Lectures on Quantum Mechanics

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Contents

Introduction

Quantum mechanics is certainly the most successful theory of the physical world at small scales. It is also one of the most mysterious.

Some notes here.

PART I

Time Independent Non-degenerate Perturbation Theory

SECTION 1

Lecture 1

Suppose we have a "known" system with Hamiltonian, eigenfunctions and eigenenergies H_0, Ψ_n and E_n respectively.

$$\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$$

where [1]

$$\langle\hat{\Psi}|\hat{H}|\hat{\Psi}\rangle = E_n, \qquad \langle\Psi_n|\Psi_{n'}\rangle = \delta_{nn'}$$

So that $\{\Psi_n\}$ forms a orthonormal basis over the Hilbert space of H_0. We apply a perturbative potential $\tilde{V}$ [2] to H_0, yielding a new Hamiltonian. for the perturbated system,

$$\tilde{H} = \hat{H}_0 + \lambda\tilde{V}, \quad \text{let } \lambda \in [0,1] \tag{1.1}$$

a "bookkeeping parameter" to keep track of the relative signs of from in order of the perturbated potential.

[1] *The student may remember the Kronecker delta from his/her Quantum Mechanics I course.*

[2] $\tilde{V}$ *is very small compared to* H_0*.*

SUBSECTION 1.1

Method

Express the wave functions and eigenenergies of the perturbated Hamiltonian H, $\tilde{\psi}$, $\tilde{E}_n$ as a power series equation in orders of λ.

$$\tilde{E}_n = \tilde{E}_0^{(0)} + \lambda\tilde{E}_n^{(1)} + \lambda^2\tilde{E}_n^{(2)} + \cdots = \sum_k \lambda^k \tilde{E}_n^{(k)}$$
$$\tilde{\psi}_n = \tilde{\psi}_n^{(0)} + \lambda\tilde{\psi}_n^{(1)} + \lambda^2\tilde{\psi}_n^{(2)} + \cdots = \sum_k \lambda^k \tilde{\psi}_n^{(k)}$$

Now we write the Time independent Schrödinger equation for the perturbated Hamiltonian,

$$\tilde{H}\Big|\tilde{\psi}_n\Big\rangle = \tilde{E}_n\Big|\tilde{\psi}_n\Big\rangle \tag{1.2}$$

$$(\hat{H}+\hat{V})\sum_k \lambda^k\Big|\psi_n^{(k)}\Big\rangle = \sum_k \lambda^k \tilde{E}_n^{(k)}\sum_k \lambda^k\Big|\psi_n^{(k)}\Big\rangle \tag{1.3}$$

$$\sum_k(\lambda^k\hat{H}_0+\lambda^{k+1}\hat{V})\Big|\hat{\psi}_n^{(k)}\Big\rangle = \sum_{k'}\sum_k \lambda^{k'+k}\hat{E}_n^{(k)}\Big|\hat{\psi}_n^{(k)}\Big\rangle \tag{1.4}$$

$$\sum_k\left(\lambda^k\hat{H}_0+\lambda^{k+1}\hat{V}-\sum_{k'}\lambda^{k'+k}\hat{E}_n^{(k')}\right)\Big|\psi_n^{(k)}\Big\rangle = 0 \tag{1.5}$$

$$\sum_k \lambda^k\left(\hat{H}_0\Big|\hat{\psi}_n^{(k)}\Big\rangle + \underbrace{(1-\delta_{k0})}_{k\neq 0}\hat{V}\Big|\hat{\psi}^{(k-1)}\Big\rangle - \sum_{k=0}^{k}\hat{E}_n^{(k')}\Big|\hat{\psi}_n^{(k-k')}\Big\rangle\right) = 0 \tag{1.6}$$

Since Equation 1.6 is true for any value of λ, it must hold for each power of λ separately:

$$\begin{aligned}
\mathcal{O}(1)_{k=0} &= \hat{H}\Big|\hat{\psi}_n^{(0)}\Big\rangle + (1-\delta_{k0})\hat{V}\Big|\hat{\psi}_n^{(-1)}\Big\rangle \\
&= \sum_{k'=0}^{0}\hat{E}_n^{(k')}\Big|\hat{\psi}_n^{(0-k')}\Big\rangle \\
\Longrightarrow \hat{H}_0\Big|\hat{\psi}_n^{(0)}\Big\rangle &= \hat{E}_n^{(0)}\Big|\hat{\psi}_n^{(0)}\Big\rangle \\
\Big\langle\psi_n\Big|\underbrace{H_0}_{\text{hermitian}}\Big|\hat{\psi}_n^{(0)}\Big\rangle &= \hat{E}_n^{(0)}\Big\langle\psi_n\Big|\hat{\psi}_n^{(0)}\Big\rangle
\end{aligned}$$

$$\Big\langle\psi_{n'}\Big|\hat{H}_0^\dagger = E_{n'}\Big\langle\psi_{n'}\Big|$$

$$(E_{n'}-\hat{E}_n^{(0)})\Big\langle\psi_{n'}\Big|\hat{\psi}_n^{(0)}\Big\rangle = 0$$

