Chapter 7. Approximation Methods – Part I

Very few problems in quantum mechanics can be solved exactly (analytically), therefore approximation methods have to be employed in almost all realistic situations. There are a small number of situations where an exact solution of a simple equation gives a remarkably accurate account of experimental data, but eventually refinement of experimental technique or previously overlooked effects will require a more complicated theoretical description, which no longer yields to an exactly analytic solution. Indeed the majority of physicists dedicate their lives to either measure or evaluate such small effects by making good approximations.

There is an enormous arsenal of approximation methods in quantum mechanics. In this class we’ll study some major analytic approximation methods, which are still widely used today and are the foundation for numerical computational methods. With the advent powerful computers, these approximation methods can be vastly more precise than was imaginable originally, providing indispensible qualitative and even quantitative understanding to complex and realistic quantum systems.

In part I we will study the WKB method, the variational principle, and the time-independent perturbation theory (Non-degenerate). In part II (Chapter 8), we will study and the degenerate perturbation theory and the time-dependent perturbation theory.

7.1 WKB

This method is also called semiclassical approximation, developed by Wentzel, Krammers and Brillouin in 1926. The basic idea is that the Schrödinger Equation can be solved easily for constant potential, so it can be solved approximately for a slowly-varying potential.

\[
\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\psi(x).
\] (7.1)

If \(V(x) = 0\), \(\psi(x) = e^{ikx} = \exp\left(i\frac{\sqrt{2mE}}{\hbar} x\right)\).

If \(V(x) = V_0\), \(\psi(x) = e^{ikx} = \exp\left(i\frac{\sqrt{2m(E - V_0)}}{\hbar} x\right)\).

Note: \(k = \sqrt{2m(E - V_0) / \hbar}\) can be real or imaginary for a piecewise potential.

We thus guess that for an arbitrary \(V(x)\)
\[ \psi(x) = e^{i\psi(x)} = \exp \left( \frac{i}{\hbar} \sigma(x) \right), \]  \tag{7.2} 

where \( \sigma(x) \) is a complex function in general.

Plugging Eq. (7.2) into Eq. (7.1) converts the equation for \( \psi(x) \) to \( \sigma(x) \):

\[ \psi'(x) = \frac{i}{\hbar} \sigma'(x) \psi(x), \]  \tag{7.3} 
\[ \psi''(x) = \left[ \frac{i}{\hbar} \sigma''(x) - \left( \frac{\sigma'(x)}{\hbar} \right)^2 \right] \psi(x), \]  \tag{7.4} 
\[ 0 = \left( \sigma' \right)^2 - i\hbar \sigma'' + 2m[V(x) - E]. \]  \tag{7.5} 

So far, no approximations are made, and Eq. (7.5) is mathematically identical to the Schrödinger Equation [Eq. 6.1(7.1)].

**The classical limit:** Quantum mechanics reduces to classical mechanics when \( \hbar \to 0 \). WKB makes good use of this to approximate solutions of Eq. (7.5), therefore it is called the *semi-classical* approximation. In particular, WKB treats \( \hbar \) as a small parameter, expanding \( \sigma(x) \) in terms of \( \hbar \):

\[ \sigma(x) = \sigma_0(x) + (-i\hbar)\sigma_1(x) + (-i\hbar)^2 \sigma_2(x) + \cdots \]  \tag{7.6} 
\[ 0 = \left[ \sigma_0' + (-i\hbar)\sigma_1' + (-i\hbar)^2 \sigma_2' + \cdots \right]^2 - i\hbar \left[ \sigma_0'' + (-i\hbar)\sigma_1'' + (-i\hbar)^2 \sigma_2'' + \cdots \right] + 2m[V(x) - E]. \]  \tag{7.7} 

Collecting the \( \hbar^n \) terms to rewrite Eq. (7.7) into the form of \( 0 = \sum_{n=0}^{\infty} \hbar^n F_n(x) \), so that we can require \( F_n(x) = 0 \) for \( n = 0, 1, 2 \cdots \); thus we obtain a set of equations:

\[ 0 = (\sigma_0')^2 + 2m[V(x) - E], \]  \tag{7.8} 
\[ 0 = 2\sigma_0'\sigma_1' + \sigma_0'', \]  \tag{7.9} 
\[ 0 = (\sigma_1')^2 + 2\sigma_0'\sigma_2' + \sigma_1'', \]  \tag{7.10} 

and so on. Usually, if \( V(x) \) doesn’t vary extremely fast, \( \sigma_2 \) and higher-order terms can be safely neglected, leading to the first-order WKB approximation:

\[ \sigma(x) \approx \sigma_0(x) - i\hbar \sigma_1(x). \]  \tag{7.11} 

Here \( \sigma_0(x) \) and \( \sigma_1(x) \) can be easily found for an arbitrary potential \( V(x) \) by solving Eqs. (7.8) and (7.9):
\[ \sigma'_0(x) = \pm p(x), \text{ where } p(x) \equiv \sqrt{2m(E - V(x))}. \quad (7.12) \]

Here \( p(x) \) is the classical momentum if \( E > V \); when \( E < V \), it is an imaginary function. Then

\[ \sigma_0(x) = \text{const. } \pm \int_{a}^{x} p(x') dx', \quad (7.13) \]

where \( a \) depends on the boundary conditions.

