THE PERTURBATION EXPANSION:

The basic idea of perturbation theory is that we adjust the energies and wavefunctions for an exactly known system by adding a small modification to the Hamiltonian. So we write the Hamiltonian as $\hat{H}=\hat{H}^0+\hat{W}$, where $\hat{H}^0$ is the Hamiltonian of the known system, and $\hat{W}$ is our perturbation.

In order to keep track of the number of times the perturbation enters our expansion, we introduce the parameter λ (which will later be set to one). So $\hat{H}=\hat{H}^0+\lambda\hat{W}$, and we assume the expansions of the exact wavefunctions and energies in terms of the perturbation parameter λ:

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \lambda^2|\psi_n^2\rangle + \cdots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

Now, expanding $H|\psi_n\rangle = E_n|\psi_n\rangle$ to second order in the perturbation:

$$(\hat{H}^0+\lambda\hat{W})(|\psi_n^0\rangle+\lambda|\psi_n^1\rangle+\lambda^2|\psi_n^2\rangle) = (E_n^0+\lambda E_n^1+\lambda^2E_n^2)(|\psi_n^0\rangle+\lambda|\psi_n^1\rangle+\lambda^2|\psi_n^2\rangle)$$

$$\hat{H}^0|\psi_n^0\rangle+\lambda\hat{H}^0|\psi_n^1\rangle+\lambda^2\hat{H}^0|\psi_n^2\rangle+\lambda\hat{W}|\psi_n^0\rangle+\lambda^2\hat{W}|\psi_n^1\rangle+\lambda^3\hat{W}|\psi_n^2\rangle$$

$$= E_n^0|\psi_n^0\rangle+\lambda E_n^0|\psi_n^1\rangle+\lambda^2E_n^0|\psi_n^2\rangle+\lambda E_n^1|\psi_n^0\rangle+\lambda^2E_n^1|\psi_n^1\rangle+\lambda^3E_n^1|\psi_n^2\rangle$$
$$+\lambda^2E_n^2|\psi_n^0\rangle+\lambda^3E_n^2|\psi_n^1\rangle+\lambda^4E_n^2|\psi_n^2\rangle$$

Collecting according to the order of the perturbation parameter, and ramping it up to 1:

λ^0: $\hat{H}_0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$

λ^1: $\hat{H}_0|\psi_n^1\rangle+\hat{W}|\psi_n^0\rangle = E_n^0|\psi_n^1\rangle + E_n^1|\psi_n^0\rangle$

λ^2: $\hat{H}_0|\psi_n^2\rangle+\hat{W}|\psi_n^1\rangle = E_n^0|\psi_n^2\rangle+E_n^1|\psi_n^1\rangle+E_n^2|\psi_n^0\rangle$

Higher orders of λ are incomplete, since we only took our expansion to second order.

The zeroth order term just gives us the Schrödinger equation for the unperturbed system

First-Order Perturbation Theory:

Correction to the Energy:

From the expression for the λ^1 equation:

$$\hat{H}^0|\psi_n^1\rangle + \hat{W}|\psi_n^0\rangle = E_n^1|\psi_n^0\rangle + E_n^0|\psi_n^1\rangle$$

We multiply on the left by the bra $\langle\psi_n^0|$:

$$\langle\psi_n^0|\hat{H}^0|\psi_n^1\rangle + \langle\psi_n^0|\hat{W}|\psi_n^0\rangle = \langle\psi_n^0|E_n^1|\psi_n^0\rangle + \langle\psi_n^0|E_n^0|\psi_n^1\rangle$$

$$E_n^0\langle\psi_n^0|\psi_n^1\rangle + \langle\psi_n^0|\hat{W}|\psi_n^0\rangle = E_n^1 + E_n^0\langle\psi_n^0|\psi_n^1\rangle$$

$$\boxed{E_n^1 = \langle\psi_n^0|\hat{W}|\psi_n^0\rangle}$$

That gives us the first order correction to the energy.

