## Review Handout

## Time Independent Perturbation Theory in Quantum Mechanics

**In this lecture you will learn:**

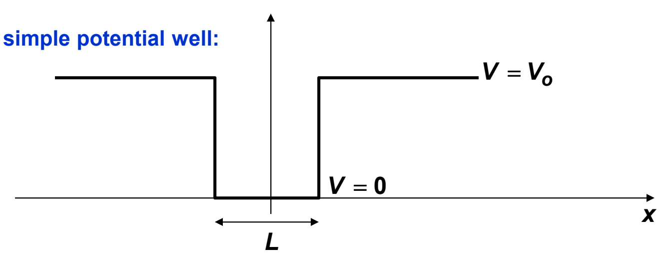
• First and Second Order Time Independent Perturbation Theory in Quantum Mechanics

Werner Heisenberg (1901-1976)



## Motivation: A Potential Well Problem

**Consider a simple potential well:**




**Suppose one has found all the eigenvalues and the eigenstates by solving the Schrodinger equation:**

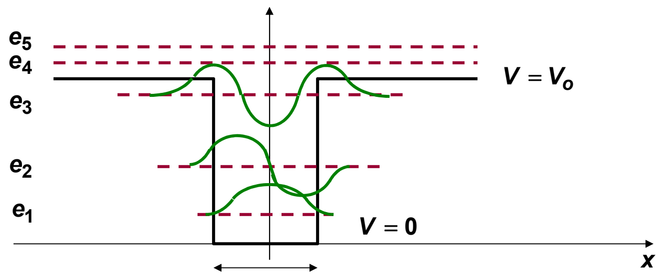
$$-\frac{\hbar^2}{2m}\nabla^2\phi(x)+V(x)\phi(x)=E\,\phi(x)$$

The eigenenergies are labeled as: $e_n$ $\{\, n = 1,2,3,\ldots\ldots$

The corresponding eigenstates are: $\phi_n(x)$ or $|\phi_n\rangle$ $\{\, n = 1,2,3,\ldots\ldots$

## Motivation: A Potential Well Problem

**Eigenstates of a simple potential well are as depicted below:**




The eigenenergies are labeled as: $e_n \quad \{ n = 1,2,3,\ldots\ldots$

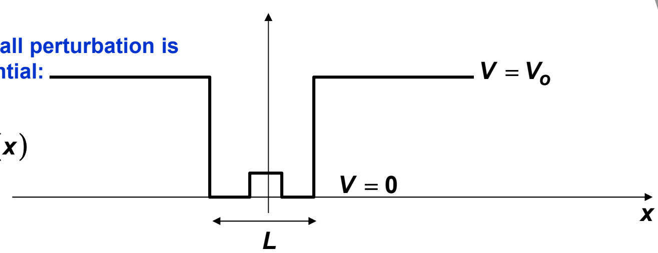
The corresponding eigenstates are: $\phi_n(x)$ or $|\phi_n\rangle \quad \{ n = 1,2,3,\ldots\ldots$



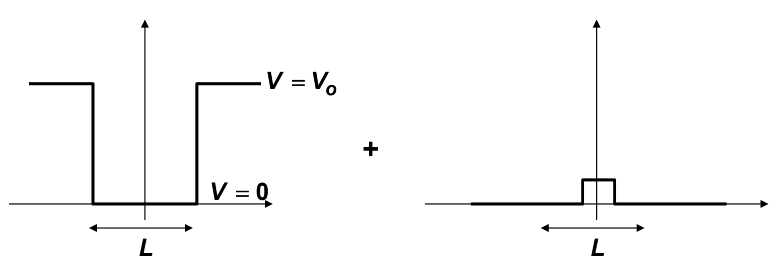
## Motivation: Addition of a Small Perturbation

**Now assume that a small perturbation is introduced in the potential:**

$$U(x) = V(x) + \Delta V(x)$$



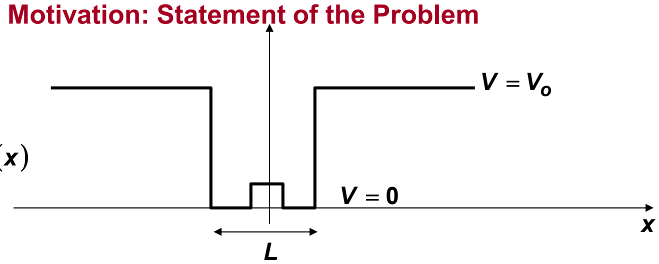

$U(x) =$




$V(x)$ $\quad\quad$ $\Delta V(x)$

## Motivation: Statement of the Problem

$U(x) = V(x) + \Delta V(x)$




How do we find the eigenstates and eigenenergies for the new potential $U(x)$ ?

