Lecture 9

Non-degenerate & Degenerate Time Independent and Time Dependent Perturbation Theory:

Reading:

Notes and Brennan Chapter 4.1 & 4.2

Non-degenerate Time Independent Perturbation Theory

If the solution to an unperturbed system is known, including Eigenstates, $\Psi_n^{(0)}$ and Eigen energies, $E_n^{(0)}$, ...

$$H_0 \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}$$

...then we seek to find the approximate solution for the same system under a slight perturbation (most commonly manifest as a change in the potential of the system).

$$H\Psi_n = E_n \Psi_n$$

To do this , we expand the Hamiltonian into modified form,

$$H = H_0 + gH_p$$

Where g is a dimensionless parameter meant to keep track of the degree of "smallness" (we will eventually set g=1, but for now, we keep it)

$$\left(H_0 + gH_p\right)\Psi_n = E_n \Psi_n$$

where H' is the perturbation term in the Hamiltonian. As $g \rightarrow 0$, then $H \rightarrow H_o$, $\Psi_n \rightarrow \Psi_n^{(0)}$ and $E_n \rightarrow E_n^{(0)}$

Non-degenerate Time Independent Perturbation Theory

If the perturbation is small enough, it is reasonable to write the wavefunction as,

$$\Psi_n = \Psi_n^{(0)} + g\Psi_n^{(1)} + g^2\Psi_n^{(2)} + ...$$

... and the energy as,

$$E_n = E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + ...$$

Thus, we can write the Schrodinger equation as,

$$H\Psi_n = E\Psi_n$$
$$\left(H_0 + gH_p\right)\left(\Psi_n^{(0)} + g\Psi_n^{(1)} + g^2\Psi_n^{(2)} + \cdots\right) = \left(E_n^{(0)} + gE_n^{(1)} + g^2E_n^{(2)} + \cdots\right)\left(\Psi_n^{(0)} + g\Psi_n^{(1)} + g^2\Psi_n^{(2)} + \cdots\right)$$

or,

$$\begin{aligned}
&H\Psi_n - E\Psi_n = 0 \\
&+ g^0\left(H_0\Psi_n^{(0)} - E_n^{(0)}\Psi_n^{(0)}\right) \\
&+ g^1\left(H_0\Psi_n^{(1)} + H_p\Psi_n^{(0)} - E_n^{(0)}\Psi_n^{(1)} - E_n^{(1)}\Psi_n^{(0)}\right) \\
&+ g^2\left(H_0\Psi_n^{(2)} + H_p\Psi_n^{(1)} - E_n^{(0)}\Psi_n^{(2)} - E_n^{(1)}\Psi_n^{(1)} - E_n^{(2)}\Psi_n^{(0)}\right) \\
&+ g^3(\cdots) \\
&+ g^4(\cdots) \\
&+ \cdots = 0
\end{aligned}$$

For any choice of g, each term in parenthesis must be equal to 0!

Non-degenerate Time Independent Perturbation Theory

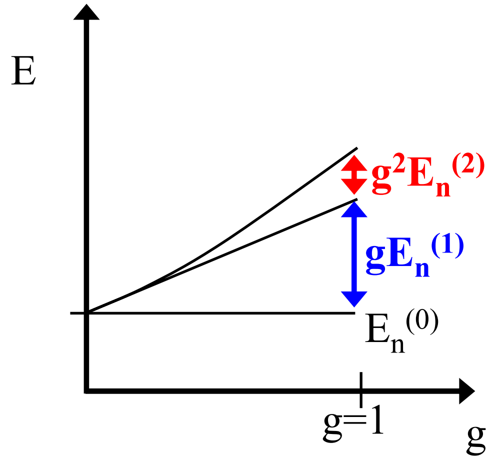
Given,

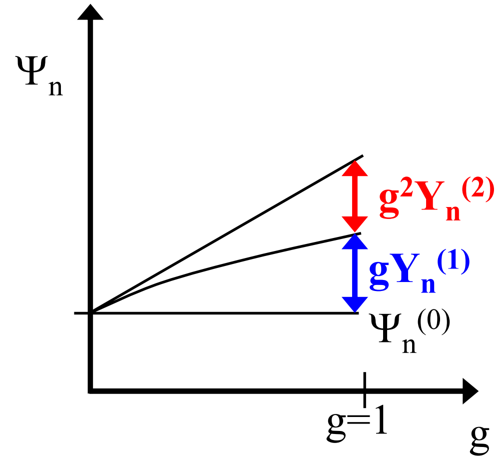
$$
\begin{aligned}
&H\Psi_n - E\Psi_n = 0 \\
&+ g^0\left(H_0\Psi_n^{(0)} - E_n^{(0)}\Psi_n^{(0)}\right) \\
&+ g^1\left(H_0\Psi_n^{(1)} + H_p\Psi_n^{(0)} - E_n^{(0)}\Psi_n^{(1)} - E_n^{(1)}\Psi_n^{(0)}\right) \\
&+ g^2\left(H_0\Psi_n^{(2)} + H_p\Psi_n^{(1)} - E_n^{(0)}\Psi_n^{(2)} - E_n^{(1)}\Psi_n^{(1)} - E_n^{(2)}\Psi_n^{(0)}\right) \\
&+ g^3(\cdots) \\
&+ g^4(\cdots) \\
&+ \cdots = 0
\end{aligned}
$$

For any choice of g, each term in parenthesis must be equal to 0!

1st order perturbation theory seeks values of $E_n^{(1)}$ and $\Psi_n^{(1)}$.

2nd order perturbation theory will seek values of $E_n^{(2)}$ and $\Psi_n^{(2)}$.





1st Order Perturbation Theory

Given the term that is 1st order in g,

$$g\left(H_0\Psi_n^{(1)} + H_p\Psi_n^{(0)} - E_n^{(0)}\Psi_n^{(1)} - E_n^{(1)}\Psi_n^{(0)}\right) = 0$$

and using the Fundamental Expansion Postulate for $\Psi_n^{(1)}$, using the basis vectors, $\Psi_j^{(0)}$'s

$$\Psi_n^{(1)} = \sum_j a_j \Psi_j^{(0)}$$

$$H_0\Psi_n^{(1)} + H_p\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(1)} + E_n^{(1)}\Psi_n^{(0)}$$

$$H_0\left(\sum_j a_j \Psi_j^{(0)}\right) + H_p\Psi_n^{(0)} = E_n^{(0)}\left(\sum_j a_j \Psi_j^{(0)}\right) + E_n^{(1)}\Psi_n^{(0)}$$

But since,

$$H_0\Psi_n^{(0)} = E_0\Psi_n^{(0)}$$

then,

$$\left(\sum_j a_j E_j^0 \Psi_j^{(0)}\right) + H_p\Psi_n^{(0)} = E_n^{(0)}\left(\sum_j a_j \Psi_j^{(0)}\right) + E_n^{(1)}\Psi_n^{(0)}$$

1^{st} Order Perturbation Theory

Cont'd,

$$\left(\sum_j a_j E_j^0 \Psi_j^{(0)}\right) + H_p \Psi_n^{(0)} = E_n^{(0)}\left(\sum_j a_j \Psi_j^{(0)}\right) + E_n^{(1)}\Psi_n^{(0)}$$

As we have done many times, we will multiply by $\Psi_m^{(0)*}$ and integrate over all space

$$\int\left(\sum_j a_j E_j^0 \Psi_m^{(0)*}\Psi_j^{(0)}\right)dv + \int \Psi_m^{(0)*} H_p \Psi_n^{(0)} dv = \int E_n^{(0)}\left(\sum_j a_j \Psi_m^{(0)*}\Psi_j^{(0)}\right)dv + \int E_n^{(1)}\Psi_m^{(0)*}\Psi_n^{(0)} dv$$

Using the fact that $\Psi_m^{(0)}$ is orthogonal to $\Psi_j^{(0)}$ unless m = j,

$$a_m E_m^0 + \int \Psi_m^{(0)*} H_p \Psi_n^{(0)} dv = E_n^{(0)} a_m + E_n^{(1)} \int \Psi_m^{(0)*}\Psi_n^{(0)} dv \quad \text{or}$$

$$a_m E_m^0 + \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle = E_n^{(0)} a_m + E_n^{(1)} \left\langle \Psi_m^{(0)} \middle| \Psi_n^{(0)} \right\rangle$$

Consider the case when m=n,

$$a_m E_m^0 + \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle = E_n^{(0)} a_m + E_n^{(1)} \left\langle \Psi_m^{(0)} \middle| \Psi_n^{(0)} \right\rangle$$

$$\Downarrow$$

$$a_m E_m^0 + \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle = E_m^{(0)} a_m + E_n^{(1)} \left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle$$

$$E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle}$$

1st Order Perturbation Theory

To find the coefficient, a_m's consider the case where m≠n,

$$a_m E_m^0 + \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle = E_n^{(0)} a_m + E_n^{(1)} \left\langle \Psi_m^{(0)} \middle| \Psi_n^{(0)} \right\rangle$$

$$\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle = \left(E_n^{(0)} - E_m^{(0)} \right) a_m + 0$$

$$a_m = \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \quad \text{which is valid for all m, n except m = n}$$

1^{st} Order Perturbation Theory

For the case m=n, we have to consider, the normalization condition,

$$\left\langle \Psi_n^{(0)} + g\Psi_n^{(1)} \middle| \Psi_n^{(0)} + g\Psi_n^{(1)} \right\rangle = 1$$

$$\Downarrow$$

$$\int \left(\Psi_n^{(0)} + g\sum_m a_m \Psi_m^{(0)} \right)^* \left(\Psi_n^{(0)} + g\sum_m a_m \Psi_m^{(0)} \right) dv = 1$$

