

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.¹

¹ *With some additional side-notes*

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 ²

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

So that $\{\Psi_n\}$ forms a orthonormal basis over the Hilbert space of H_0 . We apply a perturbative potential \tilde{V} ³ 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.

² The student may remember the Kronecker delta from his/her Quantum Mechanics I course.

³ \tilde{V} is very small compared to H_0 .

SUBSECTION 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 λ .

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

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

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

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

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

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

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

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

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

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

So,

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

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

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

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:

$$\begin{aligned} |\psi_n^{(0)}\rangle &= \sum_{k'=0}^k C_{n+k'} |\psi_{n+k'}\rangle \\ \hat{E}_n &= E_n \mathcal{O}(\lambda) \end{aligned}$$

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

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

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

$$\begin{aligned} \langle\psi_{n'}|\hat{H}_0|\hat{\psi}_n^{(1)}\rangle + \langle\psi_{n'}|\hat{V}|\hat{\psi}_n^{(0)}\rangle &= E_n^{(0)}\langle\psi_{n'}|\hat{\psi}_n^{(1)}\rangle + \hat{E}_n^{(1)}\langle\psi_{n'}|\hat{\psi}_n^{(0)}\rangle \\ \langle\psi_{n'}|\hat{H}_0 &= E_{n'}\langle\psi_{n'}| \\ |\hat{\psi}_n^{(0)}\rangle &= |\psi_n\rangle \quad (\text{non-degenerate}), \quad \hat{E}_n^{(0)} = E_n \\ (E_{n'} - E_n)\langle\psi_{n'}|\hat{\psi}_n^{(1)}\rangle + \langle\psi_{n'}|\hat{V}|\psi_n\rangle &= \hat{E}_n^{(1)}\delta_{n'n} \end{aligned} \quad (1.8)$$

if $n' = n$:

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

if $n' \neq n$:

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

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

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

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

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

SECTION 2

Lecture 2

In the previous lecture we defined the perturbed hamiltonian ⁴ 1.1 as:

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

\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:

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

\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 λ :

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

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

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

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

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

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

$$\begin{aligned}\langle \psi_{n'} | \hat{H}_0^\dagger &= E_{n'} \langle \psi_{n'} | \quad (\text{SE}) \text{ for } \hat{H}_0 \\ \implies E_{n'} \langle \psi_{n'} | \psi_n^{(0)} \rangle &= \hat{E}_0^{(0)} \langle \psi_{n'} | \psi_n^{(0)} \rangle \\ E_{n'}^{(0)} &= E_{n'} \quad \text{or} \quad \langle \psi_{n'} | \psi_n^{(0)} \rangle = 0\end{aligned}$$

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

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

If E_n is k-level degenerate, then:

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

⁴ \tilde{H} : perturbed hamiltonian,
 \hat{H}_0 : unperturbed hamiltonian,
 λ : bookkeeping parameter,
 \hat{V} : perturbing potential.

Consider \hat{H}_0 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 $n' \neq n$:

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

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 $\lambda = 0$

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

,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 $\{|\psi_n\rangle, \dots, |\psi_{n+k-1}\rangle\}$ for k-fold degenerate systems, unless the unperturbed wavefunctions are eigenstates of the perturbation.

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

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

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 λ in the (SE):

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

Set $\lambda = 1$ ⁵,

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

SUBSECTION 2.1

Two Unknowns

Use the fact that:

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

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

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

$$\begin{aligned} \langle\psi_{n'}|\hat{H}_o^\dagger|\tilde{\psi}_n^{(1)}\rangle + \langle\psi_{n'}|\hat{V}|\tilde{\psi}_n^{(0)}\rangle &= E_n\langle\psi_{n'}|\tilde{\psi}_n^{(1)}\rangle + E_n^{(1)}\underbrace{\langle\psi_{n'}|\psi_n\rangle}_{\delta_{n'n}} \\ (E_{n'} - E_n)\langle\psi_{n'}|\tilde{\psi}_n^{(1)}\rangle + \langle\psi_{n'}|\hat{V}|\psi_n\rangle &= \tilde{E}_n^{(1)}\delta_{n'n} \end{aligned} \quad (2.4)$$

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

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

If $n' = n$, 2.4 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 $n' \neq n$, 2.4 yields to: coefficients of $|\tilde{\psi}_n^{(1)}\rangle$ and $\lambda = 1$.

$$\begin{aligned} \langle\psi_{n'}|\tilde{\psi}_n^{(1)}\rangle &= \frac{\langle\psi_{n'}|\hat{V}|\psi_n\rangle}{E_n - E_{n'}} \\ |\tilde{\psi}_n^{(1)}\rangle &= \sum_{n' \neq n} \frac{\langle\psi_{n'}|\hat{V}|\psi_n\rangle}{E_n - E_{n'}} |\psi_{n'}\rangle \\ \tilde{E}_n &= E_n + \langle\psi_n|\hat{V}|\psi_n\rangle + \mathcal{O}(\lambda^2) \\ |\tilde{\psi}_n\rangle &= |\psi_n\rangle + \sum_{n' \neq n} \frac{\langle\psi_{n'}|\hat{V}|\psi_n\rangle}{E_n - E_{n'}} |\psi_{n'}\rangle + \mathcal{O}(\lambda^2) \end{aligned} \quad (2.5)$$

⁵ 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 ψ_n respectively \because the \mathcal{O}^{th} relates the k th order corrections to all previous orders.

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.

⁶ **Note:** if \hat{V} (the perturbation) is an odd function:

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

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

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

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.

$$\implies \lambda \gg 1$$

$$\mathcal{O}(\lambda^2) : \hat{H}_0 |\tilde{\psi}_n^{(2)}\rangle + \hat{V} |\tilde{\psi}_n^{(1)}\rangle = E_n |\tilde{\psi}_n^{(2)}\rangle + \tilde{E}_n^{(1)} |\tilde{\psi}_n^{(1)}\rangle + \tilde{E}_n^{(2)} |\psi_n\rangle$$

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

$$\langle \psi_{n'} | \hat{H}_0 |\tilde{\psi}_n^{(2)}\rangle + \langle \psi_{n'} | \hat{V} |\tilde{\psi}_n^{(1)}\rangle = E_n \langle \psi_{n'} | \tilde{\psi}_n^{(2)}\rangle + \tilde{E}_n^{(1)} \langle \psi_{n'} | \tilde{\psi}_n^{(1)}\rangle + \tilde{E}_n^{(2)} \langle \psi_{n'} | \psi_n \rangle$$

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

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

If $n' = n$:

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

If $n' \neq n$:

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

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

SECTION 3

Lecture 3
