Perturbation Theory with Degeneracy PhL 1.3.09

symbol grab area: $\mathcal{H}^{(m)}$ $\mathcal{H}^{\perp}$ $\mathcal{H}^{(m)} \oplus \mathcal{H}^{\perp}$ $u_{mi} \in \mathcal{H}^{(m)}$

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Degenerate Case (Schiff page 248)

I really want to "start all over" here (in the case with degeneracy) and assume nothing can be reused until it is verified. And I might as well assume some arbitrary degeneracy count N and do this all at once. But first, consider this example.

1. An Example. Suppose we have a system of two electrons that form S=0 and S=1 states, and our perturbation is a mag field. We know that the states $|1,\pm1\rangle$ will be pulled away from the other two states which remain where they were since they have $m_s = 0$. At least I think that is what will happen in first order. But this illustrates the idea that when the perturbation is turned on, the symmetry of the original H_o is broken to some extent, and certain linear combinations of states that were degenerate will prove to "hold together" and move apart from the original energy, and will be eigenstates of the perturbed Hamiltonian. So a new issue here is that you have to get the *right* linear combinations somehow so that

things are continuous as $\lambda \to 0$, just as Schiff says. [What Schiff does not seem to say but maybe I missed it is that these right linear combinations are those that diagonalize H' in the m subspace.]

2. Notation and Hilbert Spaces. This is the big problem here! If you have too much notation, you get bogged down with lots of extra symbols which conceal the simplicity of things. If you have too little, you get confused as well.

So let's start with some unperturbed states u_k which span a Hilbert Space $\mathcal{H}$. We then want to consider a subset of these states which are degenerate with energy E_m. These states span a subspace I will call $\mathcal{H}^{(m)}$. So we can write $\mathcal{H} = \mathcal{H}^{(m)} \oplus \mathcal{H}^{\perp}$ where $\mathcal{H}^{\perp}$ is just the rest of the Hilbert Space $\mathcal{H}$. It is perpendicular to $\mathcal{H}^{(m)}$ because if you pick any state in $\mathcal{H}^{(m)}$ and any state in $\mathcal{H}^{\perp}$, their inner product will be 0. I will denote states in the $\mathcal{H}^{(m)}$ subspace by the notation u_{mi} where i = 1,2...N. In fact, these u_{mi} will be assumed to span the subspace which we assume is of dimension N. States in $\mathcal{H}^{\perp}$ will just be u_k with a single subscript. There may be other subspaces within $\mathcal{H}^{\perp}$ but our effort here concerns doing perturbation theory on the states (and their energies) in a particular subspace we call $\mathcal{H}^{(m)}$.

Note added 1.19.09: This space $\mathcal{H}^{(m)}$ is one of the eigenmanifolds of a finite-dimensional complex symmetric linear operator H, a subject treated in Stakgold. His spectral theorem on page 160 formalizes the notion that each eigenvalue really does inhabit a subspace which he calls a linear manifold, and he talks about a projection theorem which says the space is partitioned into these manifolds and you can use the projection operators P_i to do manipulations. This is what Messiah does in his resolvent section.

3. Most General Expansion for ψ_{mi}.

Now, when we first "set out" to construct our perturbation theory, we write this most general possibility for how the degenerate state u_{mi} moves into state ψ_{mi} when the perturbation is turned on, where i is a degeneracy label,

$$\psi_{mi} = u_{mi} + \Sigma_{j=1,N} B_{ij} u_{mj} + \Sigma_{k \neq m} B_{ik} u_k$$

This says that when we turn on our perturbation (by gradually increasing λ from λ=0), various B coefficients will appear as shown above and our original eigenstate u_{mi} acquires corrections. The summation $\Sigma_{k \neq m}$ excludes all states in the subspace $\mathcal{H}^{(m)}$. We assume that we acquire corrections from both $\mathcal{H}^{(m)}$ states and from $\mathcal{H}^{\perp}$ states.

4. Perturbation theory set up. Our first need is to develop a "degeneracy version" of 31.4. So:

$$H_o u_{mi} = E_m u_{mi} \qquad u_{mi} \in \mathcal{H}^{(m)}$$

$$H_o u_k = E_k u_k \qquad u_k \in \mathcal{H}^{\perp}$$

$$(H_o + \lambda H')\psi_{mi} = W_{mi} \psi_{mi}$$

$$W_{mi} = \Sigma_{n=0} \lambda^n W_{mi,n} \qquad W_{mi,0} = E_m$$

$$\psi_{mi} = \Sigma_{n=0} \lambda^n \psi_{mi,n} \qquad \psi_{mi,0} = u_{mi}$$

If we now insert these λ expansions into the SE and do what we did in the Schiff Chapter 8 notes, we get this result. Nothing really is different, we have the extra label "m" stuck to everything.

$$(H_0 - E_m)\,\psi_{mi,s} = (W_{mi,1} - H')\,\psi_{mi,s-1} + \Sigma_{j=2,3..s}\, W_{mi,j}\,\psi_{mi,s-j} \qquad s = 1,2,3...$$

and now I will write them out: // this is the **new 31.4**

$$(H_0 - E_m)\,\psi_{mi,0} = 0 \qquad s = 0$$
$$(H_0 - E_m)\,\psi_{mi,1} = (W_{mi,1} - H')\,\psi_{mi,0} \qquad s = 1$$
$$(H_0 - E_m)\,\psi_{mi,2} = (W_{mi,1} - H')\,\psi_{mi,1} + W_{mi,2}\,\psi_{mi,0} \qquad s = 2$$
$$(H_0 - E_m)\,\psi_{mi,3} = (W_{mi,1} - H')\,\psi_{mi,2} + W_{mi,2}\,\psi_{mi,1} + W_{mi,3}\,\psi_{mi,0} \qquad s = 3$$

Basically I have replaced the former superscript (m) with a subscript mi. These are "the perturbation equations" upon which everything is based.