Eq. (7.9) \( \implies \sigma'_1(x) = -\frac{\sigma''_0(x)}{2\sigma'_0(x)} = -\frac{1}{2} \frac{d}{dx} \ln[\sigma'_0(x)] = -\frac{1}{2} \frac{d}{dx} \ln[\pm p(x)], \) we obtain

\[ \sigma_1(x) = \text{const. } -\frac{1}{2} \ln[\pm p(x)]. \quad (7.14) \]

Plugging Eqs. (7.14), (7.13) and (7.11) into Eq. (7.2), the (first-order) WKB approximation is

\[ \psi(x) \approx \frac{A_1}{\sqrt{p(x)}} \exp \left[ \frac{i}{\hbar} \int_{a}^{x} p(x') dx' \right] + \frac{A_2}{\sqrt{p(x)}} \exp \left[ -\frac{i}{\hbar} \int_{a}^{x} p(x') dx' \right]. \quad (7.15) \]

Remarks: (1) Classically, the momentum \( p(x) = \sqrt{2m(E - V(x))} \), and the probability of find the particle at position \( x \) is proportional to \( 1/ p(x) \). Quantum mechanically, the WKB approximation leads to \( |\psi(x)|^2 \propto 1/ p(x) \) for \( E > V \). (2) If \( V(x) = V_0 \), a constant potential, then Eq. (7.15) reduces to \( \psi(x) = B_1 e^{i p x/\hbar} + B_2 e^{-i p x/\hbar} \), with \( p = \sqrt{2m(E - V_0)} \), which are the solutions to the Schrödinger equation for a constant potential. (3) A modern topic, the path integral method, has a strong connection to the WKB approximation [Eq. (7.15)].

** Turning Points **

For an arbitrary potential \( V(x) \), we will encounter the turning-point problem when employing WKB. Consider \( V(x) \) shown in the figure on the right. Here

\[ \lim_{x \to \infty} V(x) \to \infty. \] The turning point is defined as \( x = b \), where \( E = V(b) \) and the classical momentum vanishes: \( p(b) = 0 \).

In region I \( (x > b) \), \( E > V(x) \), the phase integral starts from the turning point \( x = b \):
\[
\sigma_0(x) = \int_b^x p(x')\,dx' = \int_b^x \sqrt{2m(E-V(x'))}\,dx'.
\] (7.16)

Here \(p(x)\) is real, so \(\sigma_0\) is a pure quantum phase factor for wave function \(\psi(x)\):

\[
\psi(x) = \frac{1}{\sqrt{p(x)}} \left[ A_1 e^{i\sigma_0(x)/\hbar} + A_2 e^{-i\sigma_0(x)/\hbar} \right].
\] (7.17)

A very useful trick is to use another two parameters, \(A\) and \(\phi\), so that

\[
\psi(x) = \frac{A}{\sqrt{p(x)}} \cos \left[ \frac{\sigma_0(x)}{\hbar} + \phi \right] = \frac{A}{\sqrt{p(x)}} \cos \left[ \frac{1}{\hbar} \int_b^x p(x')\,dx' + \phi \right].
\] (7.18)

In region II \((x < b)\), \(E < V(x)\), \(p(x)\) is purely imaginary. We set \(p(x) = iq(x)\), where \(q(x) = \sqrt{2m[V(x)-E]}\), and it is real.

\[
\sigma_0(x) = \int_b^x p(x')\,dx' = i\int_b^x q(x')\,dx',
\] (7.19)

\[
\psi(x) = \frac{A_1}{\sqrt{q(x)}} \exp \left[ -\frac{1}{\hbar} \int_x^b q(x')\,dx' \right] + \frac{A_2}{\sqrt{q(x)}} \exp \left[ +\frac{1}{\hbar} \int_x^b q(x')\,dx' \right].
\] (7.20)

Here when \(x \to -\infty\), \(V(x) \to \infty\) therefore \(\psi(x) \to 0\). But the second term in Eq. (7.20) will increase exponentially as \(x \to -\infty\), thus only the first term in Eq. (7.20) survives. Set \(B = A_1\),

\[
\psi(x) = \frac{B}{\sqrt{q(x)}} \exp \left[ -\frac{1}{\hbar} \int_x^b q(x')\,dx' \right].
\] (7.21)

**Question:** How to determine the relationship between \(A\) and \(B\), and the phase shift \(\phi\)? Employing the boundary conditions at \(x = b\):

\[
\psi_I(x) \bigg|_{x=b} = \psi_{II}(x) \bigg|_{x=b},
\] (7.22)

\[
\frac{d}{dx} \psi_I(x) \bigg|_{x=b} = \frac{d}{dx} \psi_{II}(x) \bigg|_{x=b}.
\] (7.23)

However, at \(x \to b\) both \(p(x)\) and \(q(x)\) vanish, so \(\psi(x)\) and \(\frac{d}{dx} \psi(x)\) diverge, we can’t apply the boundary conditions of Eqs. (7.22) and (7.23). **Question:** Why does it break down?

Every approximation has its limit beyond which the approximation method breaks down. This is very important! Always keep in mind that you have to check if the approximation method can be safely applied (i.e., the accuracy is acceptable); otherwise, your results are misleading. So under what conditions can we apply the (first-order) WKB?
The central approximation we made in (first-order) WKB is Eq. (7.11), i.e.,
\[ \sigma(x) = \sigma_0(x) + (-i\hbar)\sigma_1(x) + (-i\hbar)^2\sigma_2(x) + \cdots \approx \sigma_0(x) - i\hbar\sigma_1(x). \]
This approximation is well held if the recursive expansion of Eq. (7.7) can be cut off at the second order:
\[ 0 = [(\sigma_0')^2 + 2m(V - E)] - i\hbar(2\sigma_0'\sigma_1' + \sigma_0'') + O(\hbar^2), \quad (7.24) \]
which requires that \(|(\sigma_0')^2 + 2m(V - E)| \gg \hbar|2\sigma_0'\sigma_1' + \sigma_0''|\). Since in the WKB solution, we require \(\sigma_0' = p(x)\), we choose \((\sigma_0')^2\) as a measure of the first term, and for the similar reasons we choose \(\sigma_0''\) as a measure of the second term. Then the validity condition for WKB is
\[ |(\sigma_0')^2| \gg \hbar|\sigma_0''|, \quad (7.25) \]
leading to \(1 \gg \hbar|\sigma_0''|(\sigma_0')^2 = \hbar \left| \frac{d}{dx} \frac{1}{\sigma_0'} \right| = \frac{d}{dx} \left( \frac{\hbar}{p(x)} \frac{1}{\sigma_0'} \right) \Rightarrow \frac{1}{2\pi} \left| \frac{d\lambda(x)}{dx} \right| \). We obtain the condition under which the WKB approximation can be applied,
\[ \frac{\left| \frac{d\lambda(x)}{dx} \right|}{1} \ll 1. \quad (7.26) \]
Physically, it means that the de Broglie wavelength varies slowly over space.