But since all cross terms of the form, $\int \Psi_m^{(0)*}\Psi_n^{(0)} dv$ or $\int \Psi_n^{(0)*}\Psi_m^{(0)} dv$, equal δ_{mn},

$$1 + ga_m + ga_m^* + g^2 \sum_m a_m a_m^* = 1$$

which is only true for all g when $a_m = a_m^* = a_n = a_n^* = 0$

Thus, the original equation,

$$\Psi_n = \Psi_n^{(0)} + g\Psi_n^{(1)}$$

$$\Psi_n = \Psi_n^{(0)} + g\sum_m a_m \Psi_m^{(0)}$$

becomes,

$$\Psi_n = \Psi_n^{(0)} + g\sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)}$$

NOTE : since $a_m = 0$ for m = n, the sum is only performed over $m \neq n$

1^{st} Order Perturbation Theory

In summary,

$$E_n = E_n^{(0)} + gE_n^{(1)}$$

$$where,$$

$$E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle}$$

$$\Psi_n = \Psi_n^{(0)} + g\Psi_n^{(1)}$$

$$where,$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)} \Psi_m^{(0)}$$

1st Order Perturbation Theory

Things to consider:

1. To calculate the perturbed nth state wavefunction, all other unperturbed wavefunctions must be known.

2. Since the denominator is the difference in the energy of the unperturbed nth energy and all other unperturbed energies, only those energies close to the unperturbed nth energy significantly contribute to the 1st order correction to the wavefunction.

3. "g" can be set equal to 1 for convenience or rigidly determined by the normalization condition on Ψ_n.

$$E_n = E_n^{(0)} + gE_n^{(1)}$$

where,

$$E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle}$$

$$\Psi_n = \Psi_n^{(0)} + g\Psi_n^{(1)}$$

where,

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)} \Psi_m^{(0)}$$

2^{nd} Order Perturbation Theory

Given the term that is 2^{nd} order in g,

$$+g^2\left(H_0\Psi_n^{(2)} + H_p\Psi_n^{(1)} - E_n^{(0)}\Psi_n^{(2)} - E_n^{(1)}\Psi_n^{(1)} - E_n^{(2)}\Psi_n^{(0)}\right) = 0$$

and using the Fundamental Expansion Postulate for $\Psi_n^{(2)}$, using the basis vectors, $\Psi_j^{(0)}$'s,

$$\Psi_n^{(2)} = \sum_j b_j \Psi_j^{(0)}$$

$$H_0\Psi_n^{(2)} + H_p\Psi_n^{(1)} - E_n^{(0)}\Psi_n^{(2)} - E_n^{(1)}\Psi_n^{(1)} - E_n^{(2)}\Psi_n^{(0)} = 0$$

$$H_0\left(\sum_j b_j\Psi_j^{(0)}\right) + H_p\left(\sum_j a_j\Psi_j^{(0)}\right) = E_n^{(0)}\left(\sum_j b_j\Psi_j^{(0)}\right) + E_n^{(1)}\left(\sum_j a_j\Psi_j^{(0)}\right) + E_n^{(2)}\Psi_n^{(0)}$$

Again, multiplying by $\Psi_m^{(0)*}$ and integrating over all space,

$$\int \Psi_m^{(0)*} H_0\left(\sum_j b_j\Psi_j^{(0)}\right)dv + \int \Psi_m^{(0)*} H_p\left(\sum_j a_j\Psi_j^{(0)}\right)dv = \cdots$$

$$\cdots \int E_n^{(0)}\left(\sum_j b_j\Psi_m^{(0)*}\Psi_j^{(0)}\right)dv + \int E_n^{(1)}\left(\sum_j a_j\Psi_m^{(0)*}\Psi_j^{(0)}\right)dv + \int E_n^{(2)}\Psi_m^{(0)*}\Psi_n^{(0)}dv$$

But since,

$$H_0\Psi_n^{(0)} = E_0\Psi_n^{(0)} \quad \text{and} \quad \int \Psi_m^{(0)*}\Psi_j^{(0)}dv = \delta_{mj}$$

then,

$$b_m E_m^{(0)} + \sum_j a_j \int \Psi_m^{(0)*} H_p \Psi_j^{(0)} dv = b_m E_n^{(0)} + a_m E_n^{(1)} + E_n^{(2)}\delta_{nm}$$

2nd Order Perturbation Theory

Cont'd,

$$b_m E_m^{(0)} + \sum_j a_j \int \Psi_m^{(0)*} H_p \Psi_j^{(0)} dv = b_m E_n^{(0)} + a_m E_n^{(1)} + E_n^{(2)} \delta_{nm} \quad \text{or}$$

$$b_m E_m^{(0)} + \sum_j a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle = b_m E_n^{(0)} + a_m E_n^{(1)} + E_n^{(2)} \delta_{nm}$$

To find the 2nd order energy correction, consider the case of m=n,

$$E_n^{(2)} = \sum_j a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle - a_n E_n^{(1)}$$

or pulling out of the summation the m = n term,

$$E_n^{(2)} = \sum_{j \neq n} a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle + a_n \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle - a_n E_n^{(1)}$$

Inserting the result for $E_n^{(1)}$ from the 1st order solution,

$$E_n^{(2)} = \sum_{j \neq n} a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle + a_n \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle - a_n \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle$$

$$E_n^{(2)} = \sum_{j \neq n} a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle$$

Inserting the result for a_j from the 1st order solution,

$$E_n^{(2)} = \sum_{j \neq n} \left(\frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)} \right) \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle$$

$$\boxed{E_n^{(2)} = \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)}\right)} \right)}$$

2^{nd} Order Perturbation Theory

To find the coefficient, b_m's consider the case where m≠n,

$$b_m E_m^{(0)} + \sum_{j\neq n} a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle = b_m E_n^{(0)} + a_m E_n^{(1)} + E_n^{(2)} \delta_{nm}$$

$$b_m \left(E_n^{(0)} - E_m^{(0)} \right) = \sum_{j\neq n} a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle - a_m E_n^{(1)}$$

$$b_m = \sum_{j\neq n} \left(\frac{a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{a_m E_n^{(1)}}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

$$b_m = \sum_{j\neq n} \left(\frac{a_j \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{a_m \left(\dfrac{\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle} \right)}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

$$b_m = \sum_{j\neq n} \left(\frac{\left(\dfrac{\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_j^{(0)} \right)} \right) \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{\left(\dfrac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \right) \left(\dfrac{\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{1} \right)}{\left(E_n^{(0)} - E_m^{(0)} \right)}$$

$$b_m = \sum_{j\neq n} \left(\frac{\left(\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right) \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_j^{(0)} \right) \left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{\left(\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right) \left(\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)}{\left(E_n^{(0)} - E_m^{(0)} \right) \left(E_n^{(0)} - E_m^{(0)} \right)}$$

2^{nd} Order Perturbation Theory

We also need to find the value of b_m for the case where m=n. To do this, we again examine the normalization condition,

$$\left\langle \Psi_n^{(0)} + g\Psi_n^{(1)} + g^2\Psi_n^{(2)} \middle| \Psi_n^{(0)} + g\Psi_n^{(1)} + g^2\Psi_n^{(2)} \right\rangle = 1$$

$$\Downarrow$$

$$\int \left(\Psi_n^{(0)} + g\sum_j a_j \Psi_j^{(0)} + g^2 \sum_j b_j \Psi_j^{(0)} \right)^* \left(\Psi_n^{(0)} + g\sum_j a_j \Psi_j^{(0)} + g^2 \sum_j b_j \Psi_j^{(0)} \right) dv = 1$$

But since all cross terms of the form, $\int \Psi_j^{(0)*}\Psi_n^{(0)} dv$ or $\int \Psi_n^{(0)*}\Psi_j^{(0)} dv$ equal δ_{mn},

$$b_n = -\frac{1}{2}\sum_j \left| a_j \right|^2 = -\frac{1}{2}\sum_{j\neq n} \frac{\left| \left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)^2}$$

Adding this to the result for b_m with m ≠ n and inserting this into the expression for $\Psi_n^{(2)}$,

$$b_m = \left[\sum_{j\neq n} \left(\frac{\left(\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right) \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_j^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{\left(\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)\left(\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)}{\left(E_n^{(0)} - E_m^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right] - \frac{1}{2}\sum_{j\neq n} \frac{\left| \left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)^2}$$

2^{nd} Order Perturbation Theory

Cont'd:

$$b_m = \left[\sum_{j \neq n} \left(\frac{\left(\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right) \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_j^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{\left(\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)\left(\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)}{\left(E_n^{(0)} - E_m^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right] - \frac{1}{2} \sum_{j \neq n} \frac{\left| \left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)^2}$$

Thus, the original equation,

$$\Psi_n = \Psi_n^{(0)} + g\Psi_n^{(1)} + g^2 \Psi_n^{(2)}$$

$$\Psi_n = \Psi_n^{(0)} + g \sum_m a_m \Psi_m^{(0)} + g^2 \sum_m b_m \Psi_m^{(0)}$$

becomes,

$$\Psi_n = \Psi_n^{(0)} + g \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)} + \cdots$$

$$\cdots g^2 \sum_m \left\{ \left[\sum_{j \neq n} \left(\frac{\left(\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right) \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_j^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{\left(\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)\left(\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)}{\left(E_n^{(0)} - E_m^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right] - \frac{1}{2} \sum_{j \neq n} \frac{\left| \left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)^2} \right\} \Psi_m^{(0)}$$

2^{nd} Order Perturbation Theory

In Summary:

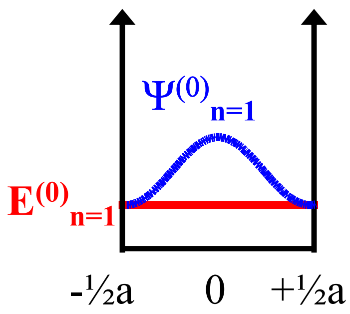
$$E_n = E_n^{(0)} + g\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle + g^2 \sum_{j\neq n} \left(\frac{\left| \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)}\right)} \right)$$

$$\Psi_n = \Psi_n^{(0)} + g \sum_{m\neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)} \Psi_m^{(0)} + \cdots$$

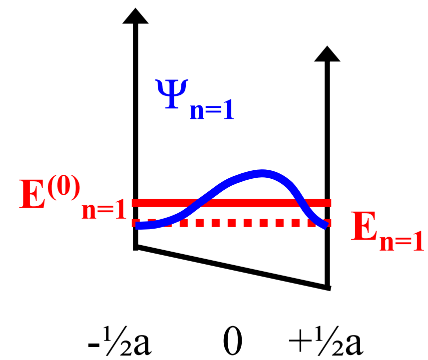
$$\cdots g^2 \sum_m \left\{ \left[\sum_{j\neq n} \left(\frac{\left(\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle\right)\left(\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle\right)}{\left(E_n^{(0)} - E_j^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)} \right) - \frac{\left(\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle\right)\left(\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle\right)}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_m^{(0)}\right)} \right] - \frac{1}{2} \sum_{j\neq n} \frac{\left| \left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)}\right)^2} \right\} \Psi_m^{(0)}$$

Perturbation Theory

Consider an important and illustrative example: Small electric field applied to an infinite potential barrier quantum well. What effect does this have on the ground state energy?



Unperturbed Well



Perturbed Well

When the electric field is applied, the energy bands bend, resulting a redistribution of the electron in the well toward the right side. Since the energy on this side of the well is lower, the new energy of the ground state is expected to be smaller than the unperturbed ground state.

We previously solved this as an asymmetric solution (0<x<L) and had states that only depended on sin functions. For reasons that will become obvious, we redefine our limits as symmetric (- ½ a <x< + ½ a) which will require wave function solutions of the form:

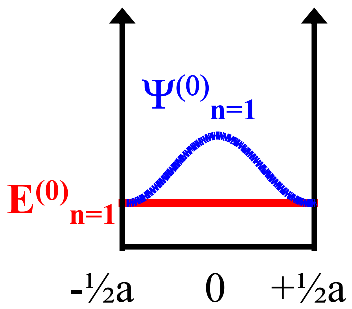
$$\Psi_m^{(0)} = \sqrt{\frac{2}{a}}\sin\left(\frac{m\pi x}{a}\right) \quad \text{for m even} \quad \text{and} \quad \Psi_m^{(0)} = \sqrt{\frac{2}{a}}\cos\left(\frac{m\pi x}{a}\right) \quad \text{for m odd}$$

$$E_{m=1}^{(0)} = \frac{(m=1)^2 \pi^2 \hbar^2}{2ma^2}$$

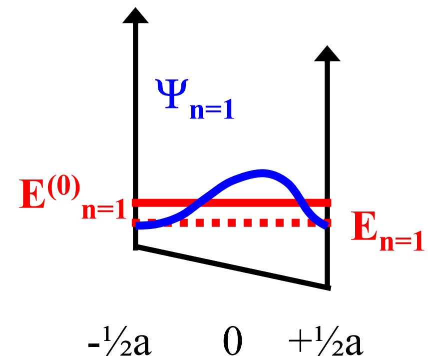
Perturbation Theory

We first attempt a 1st order perturbation solution of the form:

$$E_n = E_n^{(0)} + gE_n^{(1)} \quad where, \quad E_n^{(1)} = \frac{\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left\langle \Psi_n^{(0)} \middle| \Psi_n^{(0)} \right\rangle}$$



Unperturbed Well



Perturbed Well

Note that since our ground state wave function solution is normalized, the denominator in the above equation is equal to 1.

In this case, the perturbation Hamiltonian, $H_p = -q\varepsilon_o x$ (Electric field=Volts/meter times meters = Volts → Energy by –q). Thus, for the ground state, n=1 (odd index).

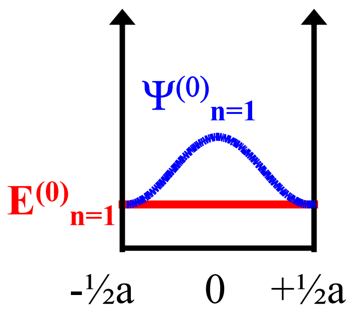
$$E_{n=1}^{(1)} = \left\langle \Psi_{n=1}^{(0)} \middle| H_p \middle| \Psi_{n=1}^{(0)} \right\rangle = \int_{-\frac{a}{2}}^{+\frac{a}{2}} \left(\Psi_{n=1}^{(0)}\right)^* (-q\varepsilon_o x)\Psi_{n=1}^{(0)} \, dx = \int_{-\frac{a}{2}}^{+\frac{a}{2}} \frac{2}{a}(-q\varepsilon_o x)\cos^2\left(\frac{(n=1)\pi x}{a}\right) dx$$

$$E_{n=1}^{(1)} = 0 \qquad \text{(integrand is an odd function)}$$

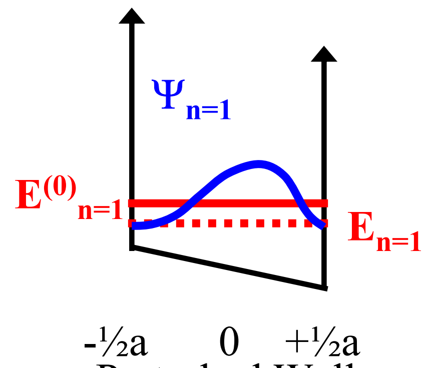
Perturbation Theory

Since our 1st order perturbation correction to the ground state energy resulted in a zero correction factor that deviated from our physical understanding of the system (i.e. we expect a lower ground state energy), we now must consider the 2nd order correction.

$$E_n = E_n^{(0)} + g\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle + g^2 \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)} \right)$$



Unperturbed Well



Perturbed Well

Note that since our 1st order correction was equal to 0, the middle term in the above equation is equal to 0.

We will examine odd and even indexes in the summation separately.

Perturbation Theory

Consider the Odd indexes in the summation:

$$E_n^{(2)} = \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_{n=1}^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_{n=1}^{(0)} - E_j^{(0)} \right)} \right)$$

$$E_n^{(2)} = \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_{n=1}^{(0)} \middle| \left(-q\varepsilon_o x \right) \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_{n=1}^{(0)} - E_j^{(0)} \right)} \right)$$

Consider for j odd,

$$\left\langle \Psi_{n=1}^{(0)} \middle| \left(-q\varepsilon_o x \right) \middle| \Psi_j^{(0)} \right\rangle = \int_{-a/2}^{+a/2} \left(\Psi_{n=1}^{(0)} \right)^* \left(-q\varepsilon_o x \right) \left(\Psi_j^{(0)} \right) dx$$

$$\left\langle \Psi_{n=1}^{(0)} \middle| \left(-q\varepsilon_o x \right) \middle| \Psi_j^{(0)} \right\rangle = \int_{-a/2}^{+a/2} \left(\sqrt{\frac{2}{a}} \cos\left(\frac{(n=1)\pi x}{a} \right) \right)^* \left(-q\varepsilon_o x \right) \left(\sqrt{\frac{2}{a}} \cos\left(\frac{j\pi x}{a} \right) \right) dx = 0$$

Perturbation Theory

Consider the Even indexes in the summation:

$$E_n^{(2)} = \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_{n=1}^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_{n=1}^{(0)} - E_j^{(0)} \right)} \right)$$

$$E_n^{(2)} = \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_{n=1}^{(0)} \middle| \left(-q\varepsilon_o x\right) \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_{n=1}^{(0)} - E_j^{(0)} \right)} \right)$$

Consider for j even,

$$\left\langle \Psi_{n=1}^{(0)} \middle| \left(-q\varepsilon_o x\right) \middle| \Psi_j^{(0)} \right\rangle = \int_{-a/2}^{+a/2} \left(\Psi_{n=1}^{(0)} \right)^* \left(-q\varepsilon_o x\right) \left(\Psi_j^{(0)} \right) dx$$

$$\left\langle \Psi_{n=1}^{(0)} \middle| \left(-q\varepsilon_o x\right) \middle| \Psi_j^{(0)} \right\rangle = \int_{-a/2}^{+a/2} \left(\sqrt{\frac{2}{a}} \cos\left(\frac{(n=1)\pi x}{a} \right) \right)^* \left(-q\varepsilon_o x\right) \left(\sqrt{\frac{2}{a}} \sin\left(\frac{j\pi x}{a} \right) \right) dx = 0$$

$$\left\langle \Psi_{n=1}^{(0)} \middle| \left(-q\varepsilon_o x\right) \middle| \Psi_j^{(0)} \right\rangle = \frac{-2q\varepsilon_o}{a} \left[\left(\frac{a}{(j-1)\pi} \right)^2 \sin\left(\frac{(j-1)\pi}{2} \right) + \left(\frac{a}{(j+1)\pi} \right)^2 \sin\left(\frac{(j+1)\pi}{2} \right) \right]$$

So the Even indexes in the summation contribute non-zero values!

