Lecture 9

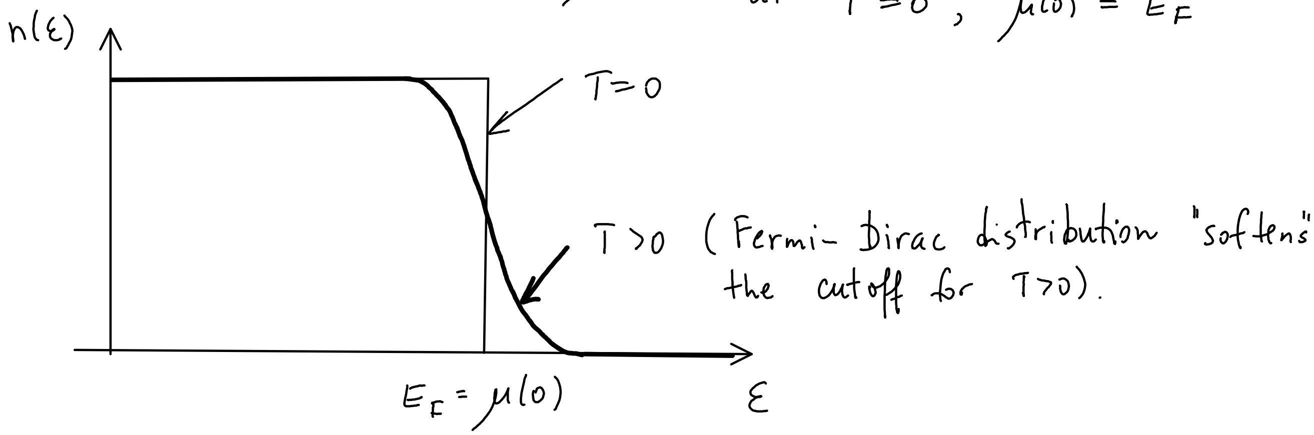
The Fermi-Dirac distribution

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1}$$

When $T \to 0 \Rightarrow e^{(\epsilon-\mu)/k_B T} \to \begin{cases} 0 & \text{if } \epsilon < \mu(0) \\ \infty & \text{if } \epsilon > \mu(0) \end{cases} \Rightarrow$

$n(\varepsilon) \to \begin{cases} 1 & \text{if } \epsilon < \mu(0) \\ 0 & \text{if } \epsilon > \mu(0) \end{cases}$ ← all states are filled up to energy $\mu(0)$ and none after

at $T = 0$, $\mu(0) = E_F$



Time-independent perturbation theory

Nondegenerate perturbation theory

General formalism of the problem:

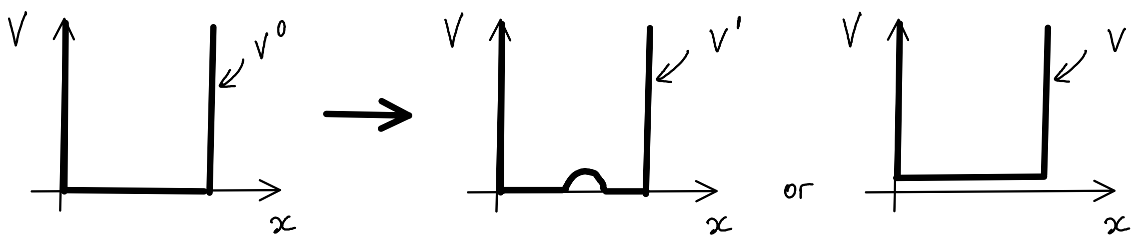
Suppose that we solved the time-independent Schrödinger equation for some potential and obtained a complete set of orthonormal eigenfunctions ψ_n^0 and corresponding eigenvalues E_n^0.

$$\boxed{\begin{aligned} H^0 \psi_n^0 &= E_n^0 \psi_n^0 \\ \langle \psi_n^0 | \psi_m^0 \rangle &= \delta_{nm} \end{aligned}}$$

This is the problem that we completely understand and know solutions for.