Close to the turning point, i.e., when \(x \to b\), \(p \to 0\), and because
\[ \left| \frac{d\lambda(x)}{dx} \right| = 2\pi \hbar \left| \frac{dp}{dx} \frac{1}{p^2} \right| = 2\pi \hbar \left| \frac{dp}{dx} \frac{1}{p^2} \right| \propto \left| \frac{1}{p^2} \right|, \quad \left| \frac{d\lambda(x)}{dx} \right| \to \infty \quad \text{violating Eq. (7.26)}. \]

**Question:** then how to treat the region close to \(x = b\)? When an approximation method breaks down, we can use (1) higher-order approximation or (2) exact method if possible. Here we can solve the Schrödinger equation near \(x = b\), where
\[ V(x) = V(b) + V'(b)(x - b), \quad (7.27) \]
for \(|x - b| < \delta \to 0\).

We have solved \(\psi(x)\) using WKB in region I \((x > b)\) and in region II \((x < b)\):
\[ \psi_1(x) = \frac{A}{\sqrt{p(x)}} \cos \left[ \frac{1}{\hbar} \int_b^x p(x') dx' + \phi \right], \quad \text{where} \quad p(x) = \sqrt{2m[E - V(x)]} \quad (7.28) \]
\[ \psi_i(x) = \frac{B}{\sqrt{q(x)}} \exp\left\{ -\frac{1}{\hbar} \int_x^b q(x') \, dx' \right\}, \text{ where } q(x) = \sqrt{2m[V(x) - E]} \] (7.29)

We need to find the relation between \( A \) and \( B \), and the phase shift \( \phi \).

1. Solving Schrödinger Eq. in \(|x - b| < \delta\) for potential \( V(x) = V(b) + V'(b)(x - b) \) to get \( \psi_0(x) \).
2. Now we can enforce the boundary conditions:
   - matching \( \psi_0(x) \) and \( \psi_I(x) \) at \( x = b + \delta \), and \( \psi_0(x) \) and \( \psi_{II}(x) \) at \( x = b - \delta \).
3. Take the limit of \( \delta \to 0 \).

The procedure and math are quite involved. The final results are

\[ A = 2B, \quad \phi = -\pi / 4 \] (7.30)

**Applications**

**Example 1.** Bound states in a potential well: \( V(x) \to \infty \) when \( x \to \pm \infty \). The key is using the boundary conditions at \( x = x_1 \) and \( x = x_2 \), the two turning points.

Start the **phase integral** from the left,

\[ \psi_I(x) = \frac{A}{\sqrt{p(x)}} \cos \left[ \frac{1}{\hbar} \int_{x_1}^x p(x') \, dx' - \frac{\pi}{4} \right]. \] (7.31)

Or we can start the phase integral from the right,

\[ \psi_I(x) = \frac{A}{\sqrt{p(x)}} \cos \left[ \frac{1}{\hbar} \int_{x_2}^x p(x') \, dx' - \frac{\pi}{4} \right] = \frac{A}{\sqrt{p(x)}} \cos \left[ \frac{1}{\hbar} \int_{x_2}^x p(x') \, dx' + \frac{\pi}{4} \right]. \] (7.32)

But Eqs. (7.31) and (7.32) should be the same eigenfunction; therefore, \( |A| = |A'| \) and

\[ \left[ \frac{1}{\hbar} \int_{x_1}^x p(x') \, dx' - \frac{\pi}{4} \right] - \left[ \frac{1}{\hbar} \int_{x_2}^x p(x') \, dx' + \frac{\pi}{4} \right] = n\pi, \text{ for } n = 0, 1, 2 \cdots \Rightarrow \]

\[ \int_{x_1}^{x_2} p(x) \, dx = (n + \frac{1}{2})\pi\hbar \] (7.33)

This is the WKB quantization condition for a potential well, very similar to the semi-empirical **Bohr-Sommerfeld quantization condition**:

\[ \int_{x_1}^{x_2} p(x) \, dx = (n + 1)\pi\hbar, \text{ for } n = 0, 1, 2 \cdots \] (7.34)
The difference rises from the treatment of boundary conditions:

Bohr-Sommerfeld: \( \psi(x) \) vanishes at \( x = x_1 \) and \( x_2 \)

WKB: \( \psi(x) \) starts to exponentially decay at \( x = x_1 \) and \( x_2 \)

Now we consider a concrete example:

\( V(x) = \alpha |x| \), with \( \alpha > 0 \). First, we compute the position of turning points for eigenenergy \( E_n : x_2 = E_n / \alpha \) and \( x_1 = -x_2 = -E_n / \alpha \).

Then, Eq. (7.33) \( \Rightarrow \)

\[
(n + \frac{1}{2})\pi \hbar = \int_{x_1}^{x_2} \sqrt{2m(E_n - \alpha |x|)} \, dx
\]

\[
= 2 \int_{0}^{x_2} \sqrt{2m(E_n - \alpha x)} \, dx = \frac{4\sqrt{2m}}{3\alpha} E_n^{3/2}
\]

We find the eigenenergies

\[
E_n = \left[ n + \frac{1}{2} \right] \frac{3\alpha \pi \hbar}{4\sqrt{2m}} \right]^{2/3}
\[
(7.35)
\]

How accurate is the WKB? We can also solve this problem numerically using a computer. If we define \( r_n \equiv \frac{E_n(\text{WKB})}{E_n(\text{exact})} \), then \( r_0 = 0.7162 \), \( r_1 = 0.9923 \), \( r_2 = 0.9942 \), \( r_3 = 0.9985 \ldots \)

For \( n \geq 10 \), the WKB energies are essentially the same as the exact values.