So,

$$\hat{E}_n^{(0)} = E_n \text{ or } \Big\langle\psi_n\Big|\hat{\psi}_n^{(0)}\Big\rangle = 0 \tag{1.7}$$

If the system $\hat{H}_0$ is nondegenerate:

$$\Longrightarrow \Big|\hat{\psi}_n^{(0)}\Big\rangle = \Big|\psi_n\Big\rangle$$

If the system is degenerate, then:

$$\hat{H}_0\Big|\psi_{n'}\Big\rangle = E_n\Big|\psi_{n'}\Big\rangle \text{ for } n'\in\{n,\cdots,n+k\}$$

Then:

$$\Big|\hat{\psi}_n^{(0)}\Big\rangle = \sum_{k'=0}^{k} C_{n+k'}\Big|\psi_{n+k'}\Big\rangle$$

$$\hat{E}_n = E_n\mathcal{O}(\lambda)$$

$$\Big|\hat{\psi}_n\Big\rangle = |\psi_n\Big\rangle + \mathcal{O}(\lambda)$$

$$\mathcal{O}(\lambda) : \hat{H}_0\Big|\hat{\psi}_n^{(1)}\Big\rangle + \hat{V}\Big|\hat{\psi}_n^{(0)}\Big\rangle = E_n^{(0)}\Big|\hat{\psi}_n^{(1)}\Big\rangle + \hat{E}_n^{(1)}\Big|\hat{\psi}_n^{(0)}\Big\rangle$$

multiply by $\Big\langle\psi_{n'}\Big|$:

$$\Big\langle\psi_{n'}\Big|\hat{H}_0\Big|\hat{\psi}_n^{(1)}\Big\rangle + \Big\langle\psi_{n'}\Big|\hat{V}\Big|\hat{\psi}_n^{(0)}\Big\rangle = E_n^{(0)}\Big\langle\psi_{n'}\Big|\hat{\psi}_n^{(1)}\Big\rangle + \hat{E}_n^{(1)}\Big\langle\psi_{n'}\Big|\hat{\psi}_n^{(0)}\Big\rangle$$

$$\Big\langle\psi_{n'}\Big|\hat{H}_0 = E_{n'}\Big\langle\psi_{n'}\Big|$$

$$\Big|\hat{\psi}_n^{(0)}\Big\rangle = \Big|\psi_n\Big\rangle \quad \text{(non-degenerate)}, \quad \hat{E}_n^{(0)} = E_n$$

$$(E_{n'} - E_n)\Big\langle\psi_{n'}\Big|\hat{\psi}_n^{(1)}\Big\rangle + \Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle = \hat{E}_n^{(1)}\delta_{n'n} \tag{1.8}$$

if $\mathbf{n'} = \mathbf{n}$:

$$\cancelto{0}{(E_{n'} - E_n)}\Big\langle\psi_{n'}\Big|\hat{\psi}_n^{(1)}\Big\rangle + \Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle = \hat{E}_n^{(1)}\delta_{n'n}$$

$$\begin{aligned}
\implies \hat{E}_n^{(1)} &= \Big\langle\psi_n\Big|\hat{V}\Big|\hat{\psi}_n^{(1)}\Big\rangle \\
\hat{E}_n &= E_n + \Big\langle\psi_{n'}\Big|\hat{V}\Big|\hat{\psi}_n^{(1)}\Big\rangle + \mathcal{O}(\lambda^2) \\
\Big|\hat{\psi}_n\Big\rangle &= \Big|\psi_n\Big\rangle + \mathcal{O}(\lambda)
\end{aligned} \tag{1.9}$$

if $\mathbf{n'} \neq \mathbf{n}$:

$$(E_{n'} - E_n)\Big\langle\psi_{n'}\Big|\hat{\psi}_n^{(1)}\Big\rangle = -\Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle + \hat{E}_n^{(1)}\cancelto{0}{\delta_{n'n}}$$

$$\Big\langle\psi_{n'}\Big|\hat{\psi}_n^{(1)}\Big\rangle = \frac{\Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle}{E_n - E_{n'}} \tag{1.10}$$

Since $\{\psi_n\}$ forms an orthonormal basis,

$$\implies \sum_{n'}\Big|\psi_{n'}\Big\rangle\Big\langle\psi_{n'}\Big| = \mathbb{1} \ \text{Identity matrix}$$

$$\begin{aligned}
\Big|\hat{\psi}_n^{(1)}\Big\rangle = \mathbb{1}\Big|\hat{\psi}_n^{(1)}\Big\rangle &= \sum_{n'}\Big|\psi_{n'}\Big\rangle\Big\langle\psi_{n'}|\hat{\psi}_n^{(1)}\Big\rangle \\
&= \sum_{n'=n}\frac{\Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle}{E_n - E_{n'}}\Big|\psi_{n'}\Big\rangle
\end{aligned} \tag{1.11}$$

Since $\Big|\hat{\psi}_n^{(0)}\Big\rangle = \Big|\psi_n\Big\rangle$, then $\Big|\hat{\psi}_n^{(1)}\Big\rangle$ cannot depend on $\Big|\psi_n\Big\rangle$.

