We've long since run out of problems where we can solve the Schrödinger equation exactly to find energy eigenstates. But we believe that QM describes all physics on small scales, regardless of whether we can ourselves solve the problems analytically.

Now we don't throw up our hands and go home; instead we devise approximation methods that, while they don't give us exact solutions, get us pretty darn close. Perturbation theory is one such method.

To keep it simple, we'll start with time independent, nondegenerate perturbation theory.

We want to solve

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

(*)

where \( \hat{H} \) is some Hamiltonian operator where we don't have an analytic solution. Well, if \( \hat{H} \) is close to a Hamiltonian \( \hat{H}_0 \) where we do know the eigenfunctions, then we can find the \( \psi_n \) in (*) by doing a perturbative expansion.
To make all this more concrete, suppose

\[ \hat{H} = \hat{H}_0 + \hat{H}' \]

where \( \hat{H} = \) total Hamiltonian, we want to find eigenfunctions + eigenvalues

\( \hat{H}_0 = \) "unperturbed Hamiltonian" whose eigenfns + eigenvalues we know:

\[ \hat{H}_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \]

\[ \uparrow \quad \uparrow \quad \uparrow \]

\[ \psi_n^{(0)} \quad \text{vs.} \quad \psi_n \]

\( \hat{H}' = \) "perturbation Hamiltonian" which is small compared to \( \hat{H}_0 \).

[Reality check: It's pretty meaningless to describe one operator as being small compared to another. In fact we mean something more specific, which we will see below. But this assumption of smallness is crucial for perturbation theory to work.]

and we want to find approximate solns to

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

\[ \uparrow \quad \uparrow \quad \uparrow \]

we want approximations to these.
The first thing to notice is that if $\hat{H}$ is small compared to $\hat{H}_0$, then $\psi_n$ and $E_n$ are probably not very different from $\psi_n^{(0)}$ and $E_n^{(0)}$, which means we can expand about the unperturbed values, i.e., we expect

$$
\psi_n = \psi_n^{(0)} + \Delta \psi_n \quad \text{with } \Delta \psi_n, \Delta E_n \text{ small}
$$

$$
E_n = E_n^{(0)} + \Delta E_n
$$

So for bookkeeping purposes, let's write $\hat{H}$ as $\lambda \hat{H}$ where $\lambda$ is a small parameter. The sole purpose of introducing $\lambda$ is to keep track of the "smallness" of various terms. Powers of $\lambda$ will correspond to orders of corrections.

(Note $\lambda \to 0$ gives the unperturbed problem and $\lambda \to 1$ is the exact problem we're trying to solve.)

Then we expand $\psi_n + E_n$ about $\psi_n^{(0)} + E_n^{(0)}$ in powers of $\lambda$:

$$
\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots
$$

$$
E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots
$$

and we want to solve for the $\psi_n^{(i)}$ and $E_n^{(i)}$.

Now substitute into $(\hat{H}_0 + \lambda \hat{H}) \psi_n = E \psi_n$ and collect orders of $\lambda$: 

\[
(H_0 + \lambda \hat{H}') \left[ \Phi^{(0)}_n + \lambda \Phi^{(1)}_n + \lambda^2 \Phi^{(2)}_n + \ldots \right]
\]
\[
= (E^{(0)}_n + \lambda E^{(1)}_n + \lambda^2 E^{(2)}_n) \left[ \Phi^{(0)}_n + \lambda \Phi^{(1)}_n + \lambda^2 \Phi^{(2)}_n + \ldots \right]
\]

and keeping terms up to order \( \lambda^2 \) we get

\[
\left[ H_0 \Psi^{(0)}_n - E^{(0)}_n \Psi^{(0)}_n \right]
\]

\[
+ \lambda \left[ H_0 \Phi^{(0)}_n + \hat{H}' \Phi^{(1)}_n - E^{(0)}_n \Phi^{(1)}_n - E^{(1)}_n \Phi^{(0)}_n \right]
\]

not necessarily = 0!

\[
+ \lambda^2 \left[ H_0 \Phi^{(2)}_n + \hat{H}' \Phi^{(1)}_n - E^{(0)}_n \Phi^{(2)}_n - E^{(1)}_n \Phi^{(1)}_n - E^{(2)}_n \Phi^{(0)}_n \right]
\]

\[\vdots\]

\[= 0\]

Now \( \lambda \) is arbitrary, and in particular suppose \( \lambda \) is very small (say \( 10^{-15} \)). For the preceding equation to be true, each term in square brackets must separately be equal to zero.