At this point in our development, we state and prove three "theorems":

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5. Theorem A: { u_{mi} must diagonalize H' in $\mathcal{H}^{(m)}$ }

Consider some eigenvalue problem $H_0 u_r = E_r u_r$ where the u_r span some Hilbert Space $\mathcal{H}$. Suppose $\mathcal{H}$ contains a degenerate subspace $\mathcal{H}^{(m)}$ of dimension N > 1, such that $\mathcal{H} = \mathcal{H}^{(m)} \oplus \mathcal{H}^{\perp}$, where $\mathcal{H}^{(m)}$ is spanned by an orthonormal subset of the u_r, which we call u_{mi}, such that $H_0 u_{mi} = E_m u_{mi}$ for i = 1,2....N (the m label just tells us the u_{mi} are u_k within $\mathcal{H}^{(m)}$). Suppose we want to do a perturbation theory analysis for the Hamiltonian $H = H_o + \lambda H'$ where λ is a smallness parameter. Theorem A says:

You cannot "do" a perturbation analysis on the states u_{mi} unless they diagonalize H' within $\mathcal{H}^{(m)}$.

We might be able to do perturbation analysis for states u_k outside $\mathcal{H}^{(m)}$, but not for states within $\mathcal{H}^{(m)}$. By "do a perturbation analysis on a state" we mean find how a state and its energy smoothly change from their λ=0 values of u_{mi} and E_m to some altered values which form a power series in λ.

Proof: This is a proof by contradiction. Assume that we *can* form a power series like so

$$\psi_{mi} = u_{mi} + \lambda\,\psi_{mi,1} + \lambda^2\,\psi_{mi,2} + \ldots. \qquad \psi_{mi,0} = u_{mi}$$

$$W_{mi} = E_m + \lambda\,W_{mi,1} + \lambda^2\,W_{mi,2} + \ldots. \qquad W_{mi,0} = E_m$$

and assume that H' is *not* diagonal within $\mathcal{H}^{(m)}$. When we insert the above expansions into the equation $(H_0+\lambda H')\psi_{mi} = W_{mi}\psi_{mi}$ and equate like powers of λ on both sides, we get a series of equations that Schiff calls 31.4 on page 245 (see above). In particular, the equation which equates λ^1 on both sides says this:

$(H_0 - E_m)\ \psi_{mi,1} = (W_{mi,1} - H')\ u_{mi}$

You can see clearly how these terms arise from $(H_0+\lambda H')\psi_{mi} = W_{mi}\psi_{mi}$. There are two terms from the LHS that are order λ, and there are two terms from the RHS that are order λ.

Suppose we close from the left with u_{mj} for $j \neq i$. We get $< u_{mj}| (H_0 - E_m) = 0$ acting to the left. Since the basis functions are orthogonal and $W_{mi,1}$ is just a number, we get only the H' term on the right. We thus find that:

$0 = <u_{mj} | H' | u_{mi}>$ for any $j \neq i$

But this says that H' must be diagonal, which contradicts our assumption. Thus, if the u_{mi} are selected in such a way that H' has off-diagonal elements, perturbation theory on u_{mi} is inconsistent. We must first find new basis functions v_{mi} which diagonalize H' within u_{mi}, and then we can do perturbation theory on these v_{mi}. On page 249 Schiff says that if you pick the wrong linear combinations in $\mathcal{H}^{(m)}$, the perturbation theory "breaks down". This theorem shows exactly how it breaks down.

[2.9.09. This bothered me a lot for a while, but resolved when I realized H' must be diagonal in the sense above if u_{mi} *are to satisfy* the perturbation equations (the EV problems derived from these equations). It is those equations that force it. If you pick some other v_{mi}, they don't satisfy the pert equations so you have to throw them out. You can *start* with some v_{mi}, but right away you arrive at *the level 1 diagonalization problem* $H'|\psi> = W_{mi,1}|\psi>$ and you have to find eigenfunctions and eigenvalues of this problem, which then leads to the diagonalizing $|\psi>= u_{mi}$.]

Notational detail: since $\mathcal{H} = \mathcal{H}^{(m)} \oplus \mathcal{H}^{\perp}$, we can decompose x in $\mathcal{H}$ as $x = x_1 + x_2$ etc. Below I keep writing $x = x_1 \oplus x_2$ as a reminder of this fact. I only use this when the thing on the left really is in $\mathcal{H}^{(m)}$ and the thing on the right is in $\mathcal{H}^{\perp}$. This notation is not official of course.

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6. Theorem B: { show 31.6: $<u_{mi}| \psi_{mi,n}> = 0$ for n > 0) } ("the normalization condition")

That is to say, it is possible to normalize ψ_{mi} such that $<u_{mi}| \psi_{mi,n}> = 0$ for $n > 0$. (This is our degeneracy version of Schiff **31.6** on page 246.)

Proof. Consider the most general change that can happen to ψ_{mi} as it leaves u_{mi}, noted above:

$\psi_{mi} = \{ u_{mi} + \Sigma_j B_{ij}\ u_{mj} \} \oplus \Sigma_{k\neq m} B_{ik}\ u_k$ $\psi_{mi} \in \mathcal{H}^{(m)} \oplus \mathcal{H}^{\perp}$

where the B_{rs} depend in some complicated way on H'. If we set H' = 0, all $B_{rs} = 0$. [the B_{rs} likely also depend on H_0 when $H' \neq 0$, I am not sure because I have never tried to make the connection.]

