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 Schrödinger equation:

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

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

The corresponding eigenstates are: \( \phi_n(x) \) or \( |\phi_n\rangle \) \(\{ n = 1,2,3,\ldots \}\)
Motivation: A Potential Well Problem

Eigenstates of a simple potential well are as depicted below:

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

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

Motivation: Addition of a Small Perturbation

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

\[
U(x) = V(x) + \Delta V(x)
\]

where \( U(x) \) is the total potential, \( V(x) \) is the original potential, and \( \Delta V(x) \) is the perturbation.
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: \( E_n \) \( \{ n = 1, 2, 3, \ldots \} \)

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

Luckily, another simpler option is available

Time Independent Perturbation Theory

Lets generalize the potential well problem a little

Suppose for a Hamiltonian \( \hat{H}_0 \) we have solved the Schrodinger equation and obtained all the eigenenergies and eigenstates:

\[ \hat{H}_0 |\phi_n\rangle = e_n |\phi_n\rangle \quad \{ n = 1, 2, 3, \ldots \} \quad \text{Orthonormality} \implies \langle \phi_n | \phi_p \rangle = \delta_{np} \]

We now want to obtain the eigenenergies and the eigenstates for the new Hamiltonian \( \hat{H} \) where \( \Delta \hat{H} \) has an added small perturbation,

\[ \hat{H} = \hat{H}_0 + \Delta \hat{H} \quad \hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \quad \{ n = 1, 2, 3, \ldots \} \]

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:

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

\[ |\psi_n\rangle = |\phi_n\rangle + \sum_{m \neq n} c_m^n |\phi_m\rangle \]

Some small correction

\[ E_n = e_n + \Delta e_n \]

Some small correction

\[ \delta_{np} \Rightarrow \langle \phi_n | \phi_p \rangle \implies \delta_{np} \]

\[ \langle \phi_n | \phi_p \rangle \implies \delta_{np} \]
A Note on the Correction Terms:

\[ E_n = e_n + \Delta e_n \]

Correction

\[ |\psi_n\rangle = |\phi_n\rangle + \sum_{m \neq n} \Delta c_m^n |\phi_m\rangle \]

Correction

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

First Order Corrections to the Eigenenergies:

Take the expressions:

\[ |\psi_n\rangle = |\phi_n\rangle + \sum_{m \neq n} \Delta c_m^n |\phi_m\rangle \quad E_n = e_n + \Delta e_n \]

Plug them into the Schrödinger equation:

\[ \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \]

And multiply both sides from the left by the bra:

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

Note that the quantities \( \Delta c_m^n \) and \( \Delta e_n \), if non-zero, are proportional to some power of \( \Delta H \) 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 \( \Delta H \). 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 \( \Delta H \).

First Order Corrections to the Eigenstates:

Now take the expressions:

\[ |\psi_n\rangle = |\phi_n\rangle + \sum_{m \neq n} \Delta c_m^n |\phi_m\rangle \quad E_n = e_n + \Delta e_n \]

Plug them into the Schrödinger equation:

\[ \hat{H}|\psi_n\rangle = E_n|\psi_n\rangle \]

And multiply both sides from the left by the bra:

\[ \langle \phi_p | (\hat{H} + \Delta \hat{H}) \left( |\phi_n\rangle + \sum_{m \neq n} \Delta c_m^n |\phi_m\rangle \right) = \langle \phi_p | (e_n + \Delta e_n) \left( |\phi_n\rangle + \sum_{m \neq n} \Delta c_m^n |\phi_m\rangle \right) \]
First Order Perturbation Theory

\[
\langle \phi_p | \left( \hat{H}_0 + \Delta \hat{H} \right) | \phi_n \rangle + \sum_{m \neq n} \Delta c_{mn}^n | \phi_m \rangle = \langle \phi_p | \left( e_n + \Delta e_n \right) | \phi_n \rangle + \sum_{m \neq n} \Delta c_{mn}^n | \phi_m \rangle
\]

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,

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

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

**Question:** What if we want more accurate eigenenergies 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 \( \Delta \hat{H} \):

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

\[
| \psi_n \rangle = | \phi_n \rangle + \sum_{m \neq n} \frac{\langle \phi_m | \Delta \hat{H} | \phi_n \rangle}{e_n - e_m} | \phi_m \rangle + \sum_{m \neq n} \Delta c_{mn}^n | \phi_m \rangle
\]

The terms containing \( \Delta c_{mn}^n \) 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

\[
\langle \phi_n \rangle \left( \mathbf{H}_0 + \Delta \mathbf{H} \right) \left( \phi_n \right) + \sum_{m \neq n} \frac{\langle \phi_m | \Delta \mathbf{H} | \phi_n \rangle}{e_n - e_m} + \sum c_m^2 \left| \phi_m \right> = 0
\]

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

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

The expression for the eigenenergies accurate to second order in \( \Delta \mathbf{H} \) is thus:

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