Section 2

Lecture 2

In the previous lecture we defined the perturbed hamiltonian [3] (Equation 1.1) as:

$$\tilde{H} = \hat{H}_0 + \lambda \hat{V}$$

[3] $\tilde{H}$: *perturbed hamiltonian*, $\hat{H}_0$: *unperturbed hamiltonian*, λ: *bookkeeping parameter*, $\hat{V}$: *perturbing potential.*

$\hat{V}$ needs to be smaller than $\hat{H}_0$, λ keeps track of this, i.e., dependence on $\hat{V}$. Writing the Schrödinger equation:

$$(\hat{H}_o + \lambda \hat{V})\hat{\psi}_n = \tilde{E}_n \tilde{\psi}_n$$

$\tilde{E}_n$ and $\tilde{\psi}_n$ are eigenenergies and wavefunctions for the perturbated hamiltonian.

Expand $\tilde{E}_n$ and $\tilde{\psi}_n$ in power of λ

$$\tilde{E}_n = \hat{E}_n^{(0)} + \lambda \tilde{E}_n^{(1)} + \lambda^2 \tilde{E}_n^{(2)} + \mathcal{O}(\lambda^3)$$
$$\tilde{\psi}_n = \hat{\psi}_n^{(0)} + \lambda \tilde{\psi}_n^{(1)} + \lambda^2 \tilde{\psi}_n^{(2)} + \mathcal{O}(\lambda^3)$$

and substitute for $\tilde{E}_0$ and $\tilde{\psi}_n$ into the (SE) and collect terms of like powers of λ.

$$\mathcal{O}(1) : \hat{H}_0 \Big| \tilde{\psi}_n^{(0)} \Big\rangle = \tilde{E}_0^{(0)} \Big| \psi_n^{(0)} \Big\rangle$$

Multiply by $\Big\langle \psi_{n'} \Big|$,

$$\Big\langle \psi_{n'} \Big| \hat{H}_0 \Big| \tilde{\psi}_n^{(0)} \Big\rangle = \tilde{E}_0^{(0)} \Big\langle \psi_{n'} \Big| \psi_n^{(0)} \Big\rangle$$

since $\hat{H}_0 = H_0^\dagger$ since $\hat{H}_0$ is hermitian

$$\Big\langle \psi_{n'} \Big| \hat{H}_0^\dagger = E_{n'} \Big\langle \psi_{n'} \Big| \text{ (SE) for } \hat{H}_0$$

$$\Longrightarrow E_{n'} \Big\langle \psi_{n'} \Big| \psi_n^{(0)} \Big\rangle = \hat{E}_0^{(0)} \Big\langle \psi_{n'} \Big| \psi_n^{(0)} \Big\rangle$$
$$E_{n'}^{(0)} = E_{n'} \quad \text{or} \quad \Big\langle \psi_{n'} \Big| \psi_n^{(0)} \Big\rangle = 0$$

$\tilde{\psi}_n^{(0)} = \sum_{n'} \Big\langle \psi_{n'} \Big| \psi_n^{(1)} \Big\rangle$

If E_n is k-level degenerate, then

$$\Big| \tilde{\psi}_n^{(0)} \Big\rangle = \sum_{n'=n}^{n+k-1} \Big\langle \psi_{n'} \Big| \psi_n^{(0)} \Big\rangle \Big| \psi_{n'} \Big\rangle \tag{2.1}$$

Consider $\hat{H}_0$ to be non-degenerate

$$\implies E_n^{(0)} = E_n, \quad \left|\left\langle \psi_n \middle| \tilde{\psi}_n^{(0)} \right\rangle\right|^2 = 0$$

$$\sum_{n'=n}^{n+k-1} \left|\left\langle \psi_{n'} \middle| \psi_n^{(0)} \right\rangle\right|^2 = 1$$

since $\left\langle \psi_{n'} \middle| \psi_n^{(0)} \right\rangle = 0$ for $n' \neq n$,

$$\implies \left| \tilde{\psi}_n^{(0)} \right\rangle = \left| \psi_{n'} \right\rangle$$

the n^{th} eigenenergy of the perturbated system (hamiltonian) $\tilde{E}_n$ is the n^{th} eigenenergy of the unperturbed system to Zeroth order in the perturbation, i.e $\mathcal{O}(\lambda^0) = \mathcal{O}(1),\ \lambda = 0$.

If we turn the perturbation off we get the eigenenergy of the unperturbed system $\because$ the n^{th} wavefunction for the perturbed hamiltonian $\tilde{\Psi}_n$ is a linear combination of the unperturbed hamiltonian's degenerate wavefunctions with energy E_n to Zeroth order in the perturbation, i.e $\mathcal{O}(\lambda^0) = \mathcal{O}(1)$ or $\lambda = 0$

$$\implies \left| \hat{\psi}_n^{(0)} \right\rangle = \sum_{n'=n}^{n+k-1} \left\langle \psi_{n'} \middle| \tilde{\psi}_n^{(0)} \right\rangle \left| \psi_{n'} \right\rangle$$

,where

$$\sum_{n'=n}^{n+k-1} \left|\left\langle \psi_{n'} \middle| \tilde{\psi}_n^{(0)} \right\rangle\right|^2 = 1$$

Even if we "turn off" the perturbation, it can still left the degeneracy of $\{\left|\psi_n\right\rangle, \cdots, \left|\psi_{n+k-1}\right\rangle\}$ for k-fold degenerate systems, unless the unperturbed wavefunctions are eigenstates of the perturbation.