**Example 2.** Tunneling rate of an energy barrier.

We have studied a tunneling rate for a square barrier; however, in reality, the energy barrier can have a rather complicated profile, as shown here.

Then how can we evaluate the tunneling rate

\[
T = \frac{|\psi(x_2)|^2}{|\psi(x_1)|^2}
\]

using the WKB approximation?
For \( x_1 < x < x_2 \), \( E < V(x) \), and \( p(x) = \sqrt{2m(E - V)} = iq(x) \), where \( p(x) \) is imaginary while \( q(x) \) is real. The WKB wavefunction:

\[
\psi(x) \approx \frac{A}{\sqrt{q(x)}} \exp\left(-\frac{1}{\hbar} \int_{x_1}^{x} q(x') \, dx' \right).
\] (7.37)

Here we omit the exponentially increasing component. The tunneling rate

\[
T \approx \left| \frac{q(x_1)}{q(x_2)} \right| \exp\left(-\frac{1}{\hbar} \int_{x_1}^{x_2} q(x) \, dx \right)^2.
\] (7.38)

Normally the tunneling rate \( T \ll 1 \) and \( q(x_1) / q(x_2) \sim 1 \), then

\[
T \approx e^{-2\gamma}, \quad \text{with} \quad \gamma = \frac{1}{\hbar} \int_{x_1}^{x_2} q(x) \, dx.
\] (7.39)

Here \( \gamma \) is Gamow’s factor. An example is alpha decay, which is your homework problem.

### 7.2 Variational Method

Perturbation theory requires exact solutions to \( H_0 \); however, it is often very difficult to solve the eigenstate problem. The variational theory offers a powerful method to estimate the ground-state energy \( E_0 \) and wavefunctions \( \psi_0(r) \).

The variational theorem: For an arbitrary wavefunction \( \phi(r) \)

\[
\frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_0.
\] (7.40)

Proof: The eigenstates of \( H \), \( \left| \psi_n \right\rangle \), form a basis to expand \( \left| \phi \right\rangle \):

\[
\left| \phi \right\rangle = \sum_n c_n \left| \psi_n \right\rangle,
\] (7.41)

where \( c_n = \langle \psi_n | \phi \rangle \). Since \( H \left| \psi_n \right\rangle = E_n \left| \psi_n \right\rangle \),

\[
\langle \phi | H | \phi \rangle = \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2,
\] (7.42)

and
\[ \langle \phi | \phi \rangle = \sum_n | c_n|^2, \]

therefore, the theorem (7.40) is proved.

The variational method is based on the variational theorem. The left hand side of (7.40),

\[ E[\phi(r)] \equiv \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \phi'(r) H \phi(r) d^3r}{\int | \phi(r) |^2 d^3r}, \]

is a functional of \( \phi(r) \). Since \( E[\phi(r)] \geq E_0 \), one can make \( E[\phi] \) as small as possible by ‘varying’ \( \phi \) to get close to \( E_0 \) [and \( \phi(r) \) also becomes close to \( \psi_0(r) \)]. \( \phi(r) \) is called the trial wavefunction, which depends on \( m \) parameters \( \lambda_1, \lambda_2, \ldots, \lambda_m \), and then \( E[\phi] \) also depends on these parameters. The minimum of \( E[\phi] \) [constrained by the expression of \( \phi(r) \) ] is found by solving the following set of \( m \) equations,

\[ \frac{\partial E}{\partial \lambda_1} = 0, \quad \frac{\partial E}{\partial \lambda_2} = 0, \quad \ldots, \quad \frac{\partial E}{\partial \lambda_m} = 0. \]  

(7.45)

A good format of \( \phi(r) \) will result in a good estimation of the ground-state energy. If \( \phi(r) \) happens to be exact, then the exact ground-state energy is obtained. But how to construct a trial wavefunction? We appeal to physical intuition — the asymptotic behaviors at boundary or large distance. Different forms of \( \phi(r) \) will give different estimation of \( E_0 \); in practice, we can use a crude method to get crude \( \phi(r) \), then we use the variational method to refine \( \phi(r) \) and \( E_0 \).

Example: the ground-state energy of the one-dimensional infinite potential well

\[ V(x) = \begin{cases} 
0, & \text{for } |x| \leq a \\
\infty, & \text{for } |x| \geq a.
\end{cases} \]  

(7.46)

We have found the exact solution

\[ \psi_0(x) = \frac{1}{\sqrt{a}} \cos \left( \frac{\pi x}{2a} \right), \]

(7.47)

\[ E_0 = \frac{\hbar^2 \pi^2}{8ma^2}. \]

(7.48)
Because wavefunction must vanish at $x = \pm a$, a trial wavefunction must satisfy $\phi(\pm a) = 0$, and we have many choices. The simplest one is $\phi(x) = A(a^2 - x^2)$, where $A$ is the normalization parameter (NOT a variational parameter). Therefore, we don’t need to solve Eq. (7.45), instead, total energy is evaluated directly from Eq. (7.44):

$$E = \frac{\int_{-a}^{a} (a^2 - x^2) \frac{d^2}{dx^2}(a^2 - x^2) \, dx}{\int_{-a}^{a} (a^2 - x^2)^2 \, dx} = \frac{10}{\pi^2} \frac{\pi^2 \hbar^2}{8ma^2} = 1.0132E_0.$$  \hspace{0.2cm} (7.49)

Next let’s try a bit more sophisticated one, $\phi(x) = A(|a|^\lambda - |x|^\lambda)$, with a variational parameter $\lambda$, which is determined by evaluating $E(\lambda)$,

$$E(\lambda) = \frac{(\lambda + 1)(2\lambda + 1)}{2\lambda - 1} \frac{\hbar^2}{4ma^2},$$  \hspace{0.2cm} (7.50)

and then solving the equation $\frac{dE(\lambda)}{d\lambda} = 0$. We find that $E(\lambda)$ has a minimum at

$$\lambda = \frac{1 + \sqrt{6}}{2} \approx 1.7247,$$

with $E_{\text{min}} = \left(\frac{5 + 2\sqrt{6}}{\pi^2}\right)E_0 \approx 1.00298 \ E_0$.