[Note added 1.29.09. Later in Messiah and below we get results like this

$C_{n'} = (V_{nn} - V_{n'n'})^{-1} \Sigma_{k \in \mathcal{E}oa\perp} V_{n'k} \ (E_a^0 - E_k)^{-1} V_{kn}$

for the B_{ij} type coefficients at level 1. They "depend on H_0" because all states here are eigenstates of H_0 and of course the energies are all eigenenergies of H_0]

We are showing things to all orders of the power series λ, and we are allowing that ψ_{mi} might leave u_{mi} in every "direction" at the same time as λ leaves the value 0. You cannot get more general that that because the u_r span the Hilbert Space $\mathcal{H}$. Now break out the u_{mi} term in the first sum so we have

$$\psi_{mi} = \{ u_{mi} + B_{ii}u_{mi} + \Sigma_{j\neq i}B_{ij}\ u_{mj} \} \oplus \Sigma_{k\neq m} B_{ik}\, u_k$$

$$= \{ (1 + B_{ii})\, u_{mi} + \Sigma_{j\neq i}B_{ij}\ u_{mj} \} \oplus \Sigma_{k\neq m} B_{ik}\, u_k$$

Then renormalize ψ into $\psi'_{mi} = \psi_{mi}/(1 + B_{ii})$ and define $B'_{rs} = B_{rs}/(1 + B_{ii})$ to get

$$\psi'_{mi} = \{ u_{mi} + \Sigma_{j\neq i}B'_{ij}\ u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik}\, u_k$$

We know that $\psi'_{mi,0} = u_{mi}$. For any higher order component we have

$$\psi'_{mi,n} = \{ \Sigma_{j\neq i}B'_{ij,n}\ u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,n}\, u_k \qquad n > 0$$

where we imagine expanding the B' just as we expand ψ' or W. Then we have

$$\langle u_{mi} | \psi'_{mi,n} \rangle = 0 \qquad n>0 \qquad \textbf{which is 31.6}$$

because $\langle u_{mi}|$ is orthogonal to all the states on the RHS. This object $\psi'_{mi,n}$ is the function we use in our perturbation theory and we **drop the prime**. Since B_{ii} is fully determined by H' (and H_0) [u_{mi} is presumed normalized] the normalization of ψ'_{mi} is fixed by the above choice, and we cannot then also require that $\langle \psi'_{mi} | \psi'_{mi} \rangle = 1$. This will in general not be true for the way we have defined ψ'_{mi}. When we are all finished with our problem, we can then adjust the normalization of ψ'_{mi} to get unity.

So the expansion we shall be using is this:

$\psi_{mi} = \{ u_{mi} + \Sigma_{j\neq i}B'_{ij}\ u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik}\, u_k$ // all orders of λ at once

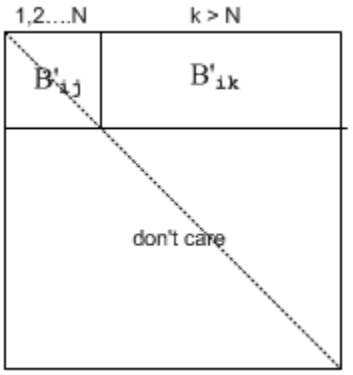
$\psi_{mi,n} = \{ \Sigma_{j\neq i}B'_{ij,n}\ u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,n}\, u_k$ // n > 0

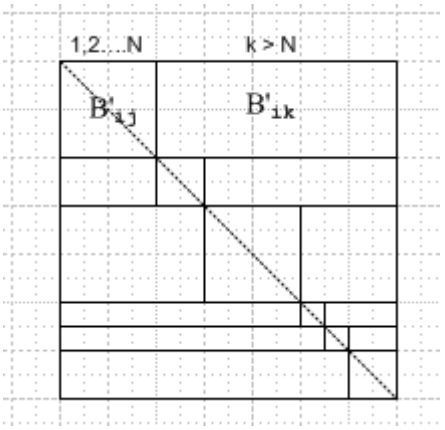
Notice that there are two distinct portions of the matrix B'_{rs} .

One portion applies within the $\mathcal{H}^{(m)}$ subspace. Here, B'_{ij} is an NxN matrix. The diagonal elements of this matrix never enter our theory due to the $\Sigma_{j\neq i}$ and the way we normalized ψ_{mi}, so if we want, we can just set $B'_{ii} = 0$. So, this inner B matrix is completely off-diagonal inside $\mathcal{H}^{(m)}$.

The other portion appearing as B'_{ik} has the first index in $\mathcal{H}^{(m)}$ and the second in $\mathcal{H}^{\perp}$.

Here are some pictures showing various parts of our B matrix. If we are only INTERESTED in doing perturbation theory on states within $\mathcal{H}^{(m)}$, then the part of the matrix marked "don't care" is never used.





But on the right we show the larger picture where there might be multiple degenerate blocks. We have shown a few singleton blocks here where "non degenerate" perturbation theory could be used. In general, you think one strip of the B matrix at a time.

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7. Theorem C: { Show 31.7: $W_{mi,s} = \langle u_{mi} | H' | \psi_{mi,s-1} \rangle$ }

(Ie, the degeneracy version of 31.7 Schiff p 246). This says that if you know the wave function to some order, you can compute the energy correction of the next higher order.