Now let's assume $\hat{H}_0$ is non-degenerate

$$\implies \left|\left\langle \psi_{n'} \middle| \tilde{\psi}_n^{(0)} \right\rangle\right|^2 = 1$$

wlog $\psi_n = \tilde{\psi}_n^{(0)}$ (Choice of 1 for phase factor),

$$\tilde{E}_n = E_n + \mathcal{O}(\lambda)$$
$$\tilde{\psi}_n = \psi_n + \mathcal{O}(\lambda)$$

and gather together terms of order 1 in λ in the (SE)

$$\mathcal{O}(\lambda) : \lambda \left(\hat{H}_0 \left| \tilde{\psi}_n^{(1)} \right\rangle + \hat{V} \left| \tilde{\psi}_n^{(0)} \right\rangle \right) = \lambda \left(E_n \left| \tilde{\psi}_n^{(1)} \right\rangle + E_n^{(1)} \left| \psi_n \right\rangle \right) \tag{2.2}$$

setting $\lambda = 1$,

$$\hat{H}_0\Big|\tilde{\psi}_n^{(1)}\Big\rangle + \hat{V}\Big|\tilde{\psi}_n^{(0)}\Big\rangle = E_n\Big|\tilde{\psi}_n^{(1)}\Big\rangle + E_n^{(1)}\Big|\psi_n\Big\rangle \tag{2.3}$$

Equation 2.3 is a recursive equation relating the 1st order corrections in $\tilde{E}_n$ and $\tilde{\psi}_n$ to the Zeroth order corrections, in the unperturbed eigenenergy and wavefunction, E_n and ψ_n respectively $\because$ the $\mathcal{O}^{th}$ relates the kth order corrections to all previous orders.

SUBSECTION 2.1

Two Unknowns

Use the fact that

$$\Big\langle\psi_{n'}\Big|\psi_n\Big\rangle = \delta_{n'n} \quad \text{and} \quad \hat{H}_o\Big|\psi_{n'}\Big\rangle = E_{n'}\Big|\psi_{n'}\Big\rangle$$

to obtain equations for $\tilde{E}_n^{(1)}$ and $\tilde{\psi}_n^{(1)}$.

Multiply by $\Big\langle\psi_{n'}\Big|$

$$\Big\langle\psi_{n'}\Big|\hat{H}_o^{\dagger}\Big|\tilde{\psi}_n^{(1)}\Big\rangle + \Big\langle\psi_{n'}\Big|\hat{V}\Big|\tilde{\psi}_n^{(0)}\Big\rangle = E_n\Big\langle\psi_{n'}\Big|\tilde{\psi}_n^{(1)}\Big\rangle + E_n^{(1)}\underbrace{\Big\langle\psi_{n'}\Big|\psi_n\Big\rangle}_{\delta_{n'n}}$$

$$\left(E_{n'} - E_n\right)\Big\langle\psi_{n'}\Big|\tilde{\psi}_n^{(1)}\Big\rangle + \Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle = \tilde{E}_n^{(1)}\delta_{n'n} \tag{2.4}$$

$\Big\langle\psi_{n'}\Big|\tilde{\psi}_n^{(1)}\Big\rangle$ is the coefficient of $\Big|\psi_{n'}\Big\rangle$.

$\tilde{E}_n^{(1)}$: First order correction to the eigenenergy.

If $n' = n$, Equation 2.4 yields to $\tilde{E}_n^{(1)}$

$$\boxed{\tilde{E}_n^{(1)} = \Big\langle\psi_n\Big|\hat{V}\Big|\psi_n\Big\rangle}$$

which is the expectation value of the perturbation in the n^{th} eigenstate of the unperturbed hamiltonian.

On the other hand, if $n' \neq n$, Equation 2.4 yields to coefficients of $\Big|\tilde{\psi}_n^{(1)}\Big\rangle$ and $\lambda = 1$.

$$\Big\langle\psi_{n'}|\hat{\psi}_n^{(1)}\Big\rangle = \frac{\Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle}{E_n - E_{n'}}$$

$$\Big|\tilde{\psi}_n^{(1)}\Big\rangle = \sum_{n'\neq n}\frac{\Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle}{E_n - E_{n'}}\Big|\psi_{n'}\Big\rangle$$

$$\tilde{E}_n = E_n + \Big\langle\psi_n\Big|\hat{V}\Big|\psi_n\Big\rangle + \mathcal{O}(\lambda^2)$$

$$\Big|\tilde{\psi}_n\Big\rangle = \Big|\psi_n\Big\rangle + \sum_{n'\neq n}\frac{\Big\langle\psi_{n'}\Big|\hat{V}\Big|\psi_n\Big\rangle}{E_n - E_{n'}}\Big|\psi_{n'}\Big\rangle + \mathcal{O}(\lambda^2) \tag{2.5}$$

The first order correction to the eigenenergy is the energy of the perturbation if you stay in the n^{th} eigenstate of the unperturbed system. So V [4] has to be "weak" so that you can remain in $\left|\psi_n\right\rangle$ under its action.