### 7.3 Time-Independent Perturbation (Non-Degenerate)

Very few problems can be solved analytically; however, practically in all realistic cases the effects of different factors are not equipollent. Thus one can first single out the most significant factors, which normally can be solved either analytically or approximately. The influence of neglected factors can then be taken into account approximately as a \textit{perturbation}.

Usually (not always), perturbations only slightly modify the wavefunctions and energy levels, so that the qualitative picture of the perturbed system retains the main features of the unperturbed one, and the changes in wavefunctions and energy levels due to perturbation can be expressed in terms of the unperturbed wavefunctions and energy levels. In this class we will focus on these \textit{well-behaved} perturbations. However, in certain cases an infinitesimal perturbation can generate significant effects on the unperturbed system, and the associated quantum chaos is currently among the frontiers in research on the foundation of quantum mechanics.

### 7.3.1 Formal Theory (Non-Degenerate)
Let’s start with Hamiltonian $H = H_0 + H'$, where $H'$ is much weaker than $H_0$.

What we know: 
1. the eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$ for $H_0$: $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$
2. $H'_{nm} = \langle n^{(0)} | H' | m^{(0)} \rangle$

**Goal:** the eigenstates $|n\rangle$ and eigenvalues $E_n$ for $H: H |n\rangle = E_n |n\rangle$, from perturbation theory in terms of $E_n^{(0)}$, $H'_{nm}$, and $|n^{(0)}\rangle$. We can write $H = H_0 + \lambda H'$, where $0 \leq \lambda \leq 1$, then

\[ E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \]  \hfill (7.51)
\[ |n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \]  \hfill (7.52)

We want to express the $j$-th order corrections to energy, $E_n^{(j)}$, and to eigenstate, $|n^{(j)}\rangle$, in terms of $E_n^{(0)}$, $H'_{nm}$, and $|n^{(0)}\rangle$. In principle, one can obtain the exact solutions to $E_n$ and $|n\rangle$ by summing all orders (from 0 to infinity) of corrections; however, in practice, we normally do first- and second-order corrections to eigenenergies, while only first-order corrections to eigenstates.

Assume all $E_n^{(0)}$ are significantly different, i.e.,

\[ |E_n^{(0)} - E_m^{(0)}| \gg |H'_{nm}| \]  \hfill (7.53)

which is the condition for applying time-independent non-degenerate perturbation theory.

\[ H |n\rangle = E_n |n\rangle \Rightarrow \left( H_0 + \lambda H' \right) |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \]
\[ = (E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots) |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \cdots \]

From the above we derive one equation for each order. We plug the zeroth-order solutions to the first-order equation to get the first-order corrections, and then plug the first-order solutions to the second-order equation to get the second-order corrections, and so on.

**Zeroth-order:** $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$

**First-order:** $\left( H_0 - E_n^{(0)} \right) |n^{(1)}\rangle = (E_n^{(1)} - H') |n^{(0)}\rangle$  \hfill (7.54)

**Second-order:** $\left( H_0 - E_n^{(0)} \right) |n^{(2)}\rangle = (E_n^{(1)} - H') |n^{(1)}\rangle + E_n^{(2)} |n^{(0)}\rangle$  \hfill (7.55)

Multiply $\langle n^{(0)} |$ on both sides of Eq. 6.43, using the zeroth-order solution $H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle$
\[
\langle n^{(0)} \vert (H_0 - E_n^{(0)}) \vert n^{(1)} \rangle = 0 = \langle n^{(0)} \vert (E_n^{(1)} - H') \vert n^{(0)} \rangle = E_n^{(1)} - \langle n^{(0)} \vert H' \vert n^{(0)} \rangle \Rightarrow \\
E_n^{(1)} = \langle n^{(0)} \vert H' \vert n^{(0)} \rangle = H'_{nn} \quad (7.56)
\]

Multiply \( \langle m^{(0)} \vert \) on both sides of Eq. (7.54), where \( m \neq n \)
\[
\langle m^{(0)} \vert (H_0 - E_n^{(0)}) \vert n^{(1)} \rangle = \langle m^{(0)} \vert (E_n^{(1)} - H') \vert n^{(0)} \rangle \\
\Rightarrow (E_m^{(0)} - E_n^{(0)}) \langle m^{(0)} \vert n^{(1)} \rangle = E_n^{(1)} \delta_{n,m} - H'_{mn} = -H'_{mn}, \text{ since } m \neq n
\]

We can express \( \vert n^{(1)} \rangle = \sum_{m} C_{nm}^{(1)} \vert m^{(0)} \rangle \), a linear combination of the basis \( \left\{ \vert n^{(0)} \rangle \right\} \), and then
\[
C_{nm}^{(1)} = \langle m^{(0)} \vert n^{(1)} \rangle = \frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}}, \text{ for } m \neq n; \text{ while } C_{nn}^{(1)} = 0. \text{ Thus we obtain}
\[
\vert n^{(1)} \rangle = \sum_{m} C_{nm}^{(1)} \vert m^{(0)} \rangle = \sum_{m \neq n} \frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}} \vert m^{(0)} \rangle \quad (7.57)
\]

Here Eqs. (7.56) and (7.57) are the first-order non-degenerate time-independent perturbations to energy levels and eigenstates, respectively. **Notes:** We can obtain this form of the first-order correction to eigenstates only if \( |E_n^{(0)} - E_m^{(0)}| \approx 0 \), i.e., non-degeneracy. When \( |E_n^{(0)} - E_m^{(0)}| \gg |H'_{mn}| \), the first-order corrections are much smaller than their corresponding unperturbed results.