Proof: When we expand the full SE in ψ and match powers, we get this result:

$$(H_0 - E_m)\,\psi_{mi,s} = (W_{mi,1} - H')\,\psi_{mi,s-1} + \Sigma_{j=2,3..s}\, W_{mi,j}\,\psi_{mi,s-j} \qquad s = 1,2,3...$$

which we can rewrite like so

$$(H_0 - E_m)\,\psi_{mi,s} = -H'\,\psi_{mi,s-1} + \Sigma_{j=1,2,3..s}\, W_{mi,j}\,\psi_{mi,s-j} \qquad s = 1,2,3...$$

If we close from the left with u_{mi}, the LHS = 0 due to the left action of $(H_0 - E_m)$. On the right we pick up a term from the H' term. What about all those other terms? The terms have this form (last factor)

$$\psi_{mi,s-1} \quad \psi_{mi,s-2} \quad \psi_{mi,s-3} \quad \cdots \quad \psi_{mi,1} \quad \psi_{mi,0} = u_{mi}$$

From Theorem B we claim that

$$\langle u_{mi} | \psi_{mi,n} \rangle = 0 \qquad n>0$$

All the factors shown have n>0 except that very last one which has n = 0. Thus, we pick up only this last term of all the terms in the second sum. That is the term with j = s, so we then have

$$0 = -\langle u_{mi} | H' | \psi_{mi,s-1} \rangle + W_{mi,s}$$ **QED**

Comment: What happens if we close from the left with some $u_{m\ell}$ with $\ell \neq i$? We would get

$$0 = -\langle u_{m\ell}| H' | \psi_{mi,s-1}\rangle + W_{mi,s}\langle u_{m\ell} | u_{mi}\rangle + \Sigma_{j=1,2,3..s-1} W_{mi,j}\langle u_{m\ell} |\psi_{mi,s-j}\rangle$$

$$\Rightarrow \quad \langle u_{m\ell}| H' | \psi_{mi,s-1}\rangle = \Sigma_{j=1,2,3..s-1} W_{mi,j}\langle u_{m\ell} |\psi_{mi,s-j}\rangle \qquad \ell \neq i$$

But now we know nothing about $\langle u_{m\ell} |\psi_{mi,s-j}\rangle$ for $\ell \neq i$ and in general all these factors will be non-zero and all we get is some kind of sum rule that is not very interesting.

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8. Finding the coefficients B'$_{ik,1}$

Apply new 31.7 with s = 1 to get

$$W_{mi,1} = \langle u_{mi} | H' | u_{mi} \rangle = \langle mi |H'|mi \rangle$$

which is now true for each state "i" in the subspace. We might have vanishing matrix elements for some i and not for others, as in our example at the start of this document.

Meanwhile, our 31.4 for s=1 says:

$$(H_0 - E_m)\, \psi_{mi,1} = (W_{mi,1} - H')\, \psi_{mi,0} \qquad s = 1$$

but from above we know that for order n = 1 we can write

$$\psi_{mi,1} = \{ \Sigma_{j\neq i} B'_{ij,1}\, u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,1}\, u_k$$

so the above says

$$(H_0 - E_m) [\{ \Sigma_{j\neq i} B'_{ij,1}\, u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,1}\, u_k] = (W_{mi,1} - H')u_{mi} \qquad (*)$$

Close (*) from the left with some $\langle u_{k'}|$ in $\mathcal{H}^{\perp}$. We know that H_0 acting to the left produces $E_{k'}\, u_{k'}$. So we then have

$$\langle u_{k'}| (E_{k'} - E_m) [\{ \Sigma_{j\neq i} B'_{ij,1} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{ik,1} |u_k\rangle] = \langle u_{k'}| (W_{mi,1} - H')|u_{mi} \rangle$$

$$\langle u_{k'}| (E_{k'} - E_m) [\Sigma_{k\neq m} B'_{ik,1} |u_k\rangle] = \langle u_{k'}| (W_{mi,1} - H')|u_{mi} \rangle$$

$$(E_{k'} - E_m)\, B'_{ik',1} = \langle u_{k'}| (W_{mi,1} - H')|u_{mi} \rangle$$

$$(E_{k'} - E_m)\, B'_{ik',1} = - \langle u_{k'}| H' |u_{mi} \rangle$$

$$(E_k - E_m)\, B'_{ik,1} = - \langle u_k| H' |u_{mi} \rangle$$

$$B'_{ik,1} = \langle u_k | H' | u_{mi} \rangle / (E_m - E_k)$$

Notice that if we close (*) from the left with some $\langle u_{mj}|$ in $\mathcal{H}^{(m)}$ the LHS = 0 and we then learn is this:

$$0 = \langle u_{mj}| (W_{mi,1} - H')|u_{mi} \rangle$$

If i = j, this duplicates our first order energy correction result. If i ≠ j, it duplicates our result that H' must be diagonal within $\mathcal{H}^{(m)}$.

9. Finding the coefficients B'$_{ij,1}$

What we are missing now is an expression for $B'_{ij,1}$ which are the correction coefficients *inside* $\mathcal{H}^{(m)}$. It seems to me that we need to learn what these are if we want to fully learn what $\psi_{mi,1}$ looks like. Schiff somehow dodges this question completely in his page 249-251 discussion.

