

# Lectures on Quantum Mechanics

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# 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.<sup>1</sup>

<sup>1</sup> *With some additional side-notes*

# Time Independent Non-degenerate Perturbation Theory

## 1 Lecture 1

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

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

where <sup>2</sup>

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

So that  $\{\Psi_n\}$  forms a orthonormal basis over the Hilbert space of  $H_0$ . We apply a perturbative potential  $\tilde{V}$  <sup>3</sup> to  $H_0$ , yielding a new Hamiltonian. for the perturbed system,

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

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

### 1.1 Method

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

$$\begin{aligned} \tilde{E}_n &= \tilde{E}_0^{(0)} + \lambda\tilde{E}_n^{(1)} + \lambda^2\tilde{E}_n^{(2)} + \dots = \sum_k \lambda^k \tilde{E}_n^{(k)} \\ \tilde{\psi}_n &= \tilde{\psi}_n^{(0)} + \lambda\tilde{\psi}_n^{(1)} + \lambda^2\tilde{\psi}_n^{(2)} + \dots = \sum_k \lambda^k \tilde{\psi}_n^{(k)} \end{aligned}$$

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

$$\tilde{H}|\tilde{\psi}_n\rangle = \tilde{E}_n|\tilde{\psi}_n\rangle \quad (1.2)$$

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

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

<sup>2</sup> The student may remember the Dirac delta function from his/her Quantum Mechanics I course.

<sup>3</sup>  $\tilde{V}$  is very small compared to  $H_0$

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

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

Since 1.6 is true for any value of  $\lambda$ , it must hold for each power of  $\lambda$  separately:

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

$$\begin{aligned} \langle \psi_{n'} | \hat{H}_0^\dagger &= E_{n'} \langle \psi_{n'} | \\ (E_{n'} - \hat{E}_n^{(0)}) \langle \psi_{n'} | \hat{\psi}_n^{(0)} \rangle &= 0 \end{aligned}$$

So,

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

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

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

If the system is degenerate, then:

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

Then:

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

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

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

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

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

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

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

$$\begin{aligned}
|\hat{\psi}_n^{(0)}\rangle &= |\psi_n\rangle \quad (\text{non-degenerate}), \quad \hat{E}_n^{(0)} = E_n \\
(E_{n'} - E_n) \langle \psi_{n'} | \hat{\psi}_n^{(1)} \rangle + \langle \psi_{n'} | \hat{V} | \psi_n \rangle &= \hat{E}_n^{(1)} \delta_{n'n}
\end{aligned} \tag{1.8}$$

if  $n' = n$ :

$$\begin{aligned}
(\cancel{E_{n'}} - E_n) \langle \psi_{n'} | \hat{\psi}_n^{(1)} \rangle + \langle \psi_{n'} | \hat{V} | \psi_n \rangle &= \hat{E}_n^{(1)} \delta_{n'n} \xrightarrow{0} \\
\implies \hat{E}_n^{(1)} &= \langle \psi_n | \hat{V} | \psi_n^{(1)} \rangle \\
\hat{E}_n &= E_n + \langle \psi_{n'} | \hat{V} | \psi_n^{(1)} \rangle + \mathcal{O}(\lambda^2) \\
|\hat{\psi}_n\rangle &= |\psi_n\rangle + \mathcal{O}(\lambda)
\end{aligned} \tag{1.9}$$

if  $n' \neq n$ :

$$\begin{aligned}
(E_{n'} - E_n) \langle \psi_{n'} | \hat{\psi}_n^{(1)} \rangle &= -\langle \psi_{n'} | \hat{V} | \psi_n \rangle + \hat{E}_n^{(1)} \delta_{n'n} \xrightarrow{0} \\
\langle \psi_{n'} | \hat{\psi}_n^{(1)} \rangle &= \frac{\langle \psi_{n'} | \hat{V} | \psi_n \rangle}{E_n - E_{n'}}
\end{aligned} \tag{1.10}$$

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

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

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

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

## 2 Lecture 2

In the previous lecture we defined the perturbed hamiltonian as: <sup>4</sup> 1.1 as:

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

<sup>4</sup>  $\tilde{H}$ : perturbed hamiltonian,  
 $\hat{H}_0$ : unperturbed hamiltonian,  
 $\lambda$ : bookkeeping parameter,  
 $\hat{V}$ : perturbing potential.

