So we find that
\[ |\psi_n^k\rangle = (\hat{R} \hat{H})^k |\psi_n^0\rangle \]  
(2.76)

Previous, we found that
\[ E_n^1 = \langle \psi_n^0 | H^* | \psi_n^0 \rangle \]  
(2.77)
\[ E_n^2 = \langle \psi_n^0 | H^* | \psi_n^1 \rangle \]  
(2.78)
\[ E_n^3 = \langle \psi_n^0 | H^* | \psi_n^2 \rangle \]  
(2.79)

In fact, we can use the same procedure to show that for \( k \)th order,
\[ E_n^k = \langle \psi_n^0 | H^* | \psi_n^{k-1} \rangle \]  
(2.80)

Because we have found that
\[ |\psi_n^{k-1}\rangle = (\hat{R} \hat{H}^*)^{k-1} |\psi_n^0\rangle \]
\[ E_n^k = \langle \psi_n^0 | H^* | \psi_n^{k-1} \rangle = \langle \psi_n^0 | H^* (\hat{R} \hat{H})^{k-1} |\psi_n^0\rangle \]  
(2.81)

So, we have
\[ E_n^1 = \langle \psi_n^0 | H^* | \psi_n^0 \rangle \]  
(2.82)
\[ E_n^2 = \langle \psi_n^0 | H^* R H^* | \psi_n^0 \rangle = \sum_{m+n} \langle \psi_n^0 | H^* | \psi_m^0 \rangle \frac{1}{E_n - E_m^0} \langle \psi_m^0 | H^* | \psi_n^0 \rangle \]  
(2.83)
\[ E_n^3 = \langle \psi_n^0 | H^* R H^* R H^* | \psi_n^0 \rangle = \sum_{m+n} \sum_{m'} \sum_{m''} \langle \psi_n^0 | H^* | \psi_m^0 \rangle \frac{1}{E_n - E_m^0} \langle \psi_m^0 | H^* | \psi_m^0 \rangle \frac{1}{E_n - E_{m'}^0} \langle \psi_{m'}^0 | H^* | \psi_n^0 \rangle \]  
(2.84)

...  
(2.85)

From these formula we see a pattern.

1. For any \( E_n^k \), if we look at the formula from right to left, one always start from unperturbed state \( |\psi_n^0\rangle \) and eventually goes back to the same state \( \langle \psi_n^0 | \).  
2. In the path from \( |\psi_n^0\rangle \) to \( \langle \psi_n^0 | \), we go through several intermediate states \( |\psi_m^0\rangle \), \( |\psi_m^0\rangle \). For \( k \)th order perturbation, we have \( k - 1 \) intermediate states.
3. To turn from a state to another along the path (e.g. from \( n \) to \( m' \) or from \( m' \) to \( m \) in \( E_n^3 \)), we use the perturbation \( H^* \)
4. For each intermediate state, we have an denominator \( \frac{1}{E_n - E_m^0} \)

2.3.3. **Diagrammatic representation**

We can represent the \( E_n^k \) using diagrams.

1. For each intermediate state, we represent \( \frac{1}{E_n - E_m^0} \) as a solid line with integer \( m \) labeling the state.
2. For each \( \langle \psi_m^0 | H^* | \psi_m^0 \rangle \), we represent it as a dot. And we use \( V_{mm'} \) to represent \( \langle \psi_m^0 | H^* | \psi_{m'}^0 \rangle \)
3. Connect everything together in the same order as in \( E_n^k \)
4. At the two ends of the line, we use two short line to present that we start from and end at the same state \( |\psi_n^0\rangle \)

First order:

![Diagram](attachment:Phys460.nb)
Second order:

\[
\begin{array}{c}
\text{n} \\
V_{nm} \\
\text{m} \\
V_{mn} \\
\text{n}
\end{array}
\]

Third order

\[
\begin{array}{c}
\text{n} \\
V_{nm} \\
\text{m} \\
V_{m'n} \\
\text{m'} \\
V_{mn} \\
\text{n}
\end{array}
\]

By making the line longer, we can write down easily perturbation terms to any order.

**Relations to QFT:**

In QFT, we use very similar diagrams, known as the Feynman diagrams. There, solid lines are propagator of a particle \( \frac{1}{\omega - \epsilon_0} \) where \( \omega \) is frequency, pretty much the same as energy \( E_n \) and \( \epsilon_0 \) is the unperturbed energy of the particle (energy ignore interactions between particles). In fiction, the diagrams we show here are baby versions of the diagrams of Feynman.