[4] ***Note:*** *if $\hat{V}$ (the perturbation) is an odd function:*

$$\hat{E}_n^{(1)} = \int d^3\vec{r} \left|\underbrace{\psi(\vec{r})}_{even}\right|^2 \overbrace{\hat{V}(\vec{r},t)}^{odd} = 0$$

The first order corrections to wavefunctions are proportional to the matrix elements of

$$\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle,$$

i.e., that under the action of the perturbation you can transition from n^{th} to n'^{th} eigenstate of the unperturbed hamiltonian and inversely proportional to the difference (energy) between the eigenenergies of the n^{th} and n'^{th} eigenstates of the perturbed hamiltonian.

Note:

$$\left|\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle\right| \ll \left|E_n - E_{n'}\right|$$

Otherwise our expression for the wavefunctions of the perturbed system won't converge.

Setting

$$\lambda \gg 1$$

$$\mathcal{O}(\lambda^2) : \hat{H}_o\left|\tilde{\psi}_n^{(2)}\right\rangle + \hat{V}\left|\tilde{\psi}_n^{(1)}\right\rangle = E_n\left|\tilde{\psi}_n^{(2)}\right\rangle + \tilde{E}_n^{(1)}\left|\tilde{\psi}_n^{(1)}\right\rangle + \tilde{E}_n^{(2)}\left|\psi_n\right\rangle$$

and multiplying by $\left\langle\psi_{n'}\right|$

$$\left\langle\psi_{n'}\middle|\hat{H}_o\middle|\tilde{\psi}_n^{(2)}\right\rangle+\left\langle\psi_{n'}\middle|\hat{V}\middle|\tilde{\psi}_n^{(1)}\right\rangle = E_n\left\langle\psi_{n'}\middle|\tilde{\psi}_n^{(2)}\right\rangle+\tilde{E}_n^{(1)}\left\langle\psi_{n'}\middle|\tilde{\psi}_n^{(1)}\right\rangle+\tilde{E}_n^{(2)}\left\langle\psi_{n'}\middle|\psi_n\right\rangle$$

$$\begin{aligned}(E_{n'} - E_n)\left\langle\psi_{n'}\middle|\hat{\psi}_n^{(2)}\right\rangle + \left\langle\psi_{n'}\middle|\hat{V}\sum_{k\neq n}\frac{\left\langle\psi_k\middle|\hat{V}\middle|\psi_n\right\rangle}{E_n - E_k}\middle|\psi_k\right\rangle \\ = \left\langle\psi_n\middle|\hat{V}\middle|\psi_n\right\rangle\left\langle\psi_{n'}\middle|\sum_{n=k}\frac{\left\langle\psi_k\middle|\hat{V}\middle|\psi_n\right\rangle}{E_n - E_k}\middle|\psi_k\right\rangle + \tilde{E}_n^{(2)}\delta_{n'n}\end{aligned}$$

$$\begin{aligned}(E_{n'} - E_n)\left\langle\psi_{n'}\middle|\hat{\psi}_n^{(2)}\right\rangle + \sum_{k=n}\frac{\left\langle\psi_k\middle|\hat{V}\middle|\psi_n\right\rangle\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_k\right\rangle}{E_n - E_k} \\ = \frac{\left\langle\psi_n\middle|\hat{V}\middle|\psi_n\right\rangle\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle}{E_n - E_{n'}}\left(1 - \delta_{n'n}\right) + \tilde{E}_n^{(2)}\delta_{n'n}\end{aligned}$$

If $n' = n$:

$$\boxed{\tilde{E}_n^{(2)} = \sum_{k\neq n}\frac{\left|\left\langle\psi_k\middle|\hat{V}\middle|\psi_n\right\rangle\right|^2}{E_n - E_k}} \tag{2.6}$$

If $n' \neq n$:

$$\boxed{\left\langle\psi_{n'}\middle|\tilde{\psi}_n^{(2)}\right\rangle = \sum_{k\neq n}\frac{\left\langle\psi_k\middle|\hat{V}\middle|\psi_n\right\rangle\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_k\right\rangle}{(E_n - E_k)(E_n - E_{n'})} + \frac{\left\langle\psi_n\middle|\hat{V}\middle|\psi_n\right\rangle\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle}{E_n - E_{n'}}} \tag{2.7}$$

$$\left|\tilde{\psi}_n^{(2)}\right\rangle = \sum_{n'\neq n} \left|\psi_{n'}\right\rangle \left[\frac{\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_k\right\rangle\left\langle\psi_k\middle|\hat{V}\middle|\psi_n\right\rangle}{(E_n - E_k)(E_n - E_{n'})} + \frac{\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle\left\langle\psi_n|\hat{V}\middle|\psi_n\right\rangle}{E_n - E_{n'}}\right] \tag{2.8}$$

Section 3

Lecture 3

Take into account Equation 1.1 where $\hat{H}_o\big|\psi_n\big\rangle = E_n\big|\psi_n\big\rangle$ and $\big\langle\psi_{n'}\big|\psi_n\big\rangle = \delta_{n'n}$.