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x) + U(x)\psi(x) = E\,\psi(x)$$

**Option:** Start from scratch again and solve the Schrodinger equation to get:

The new eigenenergies, labeled as: $E_n$ $\quad \{ n = 1,2,3,\ldots\ldots$

and the corresponding eigenstates: $\psi_n(x)$ or $|\psi_n\rangle$ $\quad \{ n = 1,2,3,\ldots\ldots$

Luckily, another simpler option is available



## Time Independent Perturbation Theory

Lets generalize the potential well problem a little

Suppose for a Hamiltonian $\hat{H}_o$ we have solved the Schrodinger equation and obtained all the eigenenergies and eigenstates:

$$\hat{H}_o|\phi_n\rangle = e_n|\phi_n\rangle \qquad \{ n = 1,2,3,\ldots\ldots \qquad \text{Orthonormality} \rightarrow \langle\phi_n|\phi_p\rangle = \delta_{np}$$

We now want to obtain the eigenenergies and the eigenstates for the new hamiltonian $\hat{H}$ where $\hat{H}$ has an added small perturbation,

$$\hat{H} = \hat{H}_o + \Delta\hat{H} \qquad \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \qquad \{ n = 1,2,3,\ldots\ldots$$

**Basic Assumption:** If $\Delta\hat{H}$ is not too large a perturbation, the new eigenenergies and eigenstates are likely close to the unperturbed values

Therefore assume:

$$|\psi_n\rangle = |\phi_n\rangle + \underbrace{\sum_{m\neq n}\Delta c_m^n|\phi_m\rangle}_{\text{Some small correction}}$$

$$E_n = e_n + \underbrace{\Delta e_n}_{\text{Some small correction}}$$

Main idea: Use the old eigenstates to construct the new eigenstates

## First Order Perturbation Theory

**A Note on the Correction Terms:**

$$E_n = e_n + \underbrace{\Delta e_n}_{\text{Correction}} \qquad\qquad |\psi_n\rangle = |\phi_n\rangle + \underbrace{\sum_{m\neq n} \Delta c_m^n |\phi_m\rangle}_{\text{Correction}}$$

We expect that the correction terms can be expended in a series where each successive term is proportional to a higher power of $\Delta\hat{H}$ . After all, the corrections should approach zero as the perturbation is made smaller, i.e. as $\Delta\hat{H} \to 0$

**First Order Corrections to the Eigenenergies:**

Take the expressions: $|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle \qquad E_n = e_n + \Delta e_n$

Plug them into the Schrodinger equation: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

And multiply both sides from the left by the bra: $\langle\phi_n|$

$$\langle\phi_n|\left(\hat{H}_o + \Delta\hat{H}\right)\left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle\right) = \langle\phi_n|\left(e_n + \Delta e_n\right)\left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle\right)$$



## First Order Perturbation Theory

$$\langle\phi_n|\left(\hat{H}_o + \Delta\hat{H}\right)\left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle\right) = \langle\phi_n|\left(e_n + \Delta e_n\right)\left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle\right)$$

Note that the quantities $\Delta c_m^n$ and $\Delta e_n$ , if non-zero, are proportional to some power of $\Delta\hat{H}$ that is equal to or greater than unity

So, as a first order approximation, we keep only those terms in the equation above that are first order in the perturbation $\Delta\hat{H}$ . This gives,

$$\Delta e_n = \langle\phi_n|\Delta\hat{H}|\phi_n\rangle$$

As expected, the first order correction to the eigenenergy is proportional to $\Delta\hat{H}$

**First Order Corrections to the Eigenstates:**

Now take the expressions: $|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle \qquad E_n = e_n + \Delta e_n$

Plug them into the Schrodinger equation: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