How might we get "access" to the B'_{ij} coefficients? In the s=1 equation 31.4 access is *blocked* by the protective operator $(H_0 - E_m)$ on the left hand side, so closing with a state in $\mathcal{H}^{(m)}$ always gives 0. What if we look at the *next equation in the ladder of equations*,

$$(H_0 - E_m)\, \psi_{mi,2} = (W_{mi,1} - H')\, \psi_{mi,1} + W_{mi,2}\, \psi_{mi,0} \qquad (**) \qquad s = 2$$

$$\psi_{mi,1} = \{ \Sigma_{j\neq i} B'_{ij,1}\, u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,1}\, u_k$$

$$\psi_{mi,2} = \{ \Sigma_{j\neq i} B'_{ij,2}\, u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,2}\, u_k$$

Insert these things into (**) then close with $\langle u_{ms}|$ in $\mathcal{H}^{(m)}$. As usual, LHS = 0 due to the projection, but this just blocks our access to the $B'_{ij,2}$ coefficients, not the $B'_{ij,1}$ coefficients! We then get

$$0 = \langle u_{ms}| \; (W_{mi,1} - H') [\{ \Sigma_{j\neq i} B'_{ij,1} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{ik,1} |u_k\rangle] + \langle u_{ms}| W_{mi,2} |u_{mi}\rangle$$

On the RHS, let's first evaluate the $W_{mi,1}$ terms:

$$W_{mi,1} \langle u_{ms}| \; [\{ \Sigma_{j\neq i} B'_{ij,1} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{ik,1} |u_k\rangle] = W_{mi,1}\, B'_{is,1} (1 - \delta_{s,i})$$

because the second term gives nothing and, if s = i, the first term also gives nothing because the sum does not include the state $|u_{mi}\rangle$.

Here we have finally "accessed" a $B'_{is,1}$ coefficient. Next, let's look at the H' terms:

$$- \Sigma_{j\neq i} B'_{ij,1} \langle u_{ms}| H' |u_{mj}\rangle - \Sigma_{k\neq m} B'_{ik,1} \langle u_{ms}| H' |u_k\rangle$$

now we use the fact that $\langle u_{ms}| H' |u_{mj}\rangle = \delta_{s,j} \langle u_{ms}| H' |u_{ms}\rangle$ so the first term above becomes

$$- \Sigma_{j\neq i} B'_{ij,1}\, \delta_{s,j} \langle u_{ms}| H' |u_{ms}\rangle = - B'_{is,1} \langle u_{ms}| H' |u_{ms}\rangle \; (1 - \delta_{s,i})$$

Again, if s = i, then the j sum does not include s and we get no hit. So the total H' terms are

$$- B'_{is,1}\, W_{ms,1}\ (1 - \delta_{s,i}) \ - \ \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{ms}| H' |u_k\rangle$$

Now we can put back our pieces to get

$$0 = W_{mi,1}\, B'_{is,1}(1 - \delta_{s,i}) \ - B'_{is,1}\, W_{ms,1}\,(1 - \delta_{s,i}) \ - \ \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{ms}| H' |u_k\rangle \ + W_{mi,2}\, \delta_{s,i}$$

where the last term comes from $\langle u_{ms}| W_{mi,2} |u_{mi}\rangle$. We can rewrite this as:

$$B'_{is,1}(W_{ms,1} - W_{mi,1})\,(1 - \delta_{s,i}) = - \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{ms}| H' |u_k\rangle \ + W_{mi,2}\, \delta_{s,i} \qquad (***)$$

Small digression: But from our theorem above we know that

$$W_{mi,s} = \langle u_{mi}| H' | \psi_{mi,s-1}\rangle \quad \Rightarrow \quad W_{mi,2} = \langle u_{mi}| H' | \psi_{mi,1}\rangle$$

So this tells us that

$$W_{mi,2} = \langle u_{mi}| H' | [\{ \ \Sigma_{j\neq i} B'_{ij,1} \ |u_{mj}\rangle \ \} \oplus \ \Sigma_{k\neq m}\, B'_{ik,1} \, |u_k \rangle \,]$$

$$= \Sigma_{j\neq i} B'_{ij,1} \langle u_{mi}| H' | u_{mj}\rangle \ + \ \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{mi}| H' \ |u_k \rangle$$

$$= \Sigma_{j\neq i} B'_{ij,1}\, \delta_{i,j} \langle u_{mj}| H' | u_{mj}\rangle \ + \ \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{mi}| H' \ |u_k \rangle$$

$$= \ \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{mi}| H' \ |u_k \rangle \qquad (****)$$

The first term gives nada because the sum does not include j = i.

Noted added 1.29.09: The gray box above shows very nicely that the $W_{mi,2}$ energy corrections have *no dependence whatsoever* on the $B'_{ij,1}$ coefficients. That is why it is easy to compute $W_{mi,2}$. Above we already found that $B'_{ik,1} = \langle u_k| H' |u_{mi}\rangle / (E_m - E_k)$ so we can stuff this in to get a simple result for $W_{mi,2}$, see below The lack of dependence arises from $\Sigma_{j\neq i}\, H'_{ij} = \Sigma_{j\neq i}\, \delta_{i,j}\ H'_{ii} = 0$, ie, from the fact that we have pre-diagonalized (if you will) the states u_{mi}, and the fact that we have normalized things as in Theorem B above.

Now go back to our (***) equation above.

First, consider it in the case the $s \neq i$. We then get

$$B'_{is,1}(W_{ms,1} - W_{mi,1}) = - \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{ms}| H' |u_k\rangle$$

Second, consider it in the case the s = i, which gives

$$0 = - \Sigma_{k\neq m}\, B'_{ik,1} \langle u_{mi}| H' |u_k\rangle \ + W_{mi,2}$$

This seems to indicate that

$$W_{mi,2} = \Sigma_{k\neq m} B'_{ik,1} \langle u_{mi}| H' |u_k\rangle$$

Thus, we have *replicated* our digression calculation above for $W_{mi,2}$, which is a confidence booster. We can use our earlier result above for the $B'_{ik,1}$ to write this as

$$W_{mi,2} = \Sigma_{k\neq m} \langle u_{mi}| H' |u_k\rangle \langle u_k| H' |u_{mi}\rangle / (E_m - E_k)$$

which says that $W_{mi,2} \neq 0$ only if $|u_{mi}\rangle$ "communicates" to itself through the amplitude product shown.