Correction to the Wavefunction:

We take the λ^1 expression, and rearrange it:

$$\hat{H}^0|\psi_n^1\rangle + \hat{W}|\psi_n^0\rangle = E_n^1|\psi_n^0\rangle + E_n^0|\psi_n^1\rangle$$

$$(\hat{H}^0 - E_n^0)|\psi_n^1\rangle = -(\hat{W} - E_n^1)|\psi_n^0\rangle$$

$$\sum_m (H^0 - E_n^0)|\psi_m^0\rangle\langle\psi_m|\psi_n^1\rangle = -(\hat{W} - E_n^1)|\psi_n^0\rangle$$

Now we note that if $m=n$, $(H^0 - E_n^0)$

$$\sum_{m\neq n} (H^0 - E_n^0)|\psi_m^0\rangle\langle\psi_m^0|\psi_n^1\rangle = -(\hat{W} - E_n^1)|\psi_n^0\rangle$$

Multiplying on the left by $\langle\psi_l^0|$:

$$\sum_{m\neq n} \langle\psi_l^0|H^0 - E_n^0|\psi_m^0\rangle\langle\psi_m^0|\psi_n^1\rangle = -\langle\psi_l^0|\hat{W}|\psi_n^0\rangle + \langle\psi_l^0|\psi_n^0\rangle E_n^1$$

$$\sum_{m\neq n} (E_l^0 - E_n^0)\langle\psi_l^0|\psi_m^0\rangle\langle\psi_m^0|\psi_n^1\rangle = -\langle\psi_l^0|\hat{W}|\psi_n^0\rangle + \langle\psi_l^0|\psi_n^0\rangle E_n^1$$

The delta function require $l=m$, but since $m\neq n$, $l\neq n$ as well:

$$(E_m^0 - E_n^0)\langle\psi_m^0|\psi_n^1\rangle = -\langle\psi_m^0|\hat{W}|\psi_n^0\rangle$$

$$\langle\psi_m^0|\psi_n^1\rangle = \langle\psi_m^0|\hat{W}|\psi_n^0\rangle / (E_n^0 - E_m^0)$$

Finally, since $|\psi_n^1\rangle = \sum_{m\neq n}\langle\psi_m^0|\psi_n^1\rangle|\psi_m^0\rangle$ from above, we obtain

$$\boxed{|\psi_n^1\rangle = \sum_{m\neq n} \frac{\langle\psi_m^0|\hat{W}|\psi_n^0\rangle}{E_n^0 - E_m^0}|\psi_m^0\rangle}$$

Second-Order Perturbation Theory

Will only worry about the corrections to the energies:

As before, we start with the second order equation:

$$\hat{H}_0|\psi_n^2\rangle + \hat{W}|\psi_n^1\rangle = E_n^0|\psi_n^2\rangle + E_n^1|\psi_n^1\rangle + E_n^2|\psi_n^0\rangle$$

and we multiply on the left by $\langle\psi_n^0|$:

$$\langle\psi_n^0|\hat{H}_0|\psi_n^2\rangle + \langle\psi_n^0|\hat{W}|\psi_n^1\rangle = \langle\psi_n^0|E_n^0|\psi_n^2\rangle + \langle\psi_n^0|E_n^1|\psi_n^1\rangle + \langle\psi_n^0|E_n^2|\psi_n^0\rangle$$

$$E_n^0\langle\psi_n^0|\psi_n^2\rangle + \langle\psi_n^0|W|\psi_n^1\rangle = E_n^0\langle\psi_n^0|\psi_n^2\rangle + E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2\langle\psi_n^0|\psi_n^0\rangle$$

$$\langle\psi_n^0|W|\psi_n^1\rangle = E_n^1\langle\psi_n^0|\psi_n^1\rangle + E_n^2$$

But we know from before that $\langle\psi_n^0|\psi_n^1\rangle = \sum_{m\neq n}\langle\psi_n^0|\psi_m^0\rangle\langle\psi_m^0|\psi_n^1\rangle = 0$, so that gives us

$$E_n^2 = \langle\psi_n^0|W|\psi_n^1\rangle = \langle\psi_n|W|\sum_{m\neq n}\frac{\langle\psi_m^0|W|\psi_n^0\rangle}{(E_n^0-E_m^0)}|\psi_m^0\rangle$$

$$= \sum_{m\neq n}\frac{\langle\psi_n^0|W|\psi_m^0\rangle\langle\psi_m^0|W|\psi_n^0\rangle}{E_n^0-E_m^0}$$

$$\boxed{E_n^2 = \sum_{m\neq n}\frac{|\langle\psi_m^0|W|\psi_n^0\rangle|^2}{E_n^0-E_m^0}}$$

And that's the expression for the second-order correction to the energy.