So we get a bunch of separate equations, one for each power of \( \lambda \). Notice that the power of \( \lambda \) corresponds to the order of \( \Phi \) and \( E \) in the \( \lambda \) equation. That means if we solve the equations sequentially we get the solutions for \( \lambda \)'s sequentially, until our patience runs out.
We knew that \( Y_n^{(0)} + E_n^{(0)} \) are the unperturbed solution. This serves as a consistency check.

At first sight, these terms look like they might cancel. But no, the wave function in there is \( Y_n^{(1)} \), not \( Y_n^{(0)} \), so we can't say. But if \( Y_n^{(1)} \) has a piece that's proportional to \( Y_n^{(0)} \), then that piece cancels in those two terms.

Another way of making this point is to note that for any soin \( Y_n^{(1)} \) to this eq'n, \( Y_n^{(1)} + a Y_n^{(0)} \) is also a solution for any \( a \). We don't want or need to muck up the works by including extra terms in the higher order soins; the unperturbed soin is already taken care of in the zero order term. So to get rid of this problem, let's just require that the higher order...
so we don't contain \( \psi^{(0)} \), by which we mean they're orthogonal:

\[
\langle \psi^{(i)}_n | \psi^{(0)}_m \rangle = 0 \quad \text{for all } i > 0 \text{ and all } n
\]

Okay, we still have to solve the 1st order eq'n. Note the \( \hat{H}_0 \) \( \psi^{(1)} \) term. We don't know what \( \hat{H}_0 \) does to \( \psi^{(1)}_n \) directly, but we do know what \( \hat{H}_0 \) does to the \( \psi^{(0)}_n \) and that they form a complete set, so we can expand \( \psi^{(1)}_n \) in terms of the \( \psi^{(0)}_n \):

\[
\psi^{(1)}_n = \sum_j c_{nj} \psi^{(0)}_j
\]

Then we substitute this expansion into the 1st order eq'n (***) on p.9.5 and we get

\[
(\hat{H}_0 - E^{(0)}_n) \sum_j c_{nj} \psi^{(0)}_j = (E^{(1)}_n - \hat{H}) \psi^{(0)}_n
\]

and now our task is to solve for the \( c_{nj} \). We do it by multiplying on the left w/ \( \langle \psi^{(0)}_j | \)

\[
\sum_j c_{nj} \left[ \langle \psi^{(0)}_j | \hat{H}_0 | \psi^{(0)}_j \rangle - E^{(0)}_n \langle \psi^{(0)}_j | \psi^{(0)}_j \rangle \right] = E^{(1)}_n \langle \psi^{(0)}_j | \psi^{(0)}_j \rangle - \langle \psi^{(0)}_j | \hat{H} | \psi^{(0)}_j \rangle
\]

\[\text{Helm}^*\]

* We are assuming that \( \psi^{(1)}_n \) (and the other \( \psi^{(n)} \)) lie in a subspace spanned by the \( \psi^{(0)}_n \). This is usually, but not always, the case.
which gives us
\[
\left[ E_0^{(0)} - E_0^{(0)} \right] c_{n,l} + H'_{l,n} = E_n^{(0)} \delta_{l,n} \quad (***)
\]
with
\[
H'_{l,n} = \langle \Psi_{n}^{(0)} | \hat{H}' | \Psi_{l}^{(0)} \rangle
\]
= the \( l \) \textit{n} matrix element of
the perturbation \textit{Hamiltonian}
in the unperturbed basis.

(***)

Now we need to solve for \( c_{n,l} \) and \( E_n^{(0)} \). For \( l \neq n \),
\( E_n^{(0)} \) drops out and we get
\[
c_{n,l} = \frac{H'_{l,n}}{E_n^{(0)} - E_l^{(0)}} \quad n \neq l
\]
and since we require \( \langle \Psi_{n}^{(1)} | \Psi_{n}^{(0)} \rangle = 0 \), then \( c_{n,n} = 0 \).

So plugging in to the expansion for \( \Psi_{n}^{(1)} \), we have
\[
\Psi_{n}^{(1)} = \sum_{j \neq n} \frac{H'_{j,n}}{E_j^{(0)} - E_n^{(0)}} \Psi_{j}^{(0)}
\]

Now to find \( E_n^{(0)} \) go back to (***) and take \( l = n \):
\[
E_n^{(0)} = H'_{n,n}
\]

Kind of a pretty result: \( \text{the 1st correction to the}
\text{energy is the corresponding diagonal matrix element}
of the \text{perturbation \textit{Hamiltonian}} \)
So we've got our approximate solution to 1st order (we set $\lambda = 1$ in the expansions for $\Psi_n$ and $E_n$):

$$
\Psi_n = \Psi_n^0 + \sum \frac{H_n'}{E_n - E_j} \Psi_j^{(0)}
$$

1st order

$$
E_n = E_n^{(0)} + H_n'
$$

and now we see what it means for $H'$ to be small. The expansion coeff's in $\Psi_n$ must be small which means the $H'$ matrix elements must be small compared to the corresponding unperturbed energy levels:

$$
|H_n'| \ll |E_n^{(0)} - E_j^{(0)}|
$$

and from $E_n$, the diagonal elements of $H'$ must be small compared to the unperturbed energies:

$$
|H_{nn}'| \ll E_n^{(0)}
$$
Now let's move on to the 2nd order solution.