Now the $s \neq i$ equation above was this:

$$B'_{is,1}(W_{ms,1} - W_{mi,1}) = -\Sigma_{k\neq m} B'_{ik,1} \langle u_{ms}| H' |u_k\rangle$$

So IF two $\mathcal{H}^{(m)}$ states pull apart in energy at first order (which is to say, H' when pre-diagonalized has different diagonal elements for s and i) , then we know that

$$B'_{is,1} = [\Sigma_{k\neq m} B'_{ik,1} \langle u_{ms}| H' |u_k\rangle] / (W_{mi,1} - W_{ms,1}) \qquad i \neq s \quad W_{mi,1} \neq W_{ms,1}$$

So we are making some progress here! This says that if $H'_{mi,mi} \neq H'_{ms,ms}$, then we have a formula for our desired coefficient $B'_{is,1}$! Recall, by the way, that earlier we found that

$$B'_{ik,1} = \langle u_k| H' |u_{mi}\rangle / (E_m - E_k) \qquad \text{for k in } \mathcal{H}^{\perp}$$

so we can rewrite the above as

$$B'_{is,1} = \Sigma_{k\neq m} \langle u_{ms}| H' |u_k\rangle\langle u_k| H' |u_{mi}\rangle / [(E_m - E_k)(W_{mi,1} - W_{ms,1})]$$

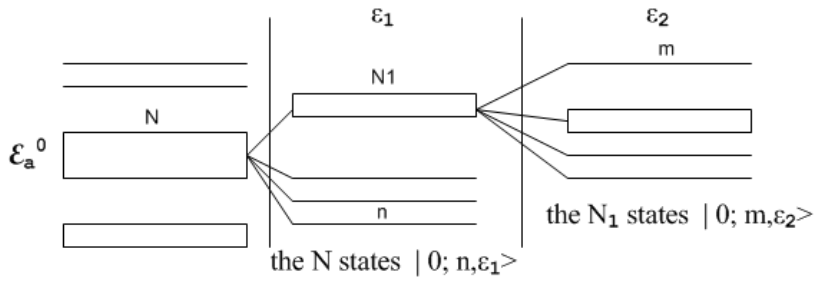
$$= (W_{mi,1} - W_{ms,1})^{-1} (H'Q_{0m}H')_{si} \qquad \text{for } i \neq s \text{ and } W_{mi,1} \neq W_{ms,1}$$

What does this tell us? It says to me this: if $|u_{mi}\rangle$ "communicates" with $|u_{ms}\rangle$ via the second order amplitude product shown (involving only intermediate states in $\mathcal{H}^{\perp}$), THEN both the states $|u_{mi}\rangle$ and $|u_{ms}\rangle$ have "corrections" within $\mathcal{H}^{(m)}$, and these are the first order correction coefficients.

Note added 1.30.09. Remember what we are doing here:

$$\psi_{mi,1} = \{ \Sigma_{j\neq i} B'_{ij,1} u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,1} u_k$$

We found the $B'_{ik,1}$ easily, and we then found the $B'_{ij,1}$ with more work when $i \neq j$. We can think of the state "i" as being singles state "n" in our later Messiah picture below, and the various j as listing the other states in the center column. So in the topology below, at least, we have our full answer for the level 1 coefficients.



10. Summary of this section on first-order degenerate perturbation theory:

• The u_k states must be selected such that H' is diagonal in $\mathcal{H}^{(m)}$ { "prediagonalization"} [You can choose not to do this, but then your first order of business is to solve the level 1 diagonalization problem to find the eigenenergies and states, and then "you have done it".]

• The first order energy corrections are simple: $W_{mi,1} = < u_i |H'| u_i > = H'_{ii}$
They are just the diagonal elements of H' in $\mathcal{H}^{(m)}$.
[the index "i" is always assumed to be in $\mathcal{H}^{(m)}$]

• Our general first-order expansion for the wave function is this, where $<u_{mi}| \psi_{mi,1} > = 0$:

$$\psi_{mi,1} = \{ \Sigma_{j\neq i} B'_{ij,1} u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,1} u_k$$

• We showed that the $\mathcal{H}^{\perp}$ coefficients are given by

$$B'_{ik,1} = <u_k| H' |u_{mi} >/ (E_m - E_k) = H'_{ki} / (E_m - E_k) \qquad k \text{ in } \mathcal{H}^{\perp}$$

[2.9.09: $B'_{ik,1} = <k| Q_{a0} V |0 > = <k|1>$ in Messiah p 689 notation.]

and we got this result from the s=1 equation closed on the left with a $u_{k'}$ state.

• In passing, we noted the *second order* energy correction for our states to be

$$W_{mi,2} = \Sigma_{k\neq m} B'_{ik,1} < u_{mi}| H' |u_k > = \Sigma_{k\neq m} <u_{mi}| H' |u_k> <u_k| H' |u_{mi} >/ (E_m - E_k)$$

$$= \Sigma_{k\neq m} B'_{ik,1} H'_{ik} = \Sigma_{k\neq m} H'_{ik} H'_{ki}/ (E_m - E_k) = \Sigma_{k\neq m} |H'_{ik}|^2 /(E_m - E_k)$$

[2.9.09: $\varepsilon_2 = <0|V|1> = <0|VQ_{a0}V|0>$ in Messiah p 700 equation F notation.]

and this comes from our "general formula" $W_{mi,2} = < u_{mi}| H' | \psi_{mi,1}>$. This is exactly the same result as obtained in the non-degenerate theory, except you don't sum over the $\mathcal{H}^{(m)}$ partners of u_{mi}. We saw how

the diagonality of H' in the u_{mi} basis, and our normalization convention, causes this $W_{mi,2}$ to not depend on the $B'_{ij,1}$ coefficients. So $W_{mi,2}$ depends on the coupling from the one state mi to the perp k states.