Perturbation Theory

Thus, the correction term for Even indexes is:

$$E_n^{(2)} = \sum_{\text{j is odd}} \left(\frac{\left| \left\langle \Psi_{n=1}^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_{n=1}^{(0)} - E_j^{(0)} \right)} \right)$$

$$E_n^{(2)} = \sum_{\text{j is odd}} \left(\frac{\left| \frac{-2q\varepsilon_o}{a} \left[\left(\frac{a}{(j-1)\pi} \right)^2 \sin\left(\frac{(j-1)\pi}{2} \right) + \left(\frac{a}{(j+1)\pi} \right)^2 \sin\left(\frac{(j+1)\pi}{2} \right) \right] \right|^2}{\left(\frac{(n=1)^2 \pi^2 \hbar^2}{2ma^2} - \frac{j^2 \pi^2 \hbar^2}{2ma^2} \right)} \right)$$

Technically, this is an infinite summation. However, since the denominator increases proportionally to j^2, the relative weight of higher order j terms rapidly decreases and the solution converges after just a few terms.

Note: Since the denominator is always negative and the numerator is always positive, the 2nd order correction is always negative resulting in a lower energy than the unperturbed ground state as expected. I.e.,

$$E_{n=1} = E_{n=1}^{(0)} + g\left\langle \Psi_{n=1}^{(0)} \middle| H_p \middle| \Psi_{n=1}^{(0)} \right\rangle + g^2 \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_{n=1}^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_{n=1}^{(0)} - E_j^{(0)} \right)} \right)$$

$$E_{n=1} = E_{n=1}^{(0)} + g(0) + g^2 (\text{Negative Number})$$

Degenerate Perturbation Theory

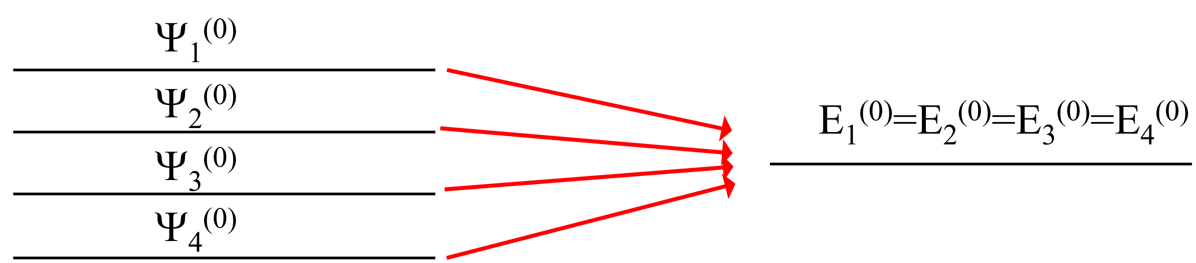
Thus far, it was assumed that the energy values of each state are never the same. If this is not the case, the correction terms can "blow up" to infinity.

$$E_n = E_n^{(0)} + g\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle + g^2 \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)} \right)$$

$$\Psi_n = \Psi_n^{(0)} + g \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)} + \cdots$$

$$\cdots g^2 \sum_m \left\{ \left[\sum_{j \neq n} \left(\frac{\left(\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right) \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_j^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{\left(\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)\left(\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right)}{\left(E_n^{(0)} - E_m^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right] - \frac{1}{2} \sum_{j \neq n} \frac{\left| \left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)^2} \right\} \Psi_m^{(0)}$$

How do we handle the case where the energy of multiple states is degenerate.



Degenerate Perturbation Theory

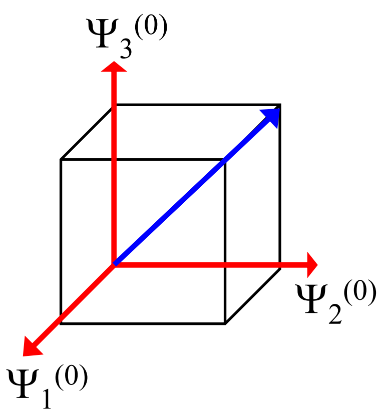
The solution to this problem is to transform the degenerate basis vectors into another set which results in zero numerator terms.

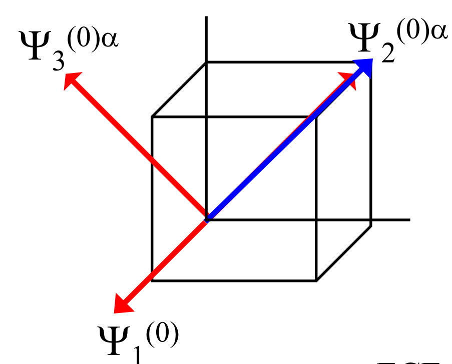
$$E_n = E_n^{(0)} + g\left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle + g^2 \sum_{j \neq n} \left(\frac{\left| \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)} \right)$$

$$\Psi_n = \Psi_n^{(0)} + g \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)} \Psi_m^{(0)} + \cdots$$

$$\cdots g^2 \sum_m \left\{ \left[\sum_{j \neq n} \left(\frac{\left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_j^{(0)} \right\rangle}{\left(E_n^{(0)} - E_j^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right) - \frac{\left\langle \Psi_m^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \left\langle \Psi_n^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)} \right)\left(E_n^{(0)} - E_m^{(0)} \right)} \right] - \frac{1}{2} \sum_{j \neq n} \frac{\left| \left\langle \Psi_j^{(0)} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle \right|^2}{\left(E_n^{(0)} - E_j^{(0)} \right)^2} \right\} \Psi_m^{(0)}$$

Simple Example: Changing to an equivalent basis set in real space. A convenient set of equivalent basis vectors can be selected for any given problem.





Degenerate Perturbation Theory

Lets assume that "h" various unperturbed states result in the same (degenerate) energies. Any specific one of these states, say the mth state can be written as:

$$\Psi_{n,m}^{(0)} \qquad \text{where m can be any value m} = 1, 2, 3, ..., h$$

n still represents the state of the electron while m represents which of the h degenerate states are being considered.

Since each of the above unperturbed states is an Eigenfunction of H_o, with h degenerate Eigen energies, $E_n^{(0)}$, any linear combination of these degenerate basis states is also an Eigenfunction of H_o (see Brennan Chapter 1). Thus, we can construct a new set of basis sets, labeled α, that are linear combinations of the degenerate Eigenstates.

$$\Psi_n^{(0)\alpha} = \sum_{m=1}^{h} b_m^{\alpha} \Psi_{n,m}^{(0)} \qquad \text{where m} = 1, 2, 3, ..., h$$

The task is simply to find the appropriate values of the coefficients, b_m^{α}. To do this, we simply find the set of b_m^{α}'s that force the numerator,

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\left\langle \Psi_m^{(0)\alpha} \middle| H_p \middle| \Psi_n^{(0)} \right\rangle}{\left(E_n^{(0)} - E_m^{(0)}\right)} \Psi_m^{(0)}$$

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\int \left(\Psi_m^{(0)\alpha}\right)^* H_p \left(\Psi_n^{(0)}\right) dx}{\left(E_n^{(0)} - E_m^{(0)}\right)} \Psi_m^{(0)}$$

to equal zero when the denominator is also zero, thus removing the singularity.

Degenerate Perturbation Theory

The problem reduces to a diagonalization of the sub-matrix of index h by defining new basis sets such that,

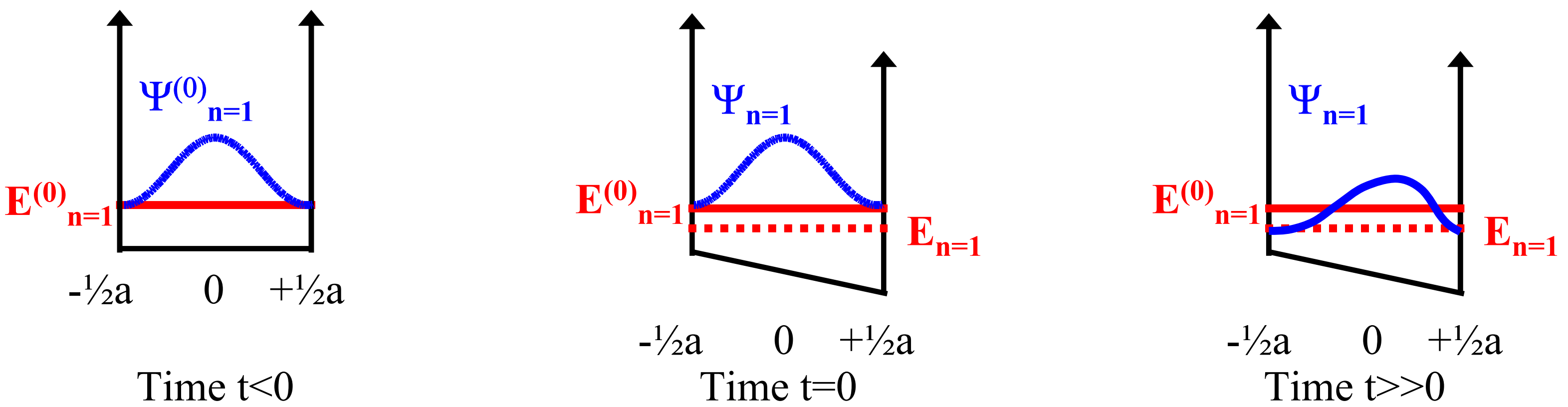
$$H_p\Psi = \begin{bmatrix} H_{11} & H_{11} & \cdots & H_{1h} & \cdots & \cdots & H_{1n} \\ H_{11} & H_{11} & & & & & \vdots \\ \vdots & & \ddots & & & & \vdots \\ H_{h1} & & & H_{hh} & & & \vdots \\ \vdots & & & & \ddots & & \vdots \\ \vdots & & & & & \ddots & \vdots \\ H_{n1} & \cdots & \cdots & \cdots & \cdots & \cdots & H_{nn} \end{bmatrix} \begin{bmatrix} \Psi^{(0)}_{n=1,m=1} \\ \Psi^{(0)}_{n=2,m=2} \\ \vdots \\ \Psi^{(0)}_{n=h,m=h} \\ \Psi^{(0)}_{n=h+1} \\ \vdots \\ \Psi^{(0)}_{n} \end{bmatrix}$$