To find it, we need to look at the $x^2$ term on p. 94: we must have the term multiplying $x^2$ be equal to zero, so putting all the $(p^{(2)})$ terms on the LHS we have

\[(\hat{H}_0^2 - E_n^{(1)}) \psi^{(2)}_n = (E_n^{(1)} - \hat{H}) \psi^{(1)}_n + E_n^{(2)} \psi^{(0)}_n\]

We know these now.

As we did above, let's expand $\psi^{(2)}_n$ in the $\hat{H}_0$ eigenstates:

\[\psi^{(2)}_n = \sum_i d_{ni} \psi^{(0)}_i\]

(We won't substitute for $E_n^{(1)} + \psi^{(1)}_n$ just yet.)

we get

\[(\hat{H}_0^2 - E_n^{(0)}) \sum_i d_{ni} \psi^{(0)}_i = (E_n^{(1)} - \hat{H}) \psi^{(1)}_n + E_n^{(2)} \psi^{(0)}_n\]

or

\[\sum_i (E_i^{(0)} - E_n^{(0)}) d_{ni} \psi^{(0)}_i = E_n^{(1)} \psi^{(1)}_n - \hat{H} \psi^{(1)}_n + E_n^{(2)} \psi^{(0)}_n\]

Taking the inner product with $\psi^{(0)}_j$, we get

\[(E_i^{(0)} - E_n^{(0)}) d_{nj} = E_n^{(1)} \langle \psi^{(0)}_j | \psi^{(1)}_n \rangle - \langle \psi^{(0)}_j | \hat{H} | \psi^{(1)}_n \rangle + E_n^{(2)} \delta_{nj}\]

\[(\star)\]
We can find $E_n^{(2)}$ by noting that the LHS cancels when $n=j$, so setting $n=j$ we have

$$E_n^{(2)} = \langle \Psi_n^{(0)} | H' | \Psi_n^{(0)} \rangle - E_n^{(1)} \langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle$$

and substituting (see p. 9.7)

$$\Psi_n^{(1)} = \sum_{i+n} \frac{H_{in}^{\dagger}}{E_n^{(0)} - E_i} \Psi_i^{(0)}$$

$$= \sum_{i+n} \frac{H_{in}^{\dagger}}{E_n^{(0)} - E_i} \langle \Psi_n^{(0)} | H^\dagger | \Psi_i^{(0)} \rangle$$

and noting that $H'$ must be Hermitian so that

$$H_{in} = (H_{ni})^*$$

$$= \sum_{i+n} \left| H_{ni} \right|^2 \frac{1}{E_n^{(0)} - E_i}$$

Now going back to (5) at the bottom of p. 9.9, we don't need to substitute this expression for $E_n^{(2)}$ to find the 1n1j. We'll take n!=j because recall that $\langle \Psi_n^{(0)} | \Psi_n^{(0)} \rangle = 0$ for all i (p. 9.5-9.6) so $\text{d}nn = 0$.

We'll substitute for $E_n^{(1)}$ in terms of the zero-order quantities.
So the spin becomes \( E_n^{(1)} \)

\[
(E_j^{(0)} - E_n^{(0)}) d_{nj} = H_{nn} \sum_{k \neq n} \frac{H_{kn}}{E_n^{(0)} - E_k^{(0)}} <\psi_j^{(0)} | H | \psi_k^{(0)}>
- \sum_{k \neq n} \frac{H_{kn}^{'}}{E_n^{(0)} - E_k^{(0)}} <\psi_j^{(0)} | H' | \psi_k^{(0)}>
+ \frac{H_{jn}^{'}}{\left(E_n^{(0)} - E_j^{(0)}\right)^2}
\]

and dividing by \((E_n^{(0)} - E_j^{(0)})\) (watch sign!)

\[
d_{nj} = \frac{1}{E_n^{(0)} - E_j^{(0)}} \sum_{k \neq n} \frac{H_{kn}^{'}}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \neq n} \frac{H_{kn}^{'}}{E_k^{(0)} - E_j^{(0)}}
- \frac{H_{jn}^{'}}{\left(E_n^{(0)} - E_j^{(0)}\right)^2}
\]