Now we derive the second-order energy corrections \( E_n^{(2)} \) from Eq. (7.55). Using the similar approach, multiply \( \langle n^{(0)} \vert \) on both sides, we get
\[
\langle n^{(0)} \vert (H_0 - E_n^{(0)}) \vert n^{(2)} \rangle = \langle n^{(0)} \vert (E_n^{(1)} - H') \vert n^{(1)} \rangle + \langle n^{(0)} \vert E_n^{(2)} \vert n^{(0)} \rangle \\
\Rightarrow \quad 0 = E_n^{(1)} \langle n^{(0)} \vert n^{(1)} \rangle - \langle n^{(0)} \vert H' \vert n^{(1)} \rangle + E_n^{(2)} \\
\Rightarrow \quad E_n^{(2)} = \langle n^{(0)} \vert H' \vert n^{(1)} \rangle - E_n^{(1)} \langle n^{(0)} \vert n^{(1)} \rangle
\]

Using the first-order results: \( \vert n^{(1)} \rangle = \sum_{m \neq n} \frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}} \vert m^{(0)} \rangle \Rightarrow \langle n^{(0)} \vert n^{(1)} \rangle = 0 \), therefore
\[
E_n^{(2)} = \langle n^{(0)} \vert H' \vert n^{(1)} \rangle = \sum_{m \neq n} C_{nm}^{(1)} \langle n^{(0)} \vert H' \vert m^{(0)} \rangle = \sum_{m \neq n} \frac{H'_{mn}^2}{E_m^{(0)} - E_n^{(0)}}. \quad (7.58)
\]
You can derive \( |n^{(2)}\rangle \), \( E_n^{(3)} \), and so on; but in practice, they are rarely used. A summary:

\[
E_n^{(1)} = H'; \quad |n^{(1)}\rangle = \sum_{m \neq n} \frac{H'_{nm}}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle
\]

\[
E_n^{(2)} = \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^{(0)} - E_m^{(0)}},
\]

\[
\Rightarrow \lambda = 1, \quad H = H_0 + H', \quad E_n \approx E_n^{(0)} + H'_{nn} + \sum_{m \neq n} \frac{|H'_{nm}|^2}{E_n^{(0)} - E_m^{(0)}} \quad |n\rangle \approx |n^{(0)}\rangle + \sum_{m \neq n} \frac{H'_{nm}}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle
\]

7.3.2 Applications of the Non-Degenerate Time-Independent Perturbation Theory

Example 1: Charged harmonic oscillator in a weak electric field. The Hamiltonian is

\[
H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 + Fx = H_0 + H',
\]

which \( H' = Fx \) and \( F = q\varepsilon \), with \( \varepsilon \) the magnitude of electric field and \( q \) the charge.

We know that \( H_0 |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle \) with \( E_n^{(0)} = (n + \frac{1}{2})\hbar\omega \).

We need to work out \( H'_{nk} = \langle n^{(0)} | x | k^{(0)} \rangle \), using the ladder operators

\[
x = x_0 (a + a^\dagger), \quad x_0 = \sqrt{\frac{\hbar}{2m\omega}}; \quad \text{then}
\]

\[
H'_{nk} = \begin{cases} 
Fx_0 \sqrt{n} & k = n - 1 \\
Fx_0 \sqrt{n+1} & k = n + 1 \\
0 & \text{Otherwise}
\end{cases}
\]

\[
E_n^{(3)} = H'_{nn} = 0,
\]

\[
E_n^{(2)} = \sum_{k \neq n} \frac{|H'_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} = \frac{|H'_{n,n-1}|^2}{E_n^{(0)} - E_{n-1}^{(0)}} + \frac{|H'_{n,n+1}|^2}{E_n^{(0)} - E_{n+1}^{(0)}}
\]

\[
= \frac{(Fx_0)^2 n}{\hbar\omega} + \frac{(Fx_0)^2 (n+1)}{-\hbar\omega} = -F^2 x_0^2 = \frac{F^2}{2m\omega^2}
\]

\[
\Rightarrow E_n \approx E_n^{(0)} + E_n^{(1)} + E_n^{(2)} = (n + \frac{1}{2})\hbar\omega - \frac{F^2}{2m\omega^2}.
\]
It is interesting to compare the exact solution, which is straightforward to obtain, since a charged simple harmonic oscillator in electric filed is still a SHO (Why? Consider the classical SHO under a constant force). Set \( y = x + \frac{F}{m\omega^2} \), the Hamiltonian

\[
H = -\frac{\hbar^2}{2m} \frac{d^2}{dy^2} + \frac{1}{2} m\omega^2 y^2 - \frac{F^2}{2m\omega^2} \Rightarrow \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dy^2} + \frac{1}{2} m\omega^2 y^2 \right\} \psi(y) = \left( E_n + \frac{F^2}{2m\omega^2} \right) \psi(y)
\]

\[
\Rightarrow E_n + \frac{F^2}{2m\omega^2} = (n + \frac{1}{2})\hbar\omega \quad \Rightarrow E_n = (n + \frac{1}{2})\hbar\omega - \frac{F^2}{2m\omega^2}.
\]

**Question:** the exact solution is the same as that using the second-order perturbation theory, why?

Next, we employ the perturbation theory to find the wavefunctions:

\[
\psi_n^{(1)}(x) = \sum_{k=\pm} C_{nk} \psi_k^{(0)}(x), \quad \text{where} \quad C_{nk} = \frac{H_{kn}}{E_n^{(0)} - E_k^{(0)}}. \tag{7.61}
\]

In this case, \( C_{nk}^{(1)} = 0 \) only for \( k = n \pm 1 \).