• We considered two states i and j within $\mathcal{H}^{(m)}$. If their first order energies are different, meaning that the two diagonal elements of H' are different, then we found that

$$B'_{ij,1} = [\Sigma_{k\neq m} B'_{ik,1}\langle u_{mj}| H' |u_k\rangle] /(W_{mi,1} - W_{mj,1}) \qquad i \neq j \quad W_{mi,1} \neq W_{mj,1}$$

$$= \Sigma_{k\neq m} \langle u_{mj}| H' |u_k\rangle\langle u_k| H' |u_{mi}\rangle / [(E_m - E_k)(W_{mi,1} - W_{mj,1})]$$

[2.9.09: Not sure how this relates to Messiah.]

However, if the two states i and j have the same first order energies, then we learn nothing about the $B'_{ij,1}$ at this level of computation. The above came from the s=2 equation.

So, this "first order" perturbation theory gives us

(1) the first order energy corrections $W_{mi,1}$

(2) the wave function corrections $B'_{ik,1}$ with k in $\mathcal{H}^{\perp}$

(3) the wave function corrections $B'_{ij,1}$ with j in $\mathcal{H}^{(m)}$ only if $W_{mi,1} \neq W_{mj,1}$

Summary of the Summary: The name of the game is to squeeze out all you can from each equation in the equation ladder 31.4. In the above the lowest equation s=1 was this

$$(H_0 - E_m)\,\psi_{mi,1} = (W_{mi,1} - H')\,\psi_{mi,0} \qquad s = 1$$

and from this equation we obtained two facts:

$$W_{mi,1} = \langle u_{mi}|\, H' \,|u_{mi}\rangle = H'_{ii} \qquad \text{// already known from "the general rule"}$$

$$B'_{ik,1} = \langle u_k| H' |u_{mi}\rangle / (E_m - E_k) = H'_{ki}/ (E_m - E_k) \qquad \text{// for k in } \mathcal{H}^{\perp}$$

We next examined the s=2 equation which was this:

$$(H_0 - E_m)\,\psi_{mi,2} = (W_{mi,1} - H')\,\psi_{mi,1} + W_{mi,2}\,\psi_{mi,0} \qquad s = 2$$

and from this equation we also obtained two facts:

$$W_{mi,2} = \Sigma_{k\neq m} B'_{ik,1} \langle u_{mi}| H' |u_k\rangle \qquad \text{// already known from the general rule}$$

$$B'_{is,1}(W_{ms,1} - W_{mi,1}) = -\Sigma_{k\neq m} B'_{ik,1}\langle u_{ms}| H' |u_k\rangle$$

and for $W_{mi,1} \neq W_{mj,1}$ this last result gave us

$$B'_{ij,1} = [\Sigma_{k\neq m} B'_{ik,1}\langle u_{mj}| H' |u_k\rangle] /(W_{mi,1} - W_{mj,1})$$

OK, let's now try to be a little more systematic.

Note added 1.30.09. Consider from above that

$$W_{mi,2} = \Sigma_{k\neq m} B'_{ik,1} \langle u_{mi}| H' |u_k\rangle = \Sigma_{k\neq m} B'_{ik,1} H'_{ik}$$

$$= \Sigma_{k\neq m} H'_{ki}/(E_m - E_k) H'_{ik} = \Sigma_{k\neq m} H'_{ik} (E_m - E_k)^{-1} H'_{ki} = (H'Q_{0m}H')_{ii}$$

This says that the second order energy corrections are the diagonal elements of operator $H'Q_{0m}H'$. I don't think this tells us that $H'Q_{0m}H'$ is a diagonal matrix in our "i" basis.

11. Systematic application of equations 31.4 (see summary a few pages below)

Here I want to try to compute the "general-n" equation 31.4 so I don't have to keep redoing things over and over again. This equation reads as follows:

$$(H_0 - E_m)\,\psi_{mi,n} = -H'\,\psi_{mi,n-1} + \Sigma_{t=1,n} W_{mi,t}\,\psi_{mi,n-t} \qquad n = 1,2,3...$$

Let's break off the very last sum term which has t = n:

$$(H_0 - E_m)\,\psi_{mi,n} = -H'\,\psi_{mi,n-1} + \Sigma_{t=1,n-1} W_{mi,t}\,\psi_{mi,n-t} + W_{mi,n}\,u_{mi}$$

If we restrict to n > 1, all wavefunctions shown will be at least first order, so we can use our general expansion which is this

$$\psi_{mi,s} = \Sigma_{j\neq i} B'_{ij,s}\,u_{mj} + \Sigma_{k\neq m} B'_{ik,s}\,u_k$$