$$\Psi = \sum_i c_i \Psi_i$$

$$H_p\Psi = \begin{bmatrix} H_{11} & 0 & \cdots & 0 & H_{1(h+1)} & \cdots & H_{1n} \\ 0 & H_{11} & 0 & 0 & & & \vdots \\ \vdots & 0 & \ddots & \vdots & & & \vdots \\ 0 & 0 & \cdots & H_{hh} & & & \vdots \\ H_{(h+1)1} & & & & \ddots & & \vdots \\ \vdots & & & & & \ddots & \vdots \\ H_{n1} & \cdots & \cdots & \cdots & \cdots & \cdots & H_{nn} \end{bmatrix} \begin{bmatrix} \Psi^{(0)\alpha}_{n=1,m=1} \\ \Psi^{(0)\alpha}_{n=2,m=2} \\ \vdots \\ \Psi^{(0)\alpha}_{n=h,m=h} \\ \Psi^{(0)}_{n=h+1} \\ \vdots \\ \Psi^{(0)}_{n} \end{bmatrix}$$

Time **Dependent** Perturbation Theory

In all previous cases, nothing observable happens because the states are assumed static – unchanging. Most useful systems require transitions between states. For example, optical absorption and electron-hole pair recombination require a change from one state to another. This inherently requires **TIME DEPENDENT** Perturbation Theory.



Given wave functions are sluggish in nature (waves do not change instantly when the perturbation changes – consider a water wave as an analogy), an instantaneous change in the perturbation results is a "more" gradual time change in the wave function and thus the distribution of particles. Note, the expectation value of the total potential energy is assumed to change instantly as the perturbation energy changes instantly but the expectation value of the kinetic energy changes "gradually".

Note: terms like "gradually" and "sluggish" are somewhat misleading in that these changes can often happen in fractions of a nanosecond. However, compared to the instantaneous perturbation these changes are considered "slower".

Time <u>Dependent</u> Perturbation Theory

The starting point for time dependent perturbation theory is the time dependent Schrodinger equation (see lecture 6).

$$\phi(x,y,z,t)=\Psi(x,y,z)e^{-i\left(\frac{Et}{\hbar}\right)}$$

$$\mathrm{H}\phi=-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \mathrm{t}}\phi$$

or

Breaking this into a time independent, H_o, part and a SMALL time dependent part, $\mathrm{H}'(\mathrm{t})$,

$$\left(\mathrm{H}_o+\mathrm{gH}'(\mathrm{t})\right)\phi=-\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \mathrm{t}}\phi$$

Considering the solution before $\mathrm{H}'(\mathrm{t})$ begins,

Since $\phi_{\mathrm{n}}^{(0)}=\Psi_{\mathrm{n}}^{(0)}\mathrm{e}^{-\mathrm{i}\left(\frac{\mathrm{E}_{\mathrm{n}}^{(0)}\mathrm{t}}{\hbar}\right)}$,

$$H_o\phi_n^{(0)}=E_n^{(0)}\phi_n^{(0)}$$

Thus, the general solution for the time dependent solution before the perturbation is :

$\phi^{(0)}=\sum_n a_n(t)\phi_{\mathrm{n}}^{(0)}$ subject to the normalization condition,

$\left\langle\phi^{(0)}\middle|\phi^{(0)}\right\rangle$ which given orthonormality of the individual eigenfunctions, $\phi_{\mathrm{n}}^{(0)}$, reduces to $\sum_n\left(a_n\right)^*\left(a_n\right)=1$

Time **Dependent** Perturbation Theory

For the time dependent solution,

$$\left(\mathrm{H_o} + \mathrm{gH'(t)}\right)\phi = -\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \mathrm{t}}\phi$$

We express the wave functions as a linear combination of the complete basis set of unperturbed wavefunctions,

$$\phi(x,t) = \sum_n a_n(t)\phi_{\mathrm{n}}^{(0)}(x,t)$$

NOTE: The time evolution of the wave function depends on the time evolution of the weighing coefficients (to be determined) and the known time evolution of the basis unperturbed states (see previous slide)

Substitution of this expression into the Schrodinger Equation yeilds,

$$\mathrm{H_o}\sum_n a_n(t)\phi_{\mathrm{n}}^{(0)}(x,t) + \mathrm{gH'(t)}\sum_n a_n(t)\phi_{\mathrm{n}}^{(0)}(x,t) = -\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial \mathrm{t}}\left(\sum_n a_n(t)\phi_{\mathrm{n}}^{(0)}(x,t)\right)$$

or

$$\sum_n a_n(t)\mathrm{H_o}\phi_{\mathrm{n}}^{(0)}(x,t) + \sum_n a_n(t)\mathrm{gH'(t)}\phi_{\mathrm{n}}^{(0)}(x,t) = -\frac{\hbar}{\mathrm{i}}\sum_n\left[\left(\frac{\partial}{\partial \mathrm{t}}a_n(t)\right)\phi_{\mathrm{n}}^{(0)}(x,t)\right] - \frac{\hbar}{\mathrm{i}}\sum_n\left[a_n(t)\left(\frac{\partial}{\partial \mathrm{t}}\phi_{\mathrm{n}}^{(0)}(x,t)\right)\right]$$

But from the unperturbed solution, the 1st and 4th terms cancel leaving :

$$\sum_n a_n(t)\mathrm{gH'(t)}\phi_{\mathrm{n}}^{(0)}(x,t) = -\frac{\hbar}{\mathrm{i}}\sum_n\left[\left(\frac{\partial}{\partial \mathrm{t}}a_n(t)\right)\phi_{\mathrm{n}}^{(0)}(x,t)\right]$$

The time dependent perturbation can be described as a time evolution of the coefficients of the basis set wave vectors.

As we have many times before, we multiply by a specific wave function, $\phi_{\mathrm{m}}^{(0)}(x,t)$, and integrate over all space,

$$-\mathrm{g}\frac{\mathrm{i}}{\hbar}\int\sum_n a_n(t)\phi_{\mathrm{m}}^{(0)}(x,t)\mathrm{H'(t)}\phi_{\mathrm{n}}^{(0)}(x,t)dv = \int\sum_n\left[\left(\frac{\partial}{\partial \mathrm{t}}a_n(t)\right)\phi_{\mathrm{m}}^{(0)}(x,t)\phi_{\mathrm{n}}^{(0)}(x,t)\right]dv$$

$$\frac{\partial}{\partial \mathrm{t}}a_m(t) = -\mathrm{g}\frac{\mathrm{i}}{\hbar}\sum_n a_n(t)\int\phi_{\mathrm{m}}^{(0)}(x,t)\mathrm{H'(t)}\phi_{\mathrm{n}}^{(0)}(x,t)dv \quad \text{or} \quad \frac{\partial}{\partial \mathrm{t}}a_m(t) = -\mathrm{g}\frac{\mathrm{i}}{\hbar}\sum_n a_n(t)\left\langle\phi_{\mathrm{m}}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}}^{(0)}(x,t)\right\rangle$$

Time <u>Dependent</u> Perturbation Theory

<u>Important Observations:</u> Since the weighting coefficients are known before the perturbation, knowing the time derivative (rate of change) of the coefficients implies full knowledge of the weighting coefficients after the perturbation occurs.

$$\frac{\partial}{\partial \mathrm{t}} a_m(t) = -\mathrm{g}\frac{\mathrm{i}}{\hbar}\sum_n a_n(t)\int \phi_{\mathrm{m}}^{(0)}(x,t)\mathrm{H}'(\mathrm{t})\phi_{\mathrm{n}}^{(0)}(x,t)dv \quad \text{or} \quad \frac{\partial}{\partial \mathrm{t}} a_m(t) = -\mathrm{g}\frac{\mathrm{i}}{\hbar}\sum_n a_n(t)\left\langle \phi_{\mathrm{m}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n}}^{(0)}(x,t)\right\rangle$$

Each individual state is “connected” through the perturbation Hamiltonian. I.e. state “m” is connected to every other state (all n states) via the perturbation Hamiltonian. If the Hamiltonian does not allow a transition from one state to another (i.e. the matrix element is zero) then the weighting coefficient for that state remains unchanged (i.e. static in time).

The change in each individual coefficient in time depends on couplings between ***<u>ALL</u>*** other available states!