So combining all orders through 2nd, we have

\[
E_n = E_n^{(0)} + H_{nn}^{(1)} + \sum_{i \neq n} \frac{|H_{ni}^{(1)}|^2}{E_i^{(0)} - E_n^{(0)}}
\]

\[
\psi_n = \psi_n^{(0)} + \sum_{i \neq n} \left[ \frac{H_{in}^{(1)}}{E_n^{(0)} - E_i^{(0)}} - \frac{H_{nn}^{(1)} H_{in}^{(1)}}{\left(E_n^{(0)} - E_i^{(0)}\right)^2} \right] \psi_i^{(0)}
+ \sum_{k \neq n} \frac{H_{kn}^{(1)} H_{kn}^{(1)}}{\left(E_n^{(0)} - E_k^{(0)}\right) \left(E_n^{(0)} - E_k^{(0)}\right)} \psi_i^{(0)}
\]
As you can see, things get pretty complicated pretty quickly, and it gets worse with each higher order. (The same problem plagues perturbative expansions in particle physics.)

So we'll stop here, and do an example.

**EX.**

Find the ground state energy for the 1-D potential energy

\[ V(x) = \begin{cases} \frac{g}{2} x & 0 \leq x \leq a \\ \infty & x < 0, x > a \end{cases} \]

This looks like a particle in a box plus a perturbing Hamiltonian \( H' = g x \). The unperturbed \( H_0 \) is

\[ H_0 = \frac{p^2}{2m} + V \quad \text{with} \quad V = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & x < 0, x > a \end{cases} \]

and the unperturbed eigenstates and energies are

\[ \phi_n^{(0)} = \sqrt{\frac{2}{a}} \sin \frac{n \pi x}{a}, \quad E_n^{(0)} = \frac{k^2 \pi^2 n^2}{2ma^2} \quad n = 1, 3, 5, \ldots \]
The 1st order correction to each of the energies is

\[ E_n^{(1)} = H_{nn} = \sum_0^\infty Y_n^{(0)} x Y_n^{(0)} \]  
\[ = g \frac{2}{a} \int_0^a x^2 \sin^2 \frac{n\pi x}{a} \ dx \]
\[ = \frac{g a^2}{4} \]

\[ = \frac{g a}{2} \]

Same for all energy levels (and note that it has units of energy). For perturbation theory to be applicable, we must have

\[ H_{nn} \ll |E_n^{(0)} - E_j^{(0)}| \]

and since \( E_j^{(0)} \) is the lowest energy, this translates to

\[ \frac{g a}{2} \ll \frac{\pi^2 \hbar^2}{2ma^2} \quad \text{or} \quad g \ll \frac{\pi^2 \hbar^2}{ma^3} = \frac{E_j^{(0)}}{a/2} \]

Now for the 2nd order correction, we have

\[ E_i^{(2)} = \frac{1}{i+1} \frac{H_{ii}^2}{E_{i+1}^{(0)} - E_i^{(0)}} \]

So we need the matrix elements \( H_{ii} \)
\[ H'_i = \frac{2g\alpha}{\pi} \int_0^\theta x \sin \frac{\pi x}{a} \sin \frac{i\pi x}{a} \, dx \]

\[
= \begin{cases} 
 0 & \text{if } i \text{ is odd} \\
 -\frac{8ga}{\pi^2} \frac{M}{(M^2-1)^2} & \text{if } M \text{ is even}
\end{cases}
\]

Now we also need \( E^{(o)}_i - E^{(o)}_L = \frac{\pi^2 h^2}{2ma^2} (1 - i^2) \)

So combining,

\[
E^{(2)}_i = \sum_{\text{even } i > 0} \left[ \frac{\frac{8ga}{\pi^2} \frac{M}{(M^2-1)^2}}{\left( \frac{\pi^2 h^2}{2ma^2} \right) (1 - i^2)} \right] E^{(o)}_{1} \]

\[
E^{(2)}_i \bigg|_{\text{even } i > 0} = -\left( \frac{8ga}{\pi} \frac{1}{E^{(o)}_1} \right) \sum_{\text{even } i > 0} \frac{i^2}{(i^2 - 1)^5}
\]

This is an infinite series, but it converges pretty quickly: the sum is 0.016483 and the i=2 and i=4 terms give 0.016482

Combining everything, we get for the ground state energy
\[ E_1 = E_1^{(0)} \left[ 1 + \frac{g a}{2 E_1^{(0)}} - 0.01083 \left( \frac{g a}{E_1^{(0)}} \right)^2 \right] \]

to 2nd order

Notice that the expansion contains successively higher powers of the small parameter g.