**Definition 2.1.** since  $\hat{V}$  needs to be smaller than  $\hat{H}_0$ ,  $\lambda$  keeps track of this, i.e., dependence on  $\hat{V}$ .

Writing the Schrödinger equation:

$$(\hat{H}_0 + \lambda \hat{V})\hat{\psi}_n = \tilde{E}_n \tilde{\psi}_n$$

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

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

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

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

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

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

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

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

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

$$\implies E_{n'} \langle \psi_{n'} | \psi_n^{(0)} \rangle = \hat{E}_0^{(0)} \langle \psi_{n'} | \psi_n^{(0)} \rangle$$

$$E_{n'}^{(0)} = E_{n'} \text{ or } \langle \psi_{n'} | \psi_n^{(0)} \rangle = 0$$

$$\mathbb{1} = \sum_{n'} |\psi_{n'}\rangle \langle \psi_{n'}|$$

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

If  $E_n$  is k-level degenerate, then:

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

Consider  $\hat{H}_o$  to be nondegenerate:

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

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

Since  $\langle \psi_{n'} | \psi_n^{(0)} \rangle = 0$  for  $n' \neq n$ :

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

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

$\iff$  If we turn the perturbation off we get the eigenenergy of the unperturbed system.

$\therefore$  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  $\lambda = 0$

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

,where

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

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

**Assuming  $\hat{H}_o$  is non-degenerate**

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

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

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

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



Gather together terms of order 1 in  $\lambda$  in the (SE):

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

Set  $\lambda = 1$ ,

$$\hat{H}_o \left| \tilde{\psi}_n^{(1)} \right\rangle + \hat{V} \left| \tilde{\psi}_n^{(0)} \right\rangle = E_n \left| \tilde{\psi}_n^{(1)} \right\rangle + E_n^{(1)} \left| \psi_n \right\rangle$$

This 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  $\psi_n$  respectively  $\because$  the  $\mathcal{O}^{th}$  relates the kth order corrections to all previous orders.

## 2.1 Two Unknowns

Use the fact that:

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

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

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

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

$$(E_{n'} - E_n) \langle \psi_{n'} | \tilde{\psi}_n^{(1)} \rangle + \langle \psi_{n'} | \hat{V} | \psi_n \rangle = \tilde{E}_n^{(1)} \delta_{n'n} \quad (2.1)$$

$\langle \psi_{n'} | \tilde{\psi}_n^{(1)} \rangle$ : Coefficient of  $|\psi_{n'}\rangle$ .

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

If  $n' = n$ , (2.2.1) yields to:  $\tilde{E}_n^{(1)}$

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

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

If  $n' \neq n$ , (2.2.1) yields to: coefficients of  $|\tilde{\psi}_n^{(1)}\rangle$  and  $\lambda = 1$ .

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

$$\begin{aligned}
|\tilde{\psi}_n^{(1)}\rangle &= \sum_{n' \neq n} \frac{\langle \psi_{n'} | \hat{V} | \psi_n \rangle}{E_n - E_{n'}} |\psi_{n'}\rangle \\
\tilde{E}_n &= E_n + \langle \psi_n | \hat{V} | \psi_n \rangle + \mathcal{O}(\lambda^2) \\
|\tilde{\psi}_n\rangle &= |\psi_n\rangle + \sum_{n' \neq n} \frac{\langle \psi_{n'} | \hat{V} | \psi_n \rangle}{E_n - E_{n'}} |\psi_{n'}\rangle + \mathcal{O}(\lambda^2)
\end{aligned}$$

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

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

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

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

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

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:**

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

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

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

for our application of perturbation theory to apply.

$$\Rightarrow \lambda \gg 1$$

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

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

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

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

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

If  $n' = n$ :

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

If  $n' \neq n$ :

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

**3    Lecture 3**