. From the first, we see that

$$|\psi^{(0)}_{n\alpha}\rangle = \sum_{r=1}^{g} U_{r\alpha}|n, r\rangle, \quad (\alpha = 1, \dots, g),$$

the "limit states" $|\psi^{(0)}_{n\alpha}\rangle$ are in general linear combinations of the unperturbed states $|n, r\rangle$.