Time Dependent Perturbation Theory

Consider an expanded form of the previous equation:

$$\frac{\partial}{\partial \mathrm{t}} a_m(t) = \text{-g}\frac{\mathrm{i}}{\hbar}\sum_n a_n(t)\left\langle \phi_{\mathrm{m}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n}}^{(0)}(x,t)\right\rangle$$

$$\Downarrow$$

$$\begin{aligned}
-\frac{\hbar}{gi}\frac{\partial}{\partial \mathrm{t}} a_{m=0}(t) &= a_{n=0}(t)\left\langle \phi_{\mathrm{m=0}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=0}}^{(0)}(x,t)\right\rangle + a_{n=1}(t)\left\langle \phi_{\mathrm{m=0}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=1}}^{(0)}(x,t)\right\rangle + \cdots + a_{n=j}(t)\left\langle \phi_{\mathrm{m=0}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=j}}^{(0)}(x,t)\right\rangle + \cdots \\
-\frac{\hbar}{gi}\frac{\partial}{\partial \mathrm{t}} a_{m=1}(t) &= a_{n=0}(t)\left\langle \phi_{\mathrm{m=1}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=0}}^{(0)}(x,t)\right\rangle + a_{n=1}(t)\left\langle \phi_{\mathrm{m=1}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=1}}^{(0)}(x,t)\right\rangle + \cdots + a_{n=j}(t)\left\langle \phi_{\mathrm{m=1}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=j}}^{(0)}(x,t)\right\rangle + \cdots \\
\vdots &= \qquad \vdots \qquad\qquad \vdots \qquad\qquad \vdots \\
-\frac{\hbar}{gi}\frac{\partial}{\partial \mathrm{t}} a_{m=j}(t) &= a_{n=0}(t)\left\langle \phi_{\mathrm{m=j}}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=0}}^{(0)}(x,t)\right\rangle + a_{n=1}(t)\left\langle \phi_{\mathrm{m}=j}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=1}}^{(0)}(x,t)\right\rangle + \cdots + a_{n=j}(t)\left\langle \phi_{\mathrm{m}=j}^{(0)}(x,t)\middle|\mathrm{H}'(\mathrm{t})\middle|\phi_{\mathrm{n=j}}^{(0)}(x,t)\right\rangle + \cdots \\
\vdots &= \qquad \vdots \qquad\qquad \vdots \qquad\qquad \vdots
\end{aligned}$$

Considering the vastness of this system of equations a simplification similar to what we did for the unperturbed system is in order. Since the wave function evolution in time is entirely determined by the coefficients, we will expand the coefficients in orders of g.

$$a_j = a_j^{(0)} + g\frac{da_j}{dg} + g^2\frac{d^2 a_j}{dg^2} + \cdots$$

or

$$a_j = a_j^{(0)} + g a_j^{'} + g^2 a_j^{''} + \cdots$$

Time **Dependent** Perturbation Theory

Using this expansion, the previous system of equations becomes:

$$-\frac{\hbar}{i}\frac{\partial}{\partial \mathrm{t}}\left(a_0^{(0)}+ga_0^{'}+g^2a_0^{''}+\cdots\right)=g\left(a_0^{(0)}+ga_0^{'}+g^2a_0^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=0}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=0}^{(0)}(x,t)\right\rangle+g\left(a_1^{(0)}+ga_1^{'}+g^2a_1^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=0}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=1}^{(0)}(x,t)\right\rangle+\cdots$$
$$\cdots+g\left(a_j^{(0)}+ga_j^{'}+g^2a_j^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=0}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=j}^{(0)}(x,t)\right\rangle\cdots$$

$$-\frac{\hbar}{i}\frac{\partial}{\partial \mathrm{t}}\left(a_1^{(0)}+ga_1^{'}+g^2a_1^{''}+\cdots\right)=g\left(a_0^{(0)}+ga_0^{'}+g^2a_0^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=1}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=0}^{(0)}(x,t)\right\rangle+g\left(a_1^{(0)}+ga_1^{'}+g^2a_1^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=1}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=1}^{(0)}(x,t)\right\rangle+\cdots$$
$$\cdots+g\left(a_j^{(0)}+ga_j^{'}+g^2a_j^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=1}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=j}^{(0)}(x,t)\right\rangle\cdots$$

$$\vdots \qquad\qquad\qquad \vdots$$

$$-\frac{\hbar}{i}\frac{\partial}{\partial \mathrm{t}}\left(a_j^{(0)}+ga_j^{'}+g^2a_j^{''}+\cdots\right)=g\left(a_0^{(0)}+ga_0^{'}+g^2a_0^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=\mathrm{j}}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=0}^{(0)}(x,t)\right\rangle+g\left(a_1^{(0)}+ga_1^{'}+g^2a_1^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=\mathrm{j}}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=1}^{(0)}(x,t)\right\rangle+\cdots$$
$$\cdots+g\left(a_j^{(0)}+ga_j^{'}+g^2a_j^{''}+\cdots\right)\left\langle\phi_{\mathrm{m}=\mathrm{j}}^{(0)}(x,t)\middle|\mathrm{H'(t)}\middle|\phi_{\mathrm{n}=j}^{(0)}(x,t)\right\rangle\cdots$$

$$\vdots \qquad\qquad\qquad \vdots$$

For our purposes we will only consider 1st order time dependent perturbation theory (**THANK GOD!**). For this we will consider only the linear terms in g. Again, for any choice of g, the terms on the left hand side must equate to the terms of equal magnitude on the right hand side. This is done on the following page...

Time **Dependent** Perturbation Theory

Considering equality of the linear terms,

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\left(a_0^{'}\right)=\left(a_0^{(0)}\right)\left\langle\phi_{m=0}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=0}^{(0)}(x,t)\right\rangle+\left(a_1^{(0)}\right)\left\langle\phi_{m=0}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=1}^{(0)}(x,t)\right\rangle+\cdots+\left(a_j^{(0)}\right)\left\langle\phi_{m=0}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=j}^{(0)}(x,t)\right\rangle\cdots$$

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\left(a_1^{'}\right)=\left(a_0^{(0)}\right)\left\langle\phi_{m=1}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=0}^{(0)}(x,t)\right\rangle+\left(a_1^{(0)}\right)\left\langle\phi_{m=1}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=1}^{(0)}(x,t)\right\rangle+\cdots+\left(a_j^{(0)}\right)\left\langle\phi_{m=1}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=j}^{(0)}(x,t)\right\rangle\cdots$$

$$\vdots \qquad\qquad \vdots$$

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\left(a_j^{'}\right)=\left(a_0^{(0)}\right)\left\langle\phi_{m=j}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=0}^{(0)}(x,t)\right\rangle+\left(a_1^{(0)}\right)\left\langle\phi_{m=j}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=1}^{(0)}(x,t)\right\rangle+\cdots+\left(a_j^{(0)}\right)\left\langle\phi_{m=j}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=j}^{(0)}(x,t)\right\rangle\cdots$$

$$\vdots \qquad\qquad \vdots$$

The importance of this equation is that it is an approximate 1^{st} order solution that only depends on the stationary unperturbed coefficients and the unperturbed basis wave functions. Thus, it depends on the initial condition (unperturbed coefficients and wave functions) of the system.

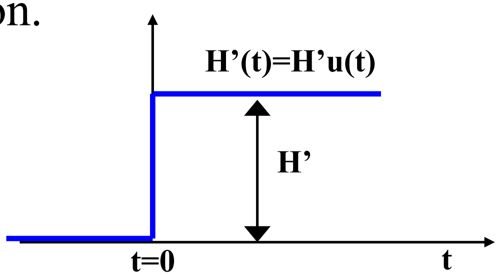
Each equation in the above system of equations represents the growth or decay of an individual Eigenfunction's magnitude and thus represents the growth or decay of the probability of the state being occupied or empty.

All states are connected via the perturbation Hamiltonian, H'(t). Thus, if a particular state, say m=3, grows (or decays) in amplitude, it must come at the expense of some other state, for example, m=11 decaying (or growing) in amplitude. The rate of growth or decay is set by the 3^{rd} and 11^{th} equations.

NOTE: this is just a simple example and in practice all states are coupled so growth and decay involves transitions from all states. In some cases, the perturbation Hamiltonian will prevent certain transitions resulting in a inability to transition between states – called forbidden transitions.

Time Dependent Perturbation Theory

Example 1: Consider the case when the initial state of a system is known to be in only the "jth" state (all zero coefficients except a_j=1) and the perturbation is turned on at time, t=0 (i.e. H'(t)=H'u(t) where H' is a constant and u(t) is a step function.



The systems of equations ...

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\left(a_0^{'}\right)=\left(a_j^{(0)}=1\right)\left\langle \phi_{m=0}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=j}^{(0)}(x,t)\right\rangle$$

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\left(a_1^{'}\right)=\left(a_j^{(0)}=1\right)\left\langle \phi_{m=1}^{(0)}(x,t)\middle|H'(t)\middle|\phi_{n=j}^{(0)}(x,t)\right\rangle$$

$$\vdots$$

... reduces to equations of the form:

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\left(a_m^{'}\right)=(1)\left\langle \Psi_m^{(0)}(x)\middle|H'\middle|\Psi_{n=j}^{(0)}(x)\right\rangle e^{i\left(E_m^{(0)}-E_j^{(0)}\right)t/\hbar} \quad \text{for } m=0,1,2,\cdots \text{ but } m\neq j \quad \text{and } \frac{\partial}{\partial t}\left(a_j^{'}\right)\approx 0$$

where we have used the fact that since $\phi_n^{(0)}=\Psi_n^{(0)}(x)e^{-i\left(\frac{E_n^{(0)}t}{\hbar}\right)}$ then,

$$\left\langle \Psi_m^{(0)}(x)e^{-i\left(\frac{E_m^{(0)}t}{\hbar}\right)}\middle|H'\middle|\Psi_j^{(0)}(x)e^{-i\left(\frac{E_j^{(0)}t}{\hbar}\right)}\right\rangle=\left\langle \Psi_m^{(0)}(x)\middle|H'\middle|\Psi_j^{(0)}(x)\right\rangle e^{-i\omega_{mj}t}, \quad \text{where } \omega_{mj}=\left(E_m^{(0)}-E_j^{(0)}\right)/\hbar$$