If

$$\left|\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle\right|^2 \ll (E_n - E_{n'})^2$$

then,

$$\hat{H}\big|\tilde{\psi}_n\big\rangle = \hat{E}_n\big|\tilde{\psi}_n\big\rangle$$

where

$$\hat{E}_n = E_n + \lambda\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle + \lambda^2 \sum_{n'\neq n} \frac{\left|\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle\right|^2}{E_n - E_{n'}} + \mathcal{O}(\lambda^3)$$

$$\psi_n = \psi_n + \lambda \sum_{n'\neq n} \frac{\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle}{E_n - E_{n'}}\big|\psi_{n'}\big\rangle + \mathcal{O}(\lambda^2)$$

here,

E_n: Unperturbed eigenenergy.

$\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle$: Expectation value of the perturbation in the unperturbed state.

$\big\langle\psi_{n'}\big|\hat{V}\big|\psi_n\big\rangle$: Matrix element fot $n \to n' \to n$

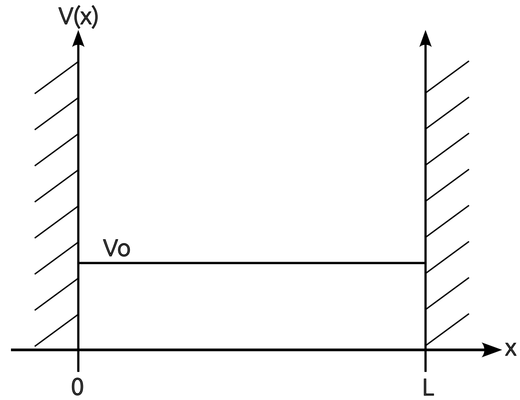
$E_n - E_{n'}$: Energy difference between ψ_n and $\psi_{n'}$.

Subsection 3.1

Example 3.1

In this example we will consider a 1D infinite square well with a perturbative potential $V = V_0$. Using Equation 1.1 we can write the perturbated hamiltonian for the infinite square well as

$$\begin{aligned}\tilde{H} &= \hat{H}_0 + \lambda\hat{V} \\ &= \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V_0, \quad x \in [0, L]\end{aligned} \tag{3.1}$$



So we have the Schrödinger equation

$$\frac{-\hbar^2}{2m}\frac{d^2\tilde{\psi}_n(x)}{dx^2} + \lambda\tilde{V}_o\tilde{\psi}_n(x) = \tilde{E}_n\tilde{\psi}_n(x)$$

for the perturbated system, and the one for the unperturbated system

$$\hat{H}_o\psi_n = E_n\psi_n$$

so, we have a well known ODE

$$\psi_n''(x) = \frac{-2mE_n\psi_n(x)}{\hbar^2} \tag{3.2}$$

whose general solution is

$$\psi_n(x) = A\cos\left(\sqrt{\frac{2mE_n}{\hbar^2}}x\right) + B\sin\left(\sqrt{\frac{2mE_n}{\hbar^2}}x\right) \tag{3.3}$$

Now, we need to apply the boundary conditions so we can find the constants A and B

$$\psi(0) = \psi(L) = 0$$

$$\psi(0) = A\cancelto{1}{\cos(0)} + B\cancelto{0}{\sin(0)} + \implies A = 0$$

$$\psi(L) = B\sin\left(\sqrt{\frac{2mE_n}{\hbar^2}}L\right) = 0 \implies \sqrt{\frac{2mE_n}{\hbar^2}}L = n\pi, \;\; n \in \mathbb{N}\ wlog$$

therefore

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \longleftarrow \text{Eigenenergies of the unperturbed infinite square well.}$$

$$\psi(x) = B \sin\left(\frac{\sqrt{2m}}{\hbar}\left(\frac{n^2\pi^2\hbar^2}{2mL^2}\right)^{1/2} x\right) = B \sin\left(\frac{n\pi x}{L}\right) \tag{3.4}$$

The Equation 3.4 is the wavefunction of the n^{th} eigenstate of the infinite square well. But this wavefunction is not normalised, so we need to normalise it.