We mark all these solutions and the Hamiltonian with "^{0}" label.

Now we slightly perturb the potential. For example, we raise a little bit the bottom of the infinite square well or put a little bump there:



The problem of the perturbation theory is to find eigenvalues and eigenfunctions of the perturbed potential, i.e. to solve approximately the following equation:

$$H \psi_n = E \psi_n , \quad H = H^0 + \underbrace{H'}_{\text{perturbation}}$$

using the known solutions of the problem

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 .$$

For now, we consider nondegenerate case, i.e. each eigenvalue corresponds to different eigenfunction.

$H = H^0 + H'$

We expand our solution as follows in terms of perturbation H' ;

$$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 + \ldots$$

$\boxed{\text{know solutions for } H^0\psi_n^0 = E_n^0\psi_n^0}$

first-order corrections (in orders of H')

second-order correction

$$E_n = E_n^0 + E_n^1 + E_n^2 + \ldots$$

first-order correction

second-order correction

We plug our expansions into $H\psi_n = E\psi_n$

$$H\psi_n = E_n\psi_n$$

$H = H^0 + H'$

$\psi_n = \psi_n^0 + \psi_n^1 + \psi_n^2 + \ldots$

$E_n = E_n^0 + E_n^1 + E_n^2 + \ldots$

$$\boxed{(H^0 + H')(\psi_n^0 + \psi_n^1 + \psi_n^2 + \ldots) = (E_n^0 + E_n^1 + E_n^2 + \ldots)(\psi_n^0 + \psi_n^1 + \psi_n^2 + \ldots)}$$

$$\begin{aligned} &H^0\psi_n^0 + H^0\psi_n^1 + H^0\psi_n^2 + H'\psi_n^0 + H'\psi_n^1 + H'\psi_n^2 + \ldots \\ &= E_n^0\psi_n^0 + E_n^0\psi_n^1 + E_n^0\psi_n^2 + \ldots \\ &+ E_n^1\psi_n^0 + E_n^1\psi_n^1 + E_n^1\psi_n^2 + \ldots \\ &+ E_n^2\psi_n^0 + E_n^2\psi_n^1 + E_n^2\psi_n^2 + \ldots \end{aligned}$$

We now separate this equation into a system of equations that are zeroth, first, second, and so on orders in perturbation potential H':

$$\underbrace{H^0\psi_n^0}_{\text{zeroth}} + \underbrace{\boxed{H^0\psi_n^1}}_{\text{first}} + \underbrace{\boxed{\boxed{H^0\psi_n^2}}}_{\text{second}} + \underbrace{\boxed{H'\psi_n^0}}_{\text{first}} + \underbrace{\boxed{\boxed{H'\psi_n^1}}}_{\text{second}} + H'\psi_n^2 + \dots$$

$$= \underbrace{E_n^0\psi_n^0}_{\text{zeroth}} + \underbrace{\boxed{E_n^0\psi_n^1}}_{\text{first}} + \underbrace{\boxed{\boxed{E_n^0\psi_n^2}}}_{\text{second}} + \dots$$

$$+ \underbrace{\boxed{E_n^1\psi_n^0}}_{\text{first}} + \underbrace{\boxed{\boxed{E_n^1\psi_n^1}}}_{\text{second}} + \underbrace{E_n^1\psi_n^2}_{\text{third}} + \dots$$

$$+ \underbrace{\boxed{\boxed{E_n^2\psi_n^0}}}_{\text{second}} + \underbrace{E_n^2\psi_n^1}_{\text{third}} + \underbrace{E_n^2\psi_n^2}_{\text{fourth}} + \dots$$

Separating the equations for zeroth, first, and second orders we get:

Zeroth order $\quad H^0\psi_n^0 = E_n^0\psi_n^0 \leftarrow$ we already solved that one

$\boxed{\text{First order}}$

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

$\boxed{\boxed{\text{Second order}}}$

$$H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0$$

If we consider more terms in the expansions for ψ_n and E_n we can write equations for third, fourth, and higher orders of perturbation theory.