Time **Dependent** Perturbation Theory

Thus, this general equation,

$$\frac{\partial}{\partial t}\left(a_m^{'}\right)=\left(\frac{-i}{\hbar}\right)1\left\langle\Psi_m^{(0)}(x)\middle|H'\middle|\Psi_{n=j}^{(0)}(x)\right\rangle e^{i\omega_{mj}t} \quad \text{for } m=0,1,2,\cdots \text{ but } m\neq j$$

can be directly integrated to result in:

$$a_m^{'}(t)=\left[\left(\frac{-1}{\hbar\omega_{mj}}\right)1\left\langle\Psi_m^{(0)}(x)\middle|H'\middle|\Psi_{n=j}^{(0)}(x)\right\rangle e^{i\omega_{mj}t} + K\right]u(t) \quad \text{for } m=0,1,2,\cdots \text{ but } m\neq j$$

The integration constant can be evaluated by restricting $a'_m(t)=0$ at $t=0$ resulting in,

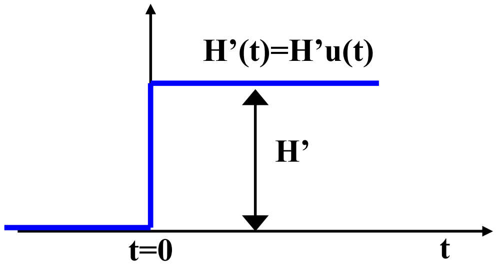
$$a_m^{'}(t)=\left[-\frac{1}{\hbar}\left\langle\Psi_m^{(0)}(x)\middle|H'\middle|\Psi_{n=j}^{(0)}(x)\right\rangle\frac{\left(e^{i\omega_{mj}t}-1\right)}{\omega_{mj}}\right]u(t) \quad \text{for } m=0,1,2,\cdots \text{ but } m\neq j$$

Finally, since the perturbation is defined as small, the j^{th} coefficient is simply,

Since for $t\leq 0$ $a_j = a_j^{(0)}$ then $a_j^{'}=0$ and,

for $t>0$, $a_j^{'}$ can be found through normalization of

the total wavefunction but in general, $a_j^{'}\approx 0$



Time Dependent Perturbation Theory

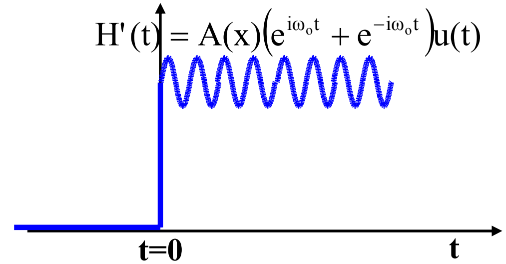
Important Observations:

$$a'_m(t) = \left[-\frac{1}{\hbar} \left\langle \Psi^{(0)}_{\mathrm{m}}(x) \middle| \mathrm{H'} \middle| \Psi^{(0)}_{\mathrm{n}=j}(x) \right\rangle \frac{\left(e^{i\omega_{mj}t} - 1\right)}{\omega_{mj}} \right] \mathrm{u(t)} \quad \text{for } m = 0, 1, 2, \cdots \text{ but } m \neq j$$

1) The matrix element in the above expression (<...> term) is known as the **transition matrix element** and describes which transitions are allowed and disallowed and how strongly the m^{th} and j^{th} states are coupled.
2) If the transition matrix element integrand is odd (a very common occurrence) the integral is 0 meaning that a transition between the m^{th} and j^{th} state is forbidden.
3) In general, this transition matrix element is responsible for a variety of "selection rules" in atomic, nuclear and semiconductor bulk/quantum well optical spectra (emission or absorption resulting from electron/hole transitions between states).
4) Even though a specific transition is forbidden from say the j^{th} state to the m^{th} state, the m^{th} state may still eventually become populated by indirect (and thus slower) transitions of the form j → k → m, etc...

Time **Dependent** Perturbation Theory

Example 2: Turning on a "Harmonic Perturbation" at time t=0. This case is important as many excitations such as electromagnetic radiation, ac electric and magnetic fields all can be periodic in nature. This problem proceeds identical to the previous example except:



$$\frac{\partial}{\partial t}\left(a_m^{'}\right)=\left(\frac{-i}{\hbar}\right)1\left\langle \Psi_m^{(0)}(x)\middle|H'(t)\middle|\Psi_{n=j}^{(0)}(x)\right\rangle e^{i\omega_{mj}t} \quad \text{for } m = 0, 1, 2, \cdots \text{ but } m \neq j$$

$$\frac{\partial}{\partial t}\left(a_m^{'}\right)=\left(\frac{-i}{\hbar}\right)\left\langle \Psi_m^{(0)}(x)\middle|A(x)\left(e^{i\omega_o t}+e^{-i\omega_o t}\right)u(t)\middle|\Psi_{n=j}^{(0)}(x)\right\rangle e^{i\omega_{mj}t} \quad \text{for } m = 0, 1, 2, \cdots \text{ but } m \neq j$$

$$\frac{\partial}{\partial t}\left(a_m^{'}\right)=\left(\frac{-i}{\hbar}\right)\left\langle \Psi_m^{(0)}(x)\middle|A(x)\middle|\Psi_{n=j}^{(0)}(x)\right\rangle e^{i\omega_{mj}t}\left(e^{i\omega_o t}+e^{-i\omega_o t}\right) \quad \text{for } m = 0, 1, 2, \cdots \text{ but } m \neq j$$

can be directly integrated to result in:

$$a_m^{'}(t)=\left(\frac{-\left\langle \Psi_m^{(0)}(x)\middle|A(x)\middle|\Psi_{n=j}^{(0)}(x)\right\rangle}{\hbar}\right)\left[\frac{\left(e^{i\left(\omega_{mj}+\omega_o\right)t}-1\right)}{\left(\omega_{mj}+\omega_o\right)}-\frac{\left(e^{i\left(\omega_{mj}-\omega_o\right)t}-1\right)}{\left(\omega_{mj}-\omega_o\right)}\right]u(t) \quad \text{for } m = 0, 1, 2, \cdots \text{ but } m \neq j$$

Where the integration constant was again evaluated by restricting $a'_m(t)=0$ at t=0.

Finally, since the perturbation is defined as small, the j^{th} coefficient is simply,

$$a_j^{'} = 0 \text{ for } t \leq 0 \text{ and } a_j^{'} \approx 0 \text{ for } t > 0$$

Time Dependent Perturbation Theory

Important Observations:

$$a_m^{'}(t)=\left(\frac{-\left\langle\Psi_{\mathrm{m}}^{(0)}(x)\middle|\mathrm{A(x)}\middle|\Psi_{\mathrm{n}=j}^{(0)}(x)\right\rangle}{\hbar}\right)\left[\frac{\left(e^{i(\omega_{mj}+\omega_o)t}-1\right)}{\left(\omega_{mj}+\omega_o\right)}-\frac{\left(e^{i(\omega_{mj}-\omega_o)t}-1\right)}{\left(\omega_{mj}-\omega_o\right)}\right]\mathrm{u(t)}\quad \text{for m} = 0, 1, 2, \cdots \text{but m} \neq \text{j}$$

1) Two resonances exist in the above coupling equation $\omega_{mj}=+/-\omega_o$ where the coupling between the mth and jth state is extremely strong. These resonances occur when the mth state is exactly $+/-\hbar\omega_o$ away from the initially occupied jth state.
2) States not on resonance still can be coupled to the initially occupied jth state, but with a lesser coupling strength than those directly on resonance.
3) While this equation predicts a strong coupling at resonance, $a'_m(t) \rightarrow \infty$, our restriction of a small perturbation (i.e. $a'_m(t)$ small) indicates that 1st order time dependent perturbation theory is insufficient to accurately describe this case and thus, it is expected that $a'_m(t)$ will NOT actually $\rightarrow \infty$ and that higher order approximations will be needed to accurately describe this condition.
4) Even though a specific transition is forbidden from say the jth state to the mth state, the mth state may still eventually become populated by indirect (and thus slower) transitions of the form j → k → m, etc...

Time Dependent Perturbation Theory

Fermi's Golden Rule:

Since the probability of state m being occupied is found by $(\Psi_m)^*(\Psi_m)$ and due to the normalization of the basis wave functions this reduces to $(a'_m(t))^*(a'_m(t))$. Thus, we need to consider the value of $(a'_m(t))^*(a'_m(t))$. To simplify this procedure, we note that only one term in the square braces need be considered for the two cases near resonance.

$$a'_m(t) = \left(\frac{-\left\langle \Psi_m^{(0)}(x) \middle| A(x) \middle| \Psi_{n=j}^{(0)}(x) \right\rangle}{\hbar} \right) \left[\frac{\left(e^{i(\omega_{mj}+\omega_o)t} - 1 \right)}{(\omega_{mj}+\omega_o)} - \frac{\left(e^{i(\omega_{mj}-\omega_o)t} - 1 \right)}{(\omega_{mj}-\omega_o)} \right] u(t) \quad \text{for } m = 0, 1, 2, \cdots \text{ but } m \neq j$$

$$\left(a'_m(t)\right)^* \left(a'_m(t)\right) \approx 4 \left(\frac{\left| \left\langle \Psi_m^{(0)}(x) \middle| A(x) \middle| \Psi_{n=j}^{(0)}(x) \right\rangle \right|^2}{\hbar^2} \right) \left[\frac{\sin^2\left(\frac{1}{2}(\omega_{mj}-\omega_o)t \right)}{(\omega_{mj}-\omega_o)^2} \right] u(t) \quad \text{for } E_m^{(0)} \approx E_j^{(0)} + \hbar\omega_o$$