**Physics meaning discussed in class:** (example: two electrons exchange photons to get E&M interactions).

### 2.3.4. How to compute the energy using Brillouin-Wigner Perturbation Theory?

First, let’s define some abbreviation to make the formula shorter,

\[
V_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle
\]

and thus

\[
E_n = E_n^0 + \lambda V_{nn} + \lambda^2 \frac{V_{nm} V_{nm}}{E_n - E_m^0} + \lambda^3 \frac{V_{nm} V_{m'n} V_{m'n}}{(E_n - E_m^0)(E_n - E_{m'}^0)} + \lambda^4 \frac{V_{nm} V_{m'n} V_{n'm'} V_{n'm'}}{(E_n - E_m^0)(E_n - E_{m'}^0)(E_n - E_{m''}^0)} + \ldots
\]

(2.87)

Here all the \( m \)s are summed over but they cannot be the same as \( n \). It may looks like that we can find \( E_n \) using this formula, but it is not quite the case yet. This is because on the r.h.s., the denominator contains also \( E_n \), i.e. IT is a equation for \( E_n \) and \( E_n \) arises on both sides.

This equation can be solved easily using iterative method (e.g. using a computer code). One start from zeroth order, and then go to first, second, third order …, every time we need \( E_n \) in the \( k \)th order calculation, we just use the \((k - 1)\)th order \( E_n \) on the r.h.s. Here is how it is done

**First run**

\[
E_n^{(1)} = E_n^0 + \lambda V_{nn}
\]

(2.88)

**Second run**

\[
E_n^{(2)} = E_n^0 + \lambda V_{nn} + \lambda^2 \frac{V_{nm} V_{mn}}{E_n^{(1)} - E_m^0}
\]

(2.89)

**Third run**

\[
E_n^{(3)} = E_n^0 + \lambda V_{nn} + \lambda^2 \frac{V_{nm} V_{mn}}{E_n^{(2)} - E_m^0} + \lambda^3 \frac{V_{nm} V_{m'n} V_{m'n}}{(E_n^{(2)} - E_m^0)(E_n^{(2)} - E_{m'}^0)}
\]

(2.90)

**Fourth run**

\[
E_n^{(4)} = E_n^0 + \lambda V_{nn} + \lambda^2 \frac{V_{nm} V_{mn}}{E_n^{(3)} - E_m^0} + \lambda^3 \frac{V_{nm} V_{m'n} V_{m'n}}{(E_n^{(3)} - E_m^0)(E_n^{(3)} - E_{m'}^0)(E_n^{(3)} - E_{m''}^0)} + \ldots
\]
Consider the following function

\[
f_n(x) = x^n \rightarrow g(x) = x^n(1 + a x + b x^2 + c x^3 + ...)
\]

If we want to keep \( f(x) \) to \( O(x^n) \), we only need to keep \( g(x) \) to \( O(x^{n-2}) \). Similarly, for the following function

\[
f(x) = x^2 g(x) = x^2(1 + a x + b x^2 + c x^3 + ...)
\]

If we want to keep \( f(x) \) to \( O(x^n) \), we only need to keep \( g(x) \) to \( O(x^{n-2}) \). This will be something that useful for us latter.

### 2.3.6. iterative method

\[
E_n = E_n^0 + \lambda V_m + \lambda^2 \frac{V_{m,n} V_{m,n}}{E_n - E_m^0} + \lambda^3 \frac{V_{m,n} V_{m,n'} V_{m,n'}}{(E_n^0 - E_m^0)(E_n^0 - E_m^0)^2} + O(\lambda^4)
\]

#### Zeroth order (no \( E_n \) on the l.h.s., so job done)

\[
E_n = E_n^0 + O(\lambda)
\]

#### First order (no \( E_n \) on the l.h.s., so job done)

\[
E_n = E_n^0 + \lambda V_m + O(\lambda^2)
\]

#### Second order, we use \( E_n \) obtained at zeroth order for the \( \lambda^2 \) term

\[
E_n = E_n^0 + \lambda V_m + \lambda^2 \frac{V_{m,n} V_{m,n}}{E_n - E_m^0} + O(\lambda^3) = E_n^0 + \lambda V_m + \lambda^2 \frac{V_{m,n} V_{m,n}}{E_n^0 - E_m^0} + O(\lambda^3)
\]

This is because the third term on the r.h.s. already has a \( \lambda^2 \) prefactor. Thus to keep to \( O(\lambda^3) \), we only need to keep the denominator to \( O(\lambda^0) \).