Degeneracies in Perturbation Theory

The basic problem of degenerate perturbation theory is the difficulty of choosing an appropriate basis for the perturbation expansion when some of the unperturbed kets have the same energy. The perturbation will have the effect of breaking the degeneracy — the degenerate states will be split.

Mathematically, this is a question of matrix representation. In the unperturbed case, any basis for the degenerate subspace is satisfactory. However, upon application of the perturbation, a specific basis emerges which diagonalizes the matrix. The challenge is that we don't know a priori what that basis will be for a perturbation.

In practice, the procedure we use to deal with degeneracies is as follows:

① Identify the degenerate subspace and construct the perturbation matrix in that subspace

② Diagonalize that matrix

③ The eigenvalues are the energy shifts

TIME DEPENDENT PERTURBATION THEORY

We approach time dependent perturbation theory by splitting our Hamiltonian $\hat{H}$ into an exactly solvable time-independent part $\hat{H}^0$ and a time-dependent perturbation $W(t)$. Before getting to the perturbative treatment, however, we'll need to look a little more closely at the time dependent Schrödinger equation.

THE TIME DEPENDENT SCHRÖDINGER EQUATION:

With the perturbation as discussed above, we write the time-dependent Schrödinger equation:

$$i\hbar \frac{d}{dt}|\Psi(t)\rangle = \left(H^0 + W(t)\right)|\Psi(t)\rangle$$

$$i\hbar \sum_n \frac{d}{dt}\langle \phi_n|\Psi(t)\rangle|\phi_n\rangle = \sum_n \left(E_n \langle\phi_n|\Psi(t)\rangle + \langle\phi_n|W(t)|\Psi(t)\rangle\right)|\phi_n\rangle$$

$$= \sum_n \left(E_n \langle\phi|\Psi(t)\rangle + \sum_k \langle\phi_n|W(t)|\phi_k\rangle\langle\phi_k|\Psi(t)\rangle\right)|\phi_n\rangle$$

Defining $c_n(t) \equiv \langle\phi_n|\Psi(t)\rangle$ and $W_{nk}(t) \equiv \langle\phi_n|W(t)|\phi_k\rangle$, this gives us

$$i\hbar \sum_n \dot{c}_n(t)|\phi_n\rangle = \sum_n \left(E_n c_n(t) + \sum_k W_{nk}(t)\, c_k(t)\right)|\phi_n\rangle$$

Since all the $|\phi_n\rangle$ are linearly independent, we separate the sum over n into different equations:

$$i\hbar\, \dot{c}_n(t) = E_n c_n(t) + \sum_k W_{nk}(t)\, c_k(t)$$

THE INTERACTION PICTURE:

Now that we have that version of the Schrödinger equation, we introduce the interaction picture of time evolution. It's less physically meaningful that the Heisenberg or Schrödinger pictures, and makes a sort of compromise between the two: the time evolution of the unperturbed states is handled in a Schrödinger-like way, while the rest of the time evolution is left in the perturbation operator. Mathematically, we "pull out" the Schrödinger part of the time evolution by defining $b_n(t)$ from the time-dependent coefficient $c_n(t)$:

$$c_n(t) = b_n(t) e^{-iE_n t/\hbar}$$

Substituting that back into the version of the time dependent Schrödinger equation from the previous section:

$$i\hbar \dot{b}_n(t) e^{-iE_n t/\hbar} + E_n b_n(t) e^{-iE_n t/\hbar} = E_n b_n(t) + \sum_k W_{nk}(t) b_k(t) e^{-iE_k t/\hbar}$$

$$i\hbar \dot{b}_n(t) e^{-iE_n t/\hbar} = \sum_k W_{nk}(t) b_k(t) e^{-iE_k t/\hbar}$$

$$i\hbar \dot{b}_n(t) = \sum_k W_{nk}(t) b_k(t) e^{-i(E_k - E_n)t/\hbar}$$

Now we define the Bohr frequency $\omega_{nk} = (E_n - E_k)/\hbar$:

$$i\hbar \dot{b}_n(t) = \sum_k W_{nk}(t) b_k(t) e^{i\omega_{nk} t}$$

This is the equation we'll actually solve with perturbation theory. Up until now, everything is actually exact quantum dynamics — no approximations have been introduced.