SUBSECTION 3.2

Normalisation

To normalise the wavefunction we need to find the constant B such that $\langle \psi_n | \psi_n \rangle = 1$.

$$\begin{aligned}
\langle \psi_n | \psi_n \rangle &= 1 \\
&= B^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx \\
&= B^2 \frac{L}{2} = 1 \\
&\boxed{B = \sqrt{\frac{2}{L}}}
\end{aligned} \tag{3.5}$$

Then, replacing B in Equation 3.4 we get

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

From our previous results we know that the first and second order corrections to the eigenenergy are given by the following equation

$$\hat{E}_n = E_n + \langle \psi_n | \hat{V} | \psi_n \rangle + \sum_{n' \neq n} \frac{\left| \langle \psi_{n'} | \hat{V} | \psi_n \rangle \right|^2}{E_n - E_{n'}} \tag{3.6}$$

Substituting the results for ψ_n and E_n into Equation 3.6 we get

$$\tilde{E}_n = \frac{n^2\pi^2\hbar^2}{2mL^2} + \int_0^L \cancelto{1}{\frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)}.V_0 dx + \sum_{n \neq n'} \frac{\left| \cancelto{0}{\int_0^L \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n,\pi x}{L}\right) dx} \right|^2}{n^2 - n'^2} V_0^2 \frac{2mL^2}{\pi^2\hbar^2}$$

$$\boxed{\tilde{E}_n = \frac{n^2\pi^2\hbar^2}{2mL} + V_0} \tag{3.7}$$

Basically, if we add a constant potential V_0 everywhere, this just shifts the eigenenergies by V_0.

The 2^{nd} order term is zero because V_0 does not alter the wavefunction ψ_n and $\left\langle \psi_{n'} \middle| \psi_n \right\rangle = \delta_{n'n}$.

Now, let's consider the case for a perturbative potential $V_0/2$. If we half the potential, the eigenenergies will be shifted by $V_0/2$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \int_0^{\frac{L}{2}} V_0 \sin^2\left(\frac{n\pi x}{L}\right)\frac{2}{L}dx + \sum_{n\neq n'} \frac{V_0^2}{n^2 - n'^2}\frac{2mL^2}{\pi^2\hbar^2}\left| \int_0^{\frac{L}{2}} \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n'\pi x}{L}\right)dx\right|^2 \left(\frac{2}{L}\right)^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + V_0\frac{2}{L}\left(\frac{L}{2\cdot 2}\right) + \frac{2mL^2}{\pi^2\hbar^2}V_0^2\sum_{n'\neq n}\frac{1}{n^2-n'^2}\cdot\left|\frac{1}{2}\int_0^{\frac{L}{2}}\cos\left(\frac{(n-n')\pi x}{L}\right) + \cos\left(\frac{(n+n')\pi x}{L}\right)dx\right|^2 \cdot \left(\frac{2}{L}\right)^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \frac{V_0}{2} + \frac{2mL^2V_0^2}{\pi^2\hbar^2}\sum_{n'\neq n}\frac{1}{n^2-n'^2}\frac{1}{4}\cdot\left|\frac{L}{\pi}\left(\frac{\sin\left(\frac{(n-n')x\pi}{L}\right)}{n-n'}\right) - \left(\frac{\sin\left(\frac{(n+n')x\pi}{L}\right)}{n+n'}\right)\Bigg|_0^{\frac{L}{2}}\right|^2\left(\frac{2}{L}\right)^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \frac{V_0}{2} + \frac{2mL^2V_0^2}{\pi^2\hbar^2}\sum_{n'\neq n}\frac{1}{n^2-n'^2}\left|\frac{\sin((n-n')\pi/2)}{n-n'} + \frac{\sin((n+n')\pi/2)}{n+n'}\right|^2$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL} + \frac{V_0}{2} + \frac{2mL^2V_0^2}{\pi^2\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left|\frac{(1-(-1)^{n-n'})}{2}\frac{(-1)^{\frac{n-n'-1}{2}}}{n-n'} + \frac{(1-(-1))^{n+n'}(-1)^{\frac{n+n'}{2}}}{n+n'}\right|^2$$

If $n+n$, is even, then $n-n$, is even.
Proof:

$$n + n' = 2k$$
$$n - n' = n + n' - 2n' = 2k - 2n' \implies \text{Which is even.}$$

If $n+n$, is odd, then $n-n$, is odd.

Proof:

$$\begin{aligned} n+n' &= 2k+1 \\ n-n' &= n+n'-2n' = 2k+1-2n' \\ &= 2(k-n')+1 \implies \text{is odd.} \end{aligned}$$

Then:

$$\frac{1-(-1)^{n-n'}}{2} = \frac{1-(-1)^{n+n'}}{2}$$

$$\tilde{E}_n^{(2)} = \frac{2mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left|\frac{1-(-1)^{n+n'}}{2}\right|\left|\frac{(-1)^{\frac{n-n'-1}{2}}}{n-n'}+\frac{(-1)^{\frac{n+n'}{2}}}{n+n'}\right|^2$$

Only when $n+n'$ is odd we have a correction.

$$\begin{aligned} \tilde{E}_n^{(2)} &= \frac{2mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left|\frac{1-(-1)^{n+n'}}{2}\right|\left|(-1)^{\frac{n+n'}{2}}\right|^2\left|\frac{1}{n+n'}-\frac{1}{n-n'}\right|^2 \\ &= \frac{2mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{1}{(n-n')(n+n')}\left(\frac{1-(-1)^{n+n'}}{2}\right)\left|\frac{n-n'-(n+n')}{(n+n')(n-n')}\right|^2 \\ &= \frac{8mL^2V_o^2}{\pi^4\hbar^2}\sum_{n'\neq n}\frac{n'^2}{(n^2-n'^2)^3}\frac{1-(-1)^{n+n'}}{2} \end{aligned}$$

We only have a 2nd order correction when we go odd $\to$ even or even $\to$ odd.