#### Third order,

\[
E_n = E_n^0 + \lambda V_m + \lambda^2 \frac{V_{m,n} V_{m,n}}{E_n - E_m^0} + \lambda^3 \frac{V_{m,n} V_{m,n'} V_{m,n'}}{(E_n^0 - E_m^0)(E_n^0 - E_m^0)^2} + O(\lambda^4)
\]

In the \( \lambda^3 \) term, we now need to keep to \( O(\lambda) \). In the \( \lambda^4 \) term, we just need to keep \( E_n \) to the zeroth order.

For the \( \lambda^2 \) term, we can expand it for small \( \lambda \)

\[
\lambda^2 \frac{V_{m,n} V_{m,n}}{(E_n^0 + \lambda V_m) - E_m^0} = \lambda^2 \frac{V_{m,n} V_{m,n}}{E_n^0 - E_m^0} - \lambda^3 \frac{V_{m,n} V_{m,n}}{E_n^0 - E_m^0} + ... + \lambda V_m + O(\lambda^3)
\]

So

\[
E_n = E_n^0 + \lambda V_m + \lambda^2 \frac{V_{m,n} V_{m,n'}}{E_n^0 - E_m^0} + \lambda^3 \left[ \frac{V_{m,n} V_{m,n'} V_{m,n'}}{(E_n^0 - E_m^0)(E_n^0 - E_m^0)} - \frac{V_{m,n} V_{m,n'} V_{m,n'}}{(E_n^0 - E_m^0)^2} \right] + O(\lambda^4)
\]
2.4. Degenerate Perturbation Theory

In the previous section, we studied the effect of a small perturbation \( \lambda H' \) on an eigenstate of \( H_0 \), \( | \psi_n^0 \rangle \). The key assumption there is that before we turn on the perturbation (i.e. at \( \lambda = 0 \)), the eigenenergies of all other eigenstates of \( H_0 \) are very far away from \( E_n^0 \)

\[
| E_n^0 - E_m^0 | > | \langle \psi_n^0 | \lambda H' | \psi_m^0 \rangle | \tag{2.103}
\]

This section, we will consider the opposite situation, where there is at least one other eigenstate of \( H_0 \) which has the same eigenenergy as \( | \psi_n^0 \rangle \). Two states having the same eigenenergy is known as “degeneracy”. So this perturbation theory is known as the degenerate perturbation theory.

2.4.1. Why non-degenerate perturbation theory fails in the presence of degeneracy?

In the presence of degeneracy, the perturbation theory that we learned before will fail. To see this, we just need to look at the second order perturbation of the eigenenergy

\[
E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots = E_n^0 + \lambda \langle \psi_n^0 | H' | \psi_n^0 \rangle + \lambda^2 \sum_{n \neq m} \frac{\langle \psi_n^0 | H' | \psi_m^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} + \ldots \tag{2.104}
\]

Here, we focus on the second order correction:

\[
\lambda^2 \sum_{n \neq m} \frac{\langle \psi_n^0 | H' | \psi_m^0 \rangle \langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \tag{2.105}
\]

If \( H_0 \) has another eigenstate \( | \psi_n^0 \rangle \) with the same eigenenergy, at least one term in this sum will have zero in the denominator and thus will diverge, i.e., when \( E_n^0 = E_m^0 \), \( \frac{1}{E_n^0 - E_m^0} \rightarrow \infty \), and thus the theory becomes ill-defined.

**NOTE:** the same divergence will arise also in higher order corrections. But there is no divergence in the first order correction \( E_n^1 \).