Eq. (7.60) \( \Rightarrow C_{n,n-1}^{(1)} = \frac{F x_n \sqrt{n}}{\hbar \omega} \) and \( C_{n,n+1}^{(1)} = -\frac{F x_0 \sqrt{n+1}}{\hbar \omega} \), we obtain

\[
\psi_n(x) \approx \psi_n^{(0)}(x) + \frac{F x_n}{\hbar \omega} \left[ \sqrt{n} \psi_{n-1}^{(0)}(x) - \sqrt{n+1} \psi_{n+1}^{(0)}(x) \right]. \tag{7.62}
\]

Let’s compare with the exact results for the ground state.

From perturbation theory,

\[
\psi_0(x) \approx \psi_0^{(0)}(x) - \frac{F x_0}{\hbar \omega} \psi_1^{(0)}(x) = \left( 1 - \frac{F x_0}{\hbar \omega} \right) \psi_0^{(0)}(x), \tag{7.63}
\]

since \( \psi_1^{(0)}(x) = \frac{x}{x_0} \psi_0^{(0)}(x) \). (How would you prove that?)

The exact solution:

\[
\psi_0(y) = A_0 e^{-\frac{x^2}{2x_0^2}} e^{-\frac{1}{2x_0^2} \frac{x F}{m\omega^2}}, \quad \text{with} \quad A_0 = \frac{1}{(2\pi x_0^2)^{1/4}}, \quad y = x + \frac{F}{m\omega^2}. \tag{7.64}
\]

The first-order Taylor expansion assuming small \( F \):

\[
\psi_0(x) \approx A_0 e^{-\frac{x^2}{2x_0^2}} e^{-\frac{1}{2x_0^2} \frac{x F}{m\omega^2}} \approx \psi_0^{(0)}(x) \left( 1 - \frac{1}{2x_0^2} \frac{x F}{m\omega^2} \right) = \left( 1 - \frac{F x}{\hbar \omega} \right) \psi_0^{(0)}(x). \tag{7.65}
\]
Example 2: Fine structure of the hydrogen atom

The above figure shows the hydrogen optical absorption spectral lines on a logarithmic scale, which can be accurately explained by solving the Schrödinger equation for Coulomb potential.

Specifically,

\[ E_n = -\frac{1}{n^2} E_0, \quad \text{where the Rydberg energy } E_0 = \frac{\hbar^2}{2m_e a_0^2} = 13.60 \text{ eV}. \]  

(7.66)
The eigenfunctions $\psi_{nlm}(r, \theta, \phi)$ can be written as
$$\langle r, \theta, \phi \| n, lm \rangle = R_n(r) Y_l^m(\theta, \phi). \quad (7.67)$$

However, when resolution is increased, one finds small deviations from theory. For example, for the $3s$ to $2p$ transition, using the reduced mass, you’ll get 656.47 nm for hydrogen and 656.29 nm for deuterium, respectively. But experimentally, physicists measured a small shift of 0.15 nm (0.00042 eV) with a tiny splitting of 0.016 nm (0.000045 eV). These effects are called the fine structure of H spectral lines, and the physical origins are rather complicated.

If you look even closer, you will find more complicated and even weaker effects, including the **Lamb shifts** and the **hyperfine structure**. Lamb shifts are due to electron and vacuum interaction, which are significant only for the $s$-wave, while the hyperfine structure is due to nuclear spin. The energy hierarchy is summarized on the right.

Here we will not discuss the Lamb shift and the hyperfine structure. The Hamiltonian at the fine-structure level:
$$H = H_0 + H_{KE} + H_{DW} + H_{so}.$$ \hspace{1cm} (7.68)

The perturbation $H' = H_{KE} + H_{DW} + H_{so}$, accounting for the relativistic kinetic energy, the Darwin and the spin-orbit coupling corrections, respectively.

(1) **The relativistic kinetic energy corrections.**

The kinetic energy: $K.E. = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \approx \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}, \quad (7.69)$

for low-energy electrons. Then
$$H_{KE} = -\frac{\hat{p}^4}{8m^3 c^2}, \quad (7.70)$$

$$E_{KE,nlm}^{(1)} = -\frac{1}{8m^3 c^2} \langle n, lm \| \hat{p}^4 \| n, lm \rangle. \quad (7.71)$$
You can imagine that evaluating Eq. (7.71) in real-space integrals is very difficult. Here is the trick. We note that

\[ p^4 = 4m^2 \left( \frac{p^2}{2m} \right)^2 = 4m^2 \left( H_0 + \frac{e^2}{r} \right)^2 \]  

so that

\[ \langle n, lm | \hat{p}^4 | n, lm \rangle = 4m^2 \left[ (E_n^{(0)})^2 + 2E_n^{(0)} e^2 \left( \frac{1}{r} \right) + e^4 \left( \frac{1}{r^3} \right) \right], \]  

(7.73)

where \( \left\langle \frac{1}{r} \right\rangle = \langle n, lm | \frac{1}{r} | n, lm \rangle \) and \( \left\langle \frac{1}{r^2} \right\rangle = \langle n, lm | \frac{1}{r^2} | n, lm \rangle \). We find that (Homework problem)

\[ e^2 \left\langle \frac{1}{r} \right\rangle = -2E_n^{(0)}, \]  

(7.74)

\[ e^4 \left\langle \frac{1}{r^2} \right\rangle = \frac{4nE_n^{(0)}}{l+1/2}. \]  

(7.75)

The first-order relativistic kinetic energy corrections are

\[ E_{KE,nlm}^{(1)} = -\frac{\alpha^4}{2} mc^2 \left[ -\frac{3}{4n^4} + \frac{1}{n^3(l+1/2)} \right], \]  

(7.76)

(2) The Darwin correction.