Suppose n is even:

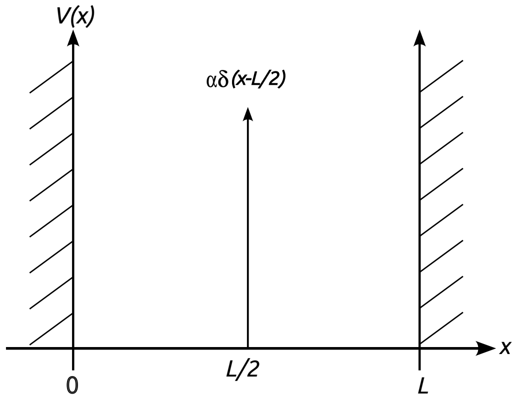
$$\begin{aligned} n = 2k \implies \Psi_{2k}\left(\frac{L}{2}\right) &= 0 \\ \Psi_{2k+1}\left(\frac{L}{2}\right) &= \pm\sqrt{\frac{2}{L}} \end{aligned}$$

Subsection 3.3

Example 3.3

Let's consider the infinite square well potential with a perturbative potential $V(x) = \alpha\delta(x-\frac{L}{2})$. From the aforementioned results we can state the criteria for using perturbation theory:

$$\boxed{\left|\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle\right|^2 \ll (E_n - E_{n'})^2}$$



$$\boxed{\psi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \qquad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$

$$\begin{aligned}
\left|\left\langle\psi_{n'}\middle|\hat{V}\middle|\psi_n\right\rangle\right|^2 &= \left|\alpha\int_0^L \frac{2}{L}\sin\left(\frac{n'\pi x}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\delta\left(x-\frac{L}{2}\right)dx\right|^2 \\
&= \frac{4}{L^2}\alpha^2\sin^2\left(\frac{n'\pi}{L}\right)\sin^2\left(\frac{n\pi}{L}\right) \\
&= \left(\frac{2\alpha}{L}\right)^2 \underbrace{\left(\frac{1-(-1)^{n'}}{2}\right)}_{\text{n' is odd}}\underbrace{\left(\frac{1-(-1)^{n}}{2}\right)}_{\text{n is odd}}
\end{aligned}$$

$$(E_n - E_{n'})^2 = \left(\frac{\pi^2\hbar^2}{2mL^2}\right)(n^2-n'^2)^2$$

$$\frac{4\alpha^2}{L^2} \ll \frac{\pi^4\hbar^4}{4m^2L^4}(n-n')^2(n+n')^2$$

$$\alpha \ll \frac{\pi^2\hbar^2}{2mL}\left|n^2-n'^2\right| = \frac{\pi^2-n'^2}{2mL}\underbrace{(n-n')}_{\geq 2}\underbrace{(n+n')}_{\geq 4}$$

$$\alpha << \frac{4\pi^2\hbar^2}{mL}$$

$$\begin{aligned}
\tilde{E}_n^{(1)} &= \left\langle\psi_n\middle|\hat{V}\middle|\psi_n\right\rangle \\
&= \int_2^L \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)\alpha\delta\left(x-\frac{L}{2}\right)dx \\
&= \frac{2}{L}\sin^2\left(\frac{n\pi L}{2L}\right)\cdot\alpha\cancelto{0}{\int_0^L \delta\left(x-\frac{L}{2}\right)} \\
&= \frac{2}{L}\left(\frac{1-(-1)^n}{2}\right)
\end{aligned}$$

$$\tilde{E}_{2k} = \frac{\pi^2\hbar^2(2k)^2}{2mL^2} + 0$$

when ψ_{2k} has no 1^{st} order correction to their eigenenergies.

$$\tilde{E}_{2k-1} = \frac{\pi^2\hbar^2(2k-1)^2}{2mL^2} + \frac{2\alpha}{L}$$

odd ψ_{2k-1} have a constant shift by $\frac{2}{L}\alpha$.

$$\psi_{2k}\left(\frac{L}{2}\right) = \sqrt{\frac{2}{L}}\sin\left(\frac{2k\pi L}{2L}\right) = \sqrt{\frac{2}{L}}\sin(\pi k) = 0$$

even n index wavefunctions all have a node @ $\frac{L}{2} \to \left(\psi_{2k}\left(\frac{L}{2}\right) = 0\right)$.

Since $V(x) = \alpha\delta\left(x - \frac{2}{L}\right)$ is non-zero only @ $\frac{L}{2}$ it does nothing to the even n wavefunctions.

$\because$ a particle in the $2k-1$, odd n, state ψ_{2k-1} has a probability $\left|\psi_{2k-1}\left(\frac{L}{2}\right)\right|^2 = \frac{2}{L}$ of being @ $\frac{L}{2}$.