And multiply both sides from the left by the bra: $\langle\phi_p| \qquad (p \neq n)$

$$\langle\phi_p|\left(\hat{H}_o + \Delta\hat{H}\right)\left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle\right) = \langle\phi_p|\left(e_n + \Delta e_n\right)\left(|\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle\right)$$

## First Order Perturbation Theory

$$\langle \phi_p | \left(\hat{H}_o + \Delta\hat{H}\right)\left( |\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle \right) = \langle \phi_p | \left(e_n + \Delta e_n\right)\left( |\phi_n\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle \right)$$

Again, as a first order approximation, we keep only those terms in the equation above that are first order in the perturbation $\Delta\hat{H}$. This gives,

$$\Delta c_p^n = \frac{\langle \phi_p | \Delta\hat{H} | \phi_n \rangle}{e_n - e_p}$$

Summing up the results obtained thus far, we can write the new eigenstates and eigenenergies in the presence of the perturbation as follows,

$$E_n = e_n + \langle \phi_n | \Delta\hat{H} | \phi_n \rangle \quad + \quad \text{terms higher order in } \Delta\hat{H}$$

$$|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} \frac{\langle \phi_m | \Delta\hat{H} | \phi_n \rangle}{e_n - e_m} |\phi_m\rangle \quad + \quad \text{terms higher order in } \Delta\hat{H}$$

**Question:** What if we want more accurate eiegenenergies and/or eigenstates?

**Answer:** One can obtain corrections to arbitrary large powers in $\Delta\hat{H}$



## Second Order Perturbation Theory

For many interesting perturbations the first order correction term to the energy vanishes, i.e.:

$$\langle \phi_n | \Delta\hat{H} | \phi_n \rangle = 0$$

For the above reason and/or also to obtain more accurate values of the eigenenergies, it is sometimes necessary to obtain corrections to the eigenenergies that are of second order in $\Delta\hat{H}$

**Second Order Corrections to the Eigenenergies:**

We take the expressions obtained that are accurate to first order in $\Delta\hat{H}$:

$$E_n = e_n + \langle \phi_n | \Delta\hat{H} | \phi_n \rangle + \Delta e_n$$

$$|\psi_n\rangle = |\phi_n\rangle + \sum_{m\neq n} \frac{\langle \phi_m | \Delta\hat{H} | \phi_n \rangle}{e_n - e_m} |\phi_m\rangle + \sum_{m\neq n} \Delta c_m^n |\phi_m\rangle$$

The terms containing $\Delta c_m^n$ and $\Delta e_n$ now represent second order corrections

We plug them into the Schrodinger equation: $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

And multiply both sides from the left by the bra: $\langle \phi_n |$

## Second Order Perturbation Theory

$$\langle \phi_n | \left(\hat{H}_o + \Delta\hat{H}\right) \left( |\phi_n\rangle + \sum_{m \neq n} \frac{\langle \phi_m | \Delta\hat{H} | \phi_n \rangle}{e_n - e_m} |\phi_m\rangle + \sum_{m \neq n} \Delta c_m^n |\phi_m\rangle \right) =$$

$$\langle \phi_n | \left(e_n + \langle \phi_n | \Delta\hat{H} | \phi_n \rangle + \Delta e_n\right) \left( |\phi_n\rangle + \sum_{m \neq n} \frac{\langle \phi_m | \Delta\hat{H} | \phi_n \rangle}{e_n - e_m} |\phi_m\rangle + \sum_{m \neq n} \Delta c_m^n |\phi_m\rangle \right)$$

We keep only those terms in the equation above that are second order or first order in the perturbation $\Delta\hat{H}$ . The terms first order in $\Delta\hat{H}$ cancel out (as they should since the solution we used was already accurate to the first order) and we get:

$$\Delta e_n = \sum_{m \neq n} \frac{\left| \langle \phi_m | \Delta\hat{H} | \phi_n \rangle \right|^2}{e_n - e_m}$$

The expression for the eigenenergies accurate to second order in $\Delta\hat{H}$ is thus:

$$E_n = e_n + \langle \phi_n | \Delta\hat{H} | \phi_n \rangle + \sum_{m \neq n} \frac{\left| \langle \phi_m | \Delta\hat{H} | \phi_n \rangle \right|^2}{e_n - e_m} + \text{terms of higher order in } \Delta\hat{H}$$



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