This is the correction due to the relativistic Dirac equation. Physically, when an electron approaches the nuclear, it will be “trembling”, a phenomenon called “zitterbewegung”. It is a consequence of the interference of the electron with its antiparticle, which appears as a virtual particle when the energy of the electron comes close to its rest energy. The consequence of the zitterbewegung is that the electron sees a smeared-out Coulomb potential of the nucleus. Mathematically, the Darwin correction is found by acting with the Laplacian on the potential.

In the case of the Coulomb potential, this yields

\[ \nabla^2 V(r) \sim \nabla^2 \left( \frac{1}{r} \right) \sim \delta(r), \]  

(7.77)

so that

\[ H_{DW} = g\delta(r), \quad \text{where} \quad g = \frac{\hbar^2 \pi^2 e^2}{2m^2 c^2}. \]  

(7.78)

\[ E_{DW,nlm}^{(1)} = \langle nlm | H_{DW} | nlm \rangle = g | \psi_{nlm}(r = 0) |^2. \]  

(7.79)
Because \( u_n(r) = rR_n(r) = rA_n \left( \frac{r}{a_0} \right)^l \exp \left\{ -\frac{Zr}{na_0} \right\} \sum_{n' = 0}^{l+1} \frac{2Zr}{na_0} \) [See Eq. (4.66) in Chapter 4], we obtain

\[
\psi_{nlm}(r = 0) = \begin{cases} 
0 & (l > 0) \\
\frac{1}{\sqrt{\pi}} \left( \frac{1}{na_0} \right)^{3/2} & (l = 0),
\end{cases}
\]

(7.80)

and

\[
E_{DW,nlm}^{(1)} = \begin{cases} 
0 & (l > 0) \\
\frac{\alpha^4}{2n^3} mc^2 & (l = 0),
\end{cases}
\]

(7.81)

which indicates that the Darwin correction is positive and only applies to the \( s \)-wave.

(3) The spin-orbit interaction.

The spin-orbit coupling Hamiltonian is

\[
H_{so} = \frac{e^2}{2m^2 c^2 r^3} \mathbf{S} \cdot \mathbf{L}
\]

(7.82)

The total angular momentum is defined as

\[
\mathbf{J} = \mathbf{S} + \mathbf{L},
\]

(7.83)

therefore

\[
\mathbf{S} \cdot \mathbf{L} = \frac{1}{2}(J^2 - L^2 - S^2).
\]

(7.84)

We need to construct the common eigenstates for \( J^2, L^2 \) and \( S^2 \), designated as \( |j, m; l, s \rangle \), where \( j = |l - s|, |l - s| + 1, \cdots, j + s - 1, j + s \) and \( m = m_j = -j, -j + 1, \cdots, j - 1, j \). In this basis,

\[
\langle j', m'; l', s | \mathbf{S} \cdot \mathbf{L} | j, m; l, s \rangle = \delta_{j, j'} \delta_{m, m'} \delta_{l, l'} \frac{\hbar^2}{2} [j(j + 1) - l(l + 1) - s(s + 1)].
\]

(7.85)

Here \( s = 1/2 \), so that \( j = l \pm 1/2 \) \((l \neq 0)\) and \( j = s = 1/2 \) \((l = 0)\). For \( l = 0 \), there is no spin-orbit coupling and \( E_{so}^{(1)} \) vanishes. For \( l \neq 0 \), we obtain
\[ E^{(1)}_{\text{so,nbm}} = \frac{\hbar^2 e^2}{4m^2 c^2} \left( \frac{1}{r^3} \right) \begin{cases} l & (j = l + 1/2) \\ -(l + 1) & (j = l - 1/2) \end{cases} \] (7.86)

Using the result of (Again your homework problem)
\[ \left( \frac{1}{r^3} \right) = \frac{1}{a_0^3 n^3 l(l + 1/2)(l + 1)} \],

one finds the first-order spin-orbit interaction corrections
\[ E^{(1)}_{\text{so,nbm}} = \frac{\alpha^4}{4} m c^2 \frac{1}{n^3 l(l + 1/2)(l + 1)} \begin{cases} l & (j = l + 1/2) \\ -(l + 1) & (j = l - 1/2) \end{cases} \] (7.88)

All these three corrections are of the \( \alpha^4 \) effects, and we combine them to write down the total fine-structure energy shifts
\[ E^{(1)}_{\text{f.s.,nj}} = -\frac{\alpha^4 m c^2}{2n^3} \left( \frac{1}{j + 1/2} - \frac{3}{4n} \right). \] (7.89)

Some remarks:
1) Here \( j = l \pm 1/2 \) for \( l > 0 \), while \( j = 1/2 \) for \( l = 0 \).
2) For \( l > 0 \), \( \Delta E^{(1)}_{\text{f.s.}} \) comes from the spin-orbit interaction and relativistic kinetic energy; however, when \( l = 0 \), i.e., for the s-wave, \( \Delta E^{(1)}_{\text{f.s.}} \) comes from the Darwin correction and relativistic kinetic energy.
3) The exact fine-structure energy levels obtained from the Dirac Equation are
\[ E_{nj} = m c^2 \left[ 1 + \left( \frac{\alpha}{n - (j + 1/2) + \sqrt{(j + 1/2)^2 - \alpha^2}} \right)^2 \right]^{-1/2} - m c^2. \] (7.90)

Expand Eq. 6.79 to order \( \alpha^4 \), we recover the perturbative results (Eq. 6.78), amazing!
4) Evaluating the correction due to the spin-orbit interaction requires the degenerate perturbation theory, which will be discussed in next Chapter.