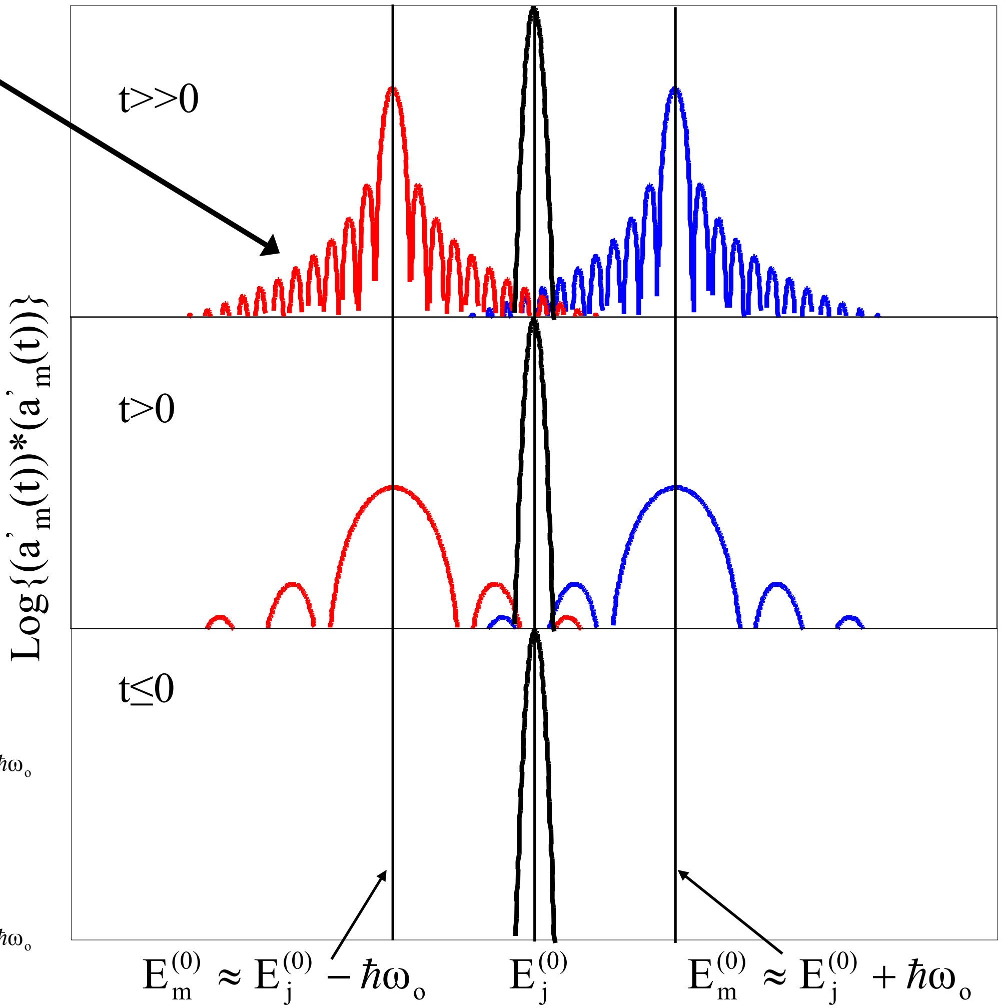
and

$$\left(a'_m(t)\right)^* \left(a'_m(t)\right) \approx 4 \left(\frac{\left| \left\langle \Psi_m^{(0)}(x) \middle| A(x) \middle| \Psi_{n=j}^{(0)}(x) \right\rangle \right|^2}{\hbar^2} \right) \left[\frac{\sin^2\left(\frac{1}{2}(\omega_{mj}+\omega_o)t \right)}{(\omega_{mj}+\omega_o)^2} \right] u(t) \quad \text{for } E_m^{(0)} \approx E_j^{(0)} - \hbar\omega_o$$

The reason we make this simplification is that in deriving Fermi's Golden Rule, the functional form of the above equations will be convenient for integration. Before we proceed lets examine these equations.

Time **Dependent** Perturbation Theory

The probability of all states including "far off-resonant" states becoming occupied increases with time.



$$\left(a'_m(t)\right)^*\left(a'_m(t)\right) \approx 4\left(\frac{\left|\left\langle \Psi_m^{(0)}(x)\middle|A(x)\middle|\Psi_{n=j}^{(0)}(x)\right\rangle\right|^2}{\hbar^2}\right)\left[\frac{\sin^2\left(\frac{1}{2}\left(\omega_{mj}-\omega_o\right)t\right)}{\left(\omega_{mj}-\omega_o\right)^2}\right]u(t) \quad \text{for } E_m^{(0)} \approx E_j^{(0)} + \hbar\omega_o$$

and

$$\left(a'_m(t)\right)^*\left(a'_m(t)\right) \approx 4\left(\frac{\left|\left\langle \Psi_m^{(0)}(x)\middle|A(x)\middle|\Psi_{n=j}^{(0)}(x)\right\rangle\right|^2}{\hbar^2}\right)\left[\frac{\sin^2\left(\frac{1}{2}\left(\omega_{mj}+\omega_o\right)t\right)}{\left(\omega_{mj}+\omega_o\right)^2}\right]u(t) \quad \text{for } E_m^{(0)} \approx E_j^{(0)} - \hbar\omega_o$$

Time **Dependent** Perturbation Theory

Instead of discrete state to state transitions, it is often useful to consider a discrete state to "band of states" transition. Examples of this are donor states to conduction band transitions, acceptor states to valence band transitions or simply defect/impurity states to either conduction/valence band transitions.
These bands can be described by their density per unit energy (see lecture 7) or since $E=\hbar\omega$, the density (number) per frequency ω centered around the transition frequency $= \rho(\omega_{mj})$.

Assuming that this density of states, $\rho(\omega_{mj})$, does not change quickly with ω_{mj}, we can find the new probability density of state m by integrating the previous expression over ω_{mj}. For example,

$$\left(a'_m(t)\right)^* \left(a'_m(t)\right) \approx \int \left(\frac{\left| \left\langle \Psi_m^{(0)}(x) \middle| A(x) \middle| \Psi_{n=j}^{(0)}(x) \right\rangle \right|^2}{\hbar^2} \right) \left[\frac{\sin^2\left(\frac{1}{2}\left(\omega_{mj} - \omega_o\right)t\right)}{\left[\frac{1}{2}\left(\omega_{mj} - \omega_o\right)\right]^2} \right] \rho\left(\omega_{mj}\right) d\omega_{mj} \quad \text{for } E_m^{(0)} \approx E_j^{(0)} + \hbar\omega_o$$

Time **Dependent** Perturbation Theory

$$\left(a'_m(t)\right)^*\left(a'_m(t)\right) \approx \int \left(\frac{\left|\left\langle \Psi_m^{(0)}(x) \middle| A(x) \middle| \Psi_{n=j}^{(0)}(x) \right\rangle\right|^2}{\hbar^2} \right) \left[\frac{\sin^2\left(\frac{1}{2}\left(\omega_{mj} - \omega_o\right)t\right)}{\left[\frac{1}{2}\left(\omega_{mj} - \omega_o\right)\right]^2} \right] \rho\left(\omega_{mj}\right) d\omega_{mj} \quad \text{for } E_m^{(0)} \approx E_j^{(0)} + \hbar\omega_o$$

Making some assumptions about this function:

1) The transition matrix element is a slowly varying function of ω_{mj}.
2) The density of states, $\rho(\omega_{mj})$, also does not change quickly with ω_{mj}.
3) Both of the above two conditions can be achieved by noting that since the [$\sin^2$...] function sharpens in in ω_{mj} with increasing time, we can always wait long enough in time to make this part of the integrand the most rapidly varying portion of the integrand in ω_{mj}.

...

Time **Dependent** Perturbation Theory

...with these assumptions, the above expression becomes:

$$\left(a'_m(t)\right)^*\left(a'_m(t)\right) \approx \left(\frac{\left|\left\langle \Psi_m^{(0)}(x)\left|A(x)\right|\Psi_{n=j}^{(0)}(x)\right\rangle\right|^2}{\hbar^2}\right)\rho(\omega_{mj})\int\left[\frac{\sin^2\left(\frac{1}{2}(\omega_{mj}-\omega_o)t\right)}{\left[\frac{1}{2}(\omega_{mj}-\omega_o)\right]^2}\right]d\omega_{mj} \quad \text{for } E_m^{(0)} \approx E_j^{(0)} + \hbar\omega_o$$

$$\left(a'_m(t)\right)^*\left(a'_m(t)\right) \approx \left(\frac{\left|\left\langle \Psi_m^{(0)}(x)\left|A(x)\right|\Psi_{n=j}^{(0)}(x)\right\rangle\right|}{\hbar^2}\right)^2\rho(\omega_{mj})[2\pi t] \quad \text{for } E_m^{(0)} \approx E_j^{(0)} + \hbar\omega_o$$

Hence the rate of change from a discrete state to a band of states is merely the time derivative of the above expression,

Fermi's Golden Rule:

$$W_{j\to m} = \frac{d}{dt}\left|a'_m(t)\right|^2 \approx \frac{2\pi}{\hbar}\left|\left\langle \Psi_m^{(0)}(x)\left|A(x)\right|\Psi_{n=j}^{(0)}(x)\right\rangle\right|^2 \rho\left(E = E_j^{(0)} + \hbar\omega_o\right)$$

Where, since E=ħω, we have replaced ρ(ω) by the equivalent energy density of states, ρ(ω) → ħρ(E).

One Final Note: Since Fermi's Golden Rule was derived from 1st order time dependent perturbation theory, it is only valid for "short" times for which the initial state occupancy does not significantly change. If you wait long enough after a perturbation this will eventually not be the case and higher order theories will be required.