In power-law expansions, infinite coefficient doesn’t always mean singularity. It means that we missed something in the lower order correction. Here is a simple example: Let’s consider a function \( f(x) \), which can be written as the following Taylor expansion at small \( x \)

\[
f(x) = a_0 + a_1 x + a_2 x^2 + \ldots \tag{2.106}
\]

Now, assume that I made a mistake in the Taylor expansion for the coefficient \( a_1 \). Instead of the correction value, \( a_1 \), I used a wrong coefficient for the linear term, say \( b_1 \).

\[
f(x) = a_0 + b_1 x + (a_1 - b_1) x + a_2 x^2 + \ldots \tag{2.107}
\]

In other words, here I missed part of the linear term, \((a_1 - b_1)x\). And thus coefficients of the higher order terms will also need to be adjusted to absorb this mistake. Let’s try to use the \( x^2 \) term to correct this error, i.e.

\[
f(x) = a_0 + b_1 x + \left( \frac{a_1 - b_1}{x} + a_2 \right) x^2 + \ldots \tag{2.108}
\]
Let me define \( b_2 = a_2 + \frac{a- b_1}{x} \)
\[
f(x) = a_0 + b_1 x + b_2 x^2 + \ldots
\]
(2.109)

Now, once again, I wrote my function as a power-law expansion. Because I used a wrong coefficient for the linear term, \( b_1 \), my second order term needs to use this new coefficient. This new coefficient \( b_2 \) is infinite at small \( x \). This is transparent if we notice that when \( x \to 0 \)
\[
b_2 = a_2 + \frac{a_1 - b_1}{x} \to \infty
\]
(2.110)

**Bottom line:** infinite coefficient in the second order term (and higher order term) means that the first order result is incorrect and needs to be revised.

### 2.4.2. What to do?

Here, let’s first take another look at the second order correction
\[
E_n^2 = \sum_{m \neq n} \frac{\langle \psi_m \, | \, H' \, | \, \psi_n \rangle \langle \psi_n \, | \, H' \, | \, \psi_m \rangle}{E_m^0 - E_n^0}
\]
(2.111)

As we know, the problem arises because \( E_n^0 = E_m^0 \) for certain \( m \), and thus we get \( \frac{1}{0} = \infty \). To avoid this singularity, the only thing that we need to do is to request that the numerator also vanish whenever the denominator is zero. i.e., if \( E_n^0 = E_m^0 \), we must make sure that \( \langle \psi_m \, | \, H' \, | \, \psi_n \rangle = 0 \).

**NOTE:** the two factors in the numerator are complex conjugate to each other: \( \langle \psi_m \, | \, H' \, | \, \psi_n \rangle = \langle \psi_n \, | \, H' \, | \, \psi_m \rangle^* \), and thus if one of them is zero, the other is also zero.

**Bottom line:** For degenerate states, before we start the procedure described in the non-degenerate perturbation theory, we need to first make sure that for any degenerate states, \( \langle \psi_m \, | \, H' \, | \, \psi_n \rangle = 0 \)

### 2.4.3. Whenever there is an degeneracy, we have an option to choose the basis

A good example, a free particle. Consider a free particle with mass \( m \).
\[
H_0 = \frac{p^2}{2 m} = -\frac{\hbar^2}{2 m} \frac{d^2}{dx^2}
\]
(2.112)

The eigenstates of \( H_0 \) arises in pairs (i.e. there is a degeneracy for any excited states). The static Schrodinger equation here is
\[
-\frac{\hbar^2}{2 m} \frac{d^2}{dx^2} \psi(x) = E \psi(x)
\]
(2.113)

It is a second order differential equation and we know the solution are just plane waves
\[
\psi = A e^{ikx} + B e^{-ikx}
\]
(2.114)

The eigenenergy for this state is \( E = p^2 / 2 m = (\hbar k)^2 / 2 m \), i.e. the kinetic energy. Here, \( A \) and \( B \) are two arbitrary coefficients.

For each fixed \( k \), we have one eigenenergy \( E = (\hbar k)^2 / 2 m \), but infinite number of eigenstates \( \psi = A e^{ikx} + B e^{-ikx} \), i.e. a **degeneracy**. This example is known as two-fold degeneracy, or we say that two states have the same energy. The reason we say “two states” here is because not all the eigenstates are linear independent. In fact, we just need two states, \( e^{ikx} \) and \( e^{-ikx} \), all other eigenstates can be written as linear superposition of these two. **Bottom line:** two-fold degeneracy means that any linear combination of these two states is an eigenstate of \( H_0 \) with the same eigenenergy.

Now, let’s look at the same second order differential equation again.
\[
-\frac{\hbar^2}{2 m} \frac{d^2}{dx^2} \psi(x) = E \psi(x)
\]
(2.115)

we know that we can also write the solution for this equation as
\[
\psi = C \cos kx + D \sin ky
\]
(2.116)