First-order perturbation theory

$$H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$$

We are going to multiply this equation by $\left(\psi_n^0\right)^*$ and integrate:

$$\int (\psi_n^0)^* H^0 \psi_n^1 d^3r + \int (\psi_n^0)^* H' \psi_n^0 d^3r = E_n^0 \int (\psi_n^0)^* \psi_n^1 d^3r + E_n^1 \int (\psi_n^0)^* \psi_n^0 d^3r$$

$$\downarrow$$

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \langle \psi_n^0 | \psi_n^0 \rangle$$

in $\langle | \rangle$ designations (remember $\int \psi_1^* H \psi_2 d^3r = \langle \psi_1 | H \psi_2 \rangle$ [or $\langle \psi_1 | H | \psi_2 \rangle$].

$$\boxed{\langle \psi_n^0 | H^0 \psi_n^1 \rangle} + \langle \psi_n^0 | H' \psi_n^0 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^1 \underbrace{\langle \psi_n^0 | \psi_n^0 \rangle}_{=1}$$

cancels with this term

H^0 is hermitian

$$\langle \psi_n^0 | H^0 \psi_n^1 \rangle = \langle H^0 \psi_n^0 | \psi_n^1 \rangle = \langle E_n^0 \psi_n^0 | \psi_n^1 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^1 \rangle$$

Therefore, **the first-order energy is given by**:

$$\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle}$$

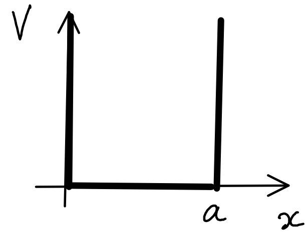
fundamental result of perturbation theory

Note: designations $\langle \psi_1 | H \psi_2 \rangle$ and $\langle \psi_1 | H | \psi_2 \rangle$ are equivalent.

insert "|"

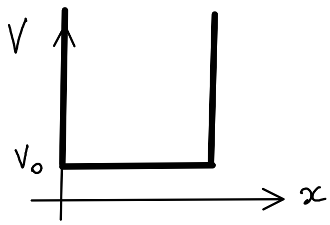
Problem #1

The solutions for the infinite square well are:



$$\psi_n^0(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a} x\right)$$

Find the first-order correction to the energies for the potential



$$H' = V_0$$

Solution:

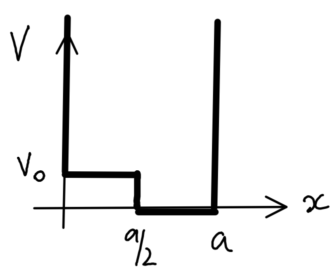
$$E_n^1 = \langle \psi_n^0 | V_0 | \psi_n^0 \rangle = V_0 \langle \psi_n^0 | \psi_n^0 \rangle = V_0$$

Corrected energy levels are

$E_n \cong E_n^0 + E_n^1 = E_n^0 + V_0$ (in this case, it it exact answer).

Problem #2

The same for the potential



$$H' = \begin{cases} V_0 & 0 < x < a/2 \\ 0 & a/2 < x < a \end{cases}$$

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle = \frac{2}{a} \int_0^{a/2} V_0 \sin^2\left(\frac{\pi n}{a} x\right) dx$$

$$= \frac{2V_0}{a} \left\{ -\frac{1}{2\frac{\pi n}{a}} \cos\left(\frac{\pi n}{a} x\right) \sin\left(\frac{\pi n}{a} x\right) + \frac{x}{2} \right\} \Bigg|_0^{a/2} = \frac{2V_0}{\cancel{a}} \frac{\cancel{a}}{4} = \frac{V_0}{2}$$

$$\boxed{\int \sin^2(ax)\,dx = -\frac{1}{2a} \cos(ax) \sin(ax) + \frac{x}{2}}$$

$E_n \approx E_n^0 + \frac{V_0}{2}$
(approximate)

First-order correction to the wave function ψ_n^1

$$H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$$

$$H^0\psi_n^1 - E_n^0\psi_n^1 = -H'\psi_n^0 + E_n^1\psi_n^0$$

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0 \qquad (1)$$

ψ_n^1 can be expanded as a linear combination of functions ψ_n^0 since they constitute a complete set.

$$\psi_n^1 = \sum_{m\neq n} C_m^{(n)}\psi_m^0 \qquad (2)$$

no need to include $m=n$ term in the sum, since if ψ_n^1 is a solution, then $\psi_n^1 + \alpha\psi_n^0$ is a solution of (1) for any α.