It is also in this last equation that we see the point of the interaction picture: the time evolution of the perturbed state, with the $b_n(t)$ coefficients, is only dependent on the time dependent on the time dependent perturbation, not on the unperturbed energy term. This comes about by choosing $b_n(t)$ such that the differentiation product rule makes the unperturbed energy term fall out.

Time Dependent Perturbation Expansion:

As with time independent perturbation theory, we introduce the perturbation parameter λ, so the Hamiltonian becomes $H^0 + \lambda W$ and we expand the coefficient $b_n(t)$ as we did previously for the wavefunction:

$$b_n(t) = b_n^{(0)}(t) + \lambda b_n^{(1)}(t) + \lambda^2 b_n^{(2)}(t) + \dots$$

The equation from the previous section becomes

$$i\hbar \left(\dot{b}_n^{(0)}(t) + \lambda \dot{b}_n^{(1)}(t) + \lambda^2 \dot{b}_n^{(2)}(t) \right) = \sum_k e^{i\omega_{nk}t} W_{nk}(t)\, \lambda \left(b_n^{(0)}(t) + \lambda b_n^{(1)}(t) + \lambda^2 b_n^{(2)}(t) \right)$$

Grouping by powers of λ, we find

$$\lambda^0: \quad i\hbar\, \dot{b}_n^{(0)}(t) = 0$$

$$\lambda^1: \quad i\hbar\, \dot{b}_n^{(1)}(t) = \sum_k e^{i\omega_{nk}t} W_{nk}(t)\, b_n^{(0)}(t)$$

$$\lambda^2: \quad i\hbar\, \dot{b}_n^{(2)}(t) = \sum_k e^{i\omega_{nk}t} W_{nk}(t)\, b_n^{(1)}(t)$$

In fact, for any $\quad > 0$, we have

$$\lambda^j \quad i\hbar\, \dot{b}_n^{(j)} = \sum_k e^{i\omega_{nk}t} W_{nk}(t)\, b_n^{(j-1)}(t)$$

Solving Time Dependent Perturbation Theory

From the above, we see that each order of time dependent perturbation theory requires the order before it. So we start with λ^0: If $\dot{b}_n^{(0)}(t) = 0$, then we know that $b_n^{(0)}(t)$ must be constant. Supposing we start in state $|\phi_i\rangle$ at time $t=0$, then the overlap with state n (for which b_n is a coefficient) is δ_{ni}.

With $b_k^{(0)} = \delta_{ki}$, we start to calculate the first-order correction:

$$i\hbar\, \dot{b}_n^{(1)}(t) = \sum_k e^{i\omega_{nk}t} W_{nk}(t)\, \delta_{ki} = e^{i\omega_{ni}t} W_{ni}(t)$$

$$d b_n^{(1)} = dt \left(\frac{-i}{\hbar}\right) e^{i\omega_{ni}t} W_{ni}(t)$$

$$b_n^{(1)} = \frac{-i}{\hbar} \int_0^t dt'\, e^{i\omega_{ni}t'} W_{ni}(t')$$

Now to use that expression for the first order to solve the second order correction

$$\dot{b}_n^{(2)} = \frac{-i}{\hbar}\sum_k e^{i\omega_{nk}t} W_{nk}(t)\, b_k^{(1)}(t)$$

$$= \left(\frac{-i}{\hbar}\right)^2 \sum_k e^{i\omega_{nk}t} W_{nk}(t) \int_0^t dt'' e^{i\omega_{ki}t''} W_{ki}(t'')$$

$$d b_n^{(2)} = \left(\frac{-i}{\hbar}\right)^2 dt' \sum_k e^{i\omega_{nk}t'} W_{nk}(t') \int_0^{t'} dt'' e^{i\omega_{ki}t''} W_{ki}(t'')$$

$$b_n^{(2)} = \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt' \sum_k e^{i\omega_{nk}t'} W_{nk}(t') \int_0^{t'} dt'' e^{i\omega_{ki}t''} W_{ki}(t'')$$