Our mission now is to find coefficients $C_m^{(n)}$. To do so, we plug our expansion (2) into the first-order equation (1).

$$(H^0 - E_n^0)\sum_{m\neq n} C_m^{(n)}\psi_m^0 = -(H' - E_n^1)\psi_n^0$$

substitute for first term $\quad H^0\psi_m^0 = E_m\psi_m^0$

$$\sum_{m\neq n}(E_m^0 - E_n^0)C_m^{(n)}\psi_m^0 = -(H' - E_n^1)\psi_n^0$$

We multiply this equation from the left side by ψ_ℓ^0 and integrate. I will not explicitly write integrals here, but use inner product notations right away. It is, of course, the same.

$$\sum_{m\neq n}(E_m^0 - E_n^0)C_m^{(n)}\underbrace{\langle\psi_\ell^0|\psi_m^0\rangle}_{\delta_{\ell m}} = -\langle\psi_\ell^0|H'|\psi_n^0\rangle + E_n^1\underbrace{\langle\psi_\ell^0|\psi_n^0\rangle}_{\delta_{\ell n}}$$

$$\sum_{m \neq n} (E_m^0 - E_n^0)\, C_m^{(n)} \delta_{\ell m} = -\langle \psi_\ell^0 | H' | \psi_n^0 \rangle + E_n^1 \delta_{\ell n}$$

If $\ell = n$, we get $E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$ again,

If $\ell \neq n$, we get

$$(E_\ell^0 - E_n^0)\, C_\ell^{(n)} = -\langle \psi_\ell^0 | H' | \psi_n^0 \rangle$$

$$C_\ell^{(n)} = \frac{\langle \psi_\ell^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_\ell^0}$$

, plug back to expansion $\psi_n^1 = \sum_{n \neq m} C_m^{(n)} \psi_m^0$

First-order correction to the wave function is given by ;

$$\boxed{\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0}$$

Note that as long as m ≠n, the denominator can not be zero as long as energy levels are nondegenerate. If the energy levels are degenerate, we need degenerate perturbation theory (consider later).

Second-order correction to the energy

$$H^0 \psi_n^2 + H^1 \psi_n^1 = E_n^0 \psi_n^2 + E_n^1 \psi_n^1 + E_n^2 \psi_n^0$$

Again, we multiply the whole equation from the left by ψ_n^0 and integrate.

$$\cancel{\underbrace{\langle \psi_n^0 | H^0 \psi_n^2 \rangle}} + \langle \psi_n^0 | H' \psi_n^1 \rangle = \cancel{E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle}$$

$$+ E_n^1 \langle \psi_n^0 | \psi_n^1 \rangle + E_n^2 \underbrace{\langle \psi_n^0 | \psi_n^0 \rangle}_{=1}$$

$$= \langle H^0 \psi_n^0 | \psi_n^2 \rangle = E_n^0 \langle \psi_n^0 | \psi_n^2 \rangle$$

$$E_n^2 = \langle \psi_n^0 | H' \psi_n^1 \rangle - E_n^1 \underbrace{\langle \psi_n^0 | \psi_n^1 \rangle}$$

$$= \sum_{m \neq n} C_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle = 0 \quad (m \neq n)$$

$$E_n^2 = \langle \psi_n^0 | H' | \psi_n^1 \rangle = \sum_{m \neq n} C_m^{(n)} \langle \psi_n^0 | H' | \psi_m^0 \rangle$$

$$= \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle \langle \psi_n^0 | H' | \psi_m^0 \rangle}{E_n^0 - E_m^0}$$

The second-order correction to the energy is

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$$