So let's now insert this in all three places:

$$(H_0 - E_m)\,[\,\Sigma_{j\neq i} B'_{ij,n}\,|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n}\,|u_k\rangle] =$$

$$-H'\,[\,\Sigma_{j\neq i} B'_{ij,n-1}\,|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n-1}\,|u_k\rangle]$$

$$+\,\Sigma_{t=1,n-1} W_{mi,t}\,[\,\Sigma_{j\neq i} B'_{ij,n-t}\,|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n-t}\,|u_k\rangle]$$

$$+\,W_{mi,n}\,|u_{mi}\rangle$$

A. Close with $\langle u_{k'}|$.

A. First, let's close this with $\langle u_{k'}|$ in the perp space. We get

$$(E_{k'} - E_m)\,[\,\Sigma_{j\neq i} B'_{ij,n}\,\langle u_{k'}|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n}\,\langle u_{k'}|u_k\rangle] =$$

$$- \langle u_{k'}| H' [\Sigma_{j\neq i} B'_{ij,n-1} |u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n-1} |u_k\rangle]$$

$$+ \Sigma_{t=1,n-1} W_{mi,t} [\Sigma_{j\neq i} B'_{ij,n-t} \langle u_{k'}|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n-t} \langle u_{k'}|u_k\rangle]$$

$$+ W_{mi,n} \langle u_{k'}|u_{mi}\rangle$$

Our first rewrite is as follows

$$(E_{k'} - E_m) [0 + \Sigma_{k\neq m} B'_{ik,n} \delta_{k,k'}] =$$

$$- \langle u_{k'}| H' [\Sigma_{j\neq i} B'_{ij,n-1} |u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n-1} |u_k\rangle]$$

$$+ \Sigma_{t=1,n-1} W_{mi,t} [0 + \Sigma_{k\neq m} B'_{ik,n-t} \delta_{k,k'}]$$

Now use $\delta_{k,k'}$ to remove the $\Sigma_{k\neq m}$ sum in two places, and at the same time expand the middle line:

$$(E_{k'} - E_m) [B'_{ik',n}] =$$

$$- \Sigma_{j\neq i} B'_{ij,n-1} \langle u_{k'}| H' |u_{mj}\rangle - \Sigma_{k\neq m} B'_{ik,n-1} \langle u_{k'}| H' |u_k\rangle + \Sigma_{t=1,n-1} W_{mi,t} [B'_{ik',n-t}]$$

$$- \Sigma_{j\neq i} B'_{ij,n-1} H'_{k'j} - \Sigma_{k\neq m} B'_{ik,n-1} H'_{k'k} + \Sigma_{t=1,n-1} W_{mi,t} [B'_{ik',n-t}]$$

This tells us the "out of strip" values of the $B'_{ik',n}$ in terms of the "strip" B' of lower orders! We are missing the n = 1 equation, so let's develop it as a special case

$$(H_0 - E_m) \psi_{mi,1} = - H' u_{mi} + W_{mi,1} u_{mi} \qquad n = 1$$

Insert on the left

$$\psi_{mi,1} = \Sigma_{j\neq i} B'_{ij,1} u_{mj} + \Sigma_{k\neq m} B'_{ik,1} u_k$$

and we get

$$(H_0 - E_m) [\Sigma_{j\neq i} B'_{ij,1} |u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,1} |u_k\rangle] = - H' |u_{mi}\rangle + W_{mi,1} |u_{mi}\rangle$$

Now close with $\langle u_{k'}|$ to get

$$(E_{k'} - E_m) [\Sigma_{j\neq i} B'_{ij,1} \langle u_{k'}|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,1} \langle u_{k'}|u_k\rangle] = - \langle u_{k'}|H' |u_{mi}\rangle + W_{mi,1} \langle u_{k'}|u_{mi}\rangle$$

$$(E_{k'} - E_m) [0 + \Sigma_{k\neq m} B'_{ik,1} \delta_{k,k'}] = - \langle u_{k'}|H' |u_{mi}\rangle + 0$$

$$(E_{k'} - E_m) [B'_{ik',1}] = - H'_{k'i}$$

$$B'_{ik',1} = H'_{k'i} / (E_m - E_{k'})$$

So let's now summarize fully our result with closure with $\langle u_{k'}|$:

$$(E_{k'} - E_m)\, B'_{ik',1} = - H'_{k'i} \qquad n = 1$$

$$(E_{k'} - E_m)\, B'_{ik',n} = -\Sigma_{j\neq i} B'_{ij,n-1}\, H'_{k'j} \qquad n > 1$$

$$- \Sigma_{k\neq m}\, B'_{ik,n-1} H'_{k'k} + \Sigma_{t=1,n-1}\, W_{mi,t}\, B'_{ik',n-t}$$

So at least for the coefficients of the form $B'_{ik',n}$ we have a starting point with $B'_{ik',1}$ given by the first equation. We do not yet, however, have any starting point for the coefficients of the type $B'_{ij,n-1}$. Notice how I am relying on k and j to keep track of which group of coefficients we are dealing with.

B. Close with $\langle u_{ms}|$ and then look at s = i and s≠i as separate cases

B. Second, let's close this with $\langle u_{ms}|$ in the m subspace. We start with

$$(H_0 - E_m)\, [\, \Sigma_{j\neq i} B'_{ij,n}\, |u_{mj}\rangle + \Sigma_{k\neq m}\, B'_{ik,n}\, |u_k\rangle] =$$

$$- H' [\, \Sigma_{j\neq i} B'_{ij,n-1}\, |u_{mj}\rangle + \Sigma_{k\neq m}\, B'_{ik,n-1}\, |u_k\rangle]$$

$$+ \Sigma_{t=1,n-1}\, W_{mi,t}\, [\, \Sigma_{j\neq i} B'_{ij,n-t}\, |u_{mj}\rangle + \Sigma_{k\neq m}\, B'_{ik,n-t}\, |u_k\rangle]$$

$$+ W_{mi,n}\, |u_{mi}\rangle \qquad n>1$$

Closure at once causes LHS = 0, so we are left with

$$0 =$$

$$- \langle u_{ms}| H' [\, \Sigma_{j\neq i} B'_{ij,n-1}\, |u_{mj}\rangle + \Sigma_{k\neq m}\, B'_{ik,n-1}\, |u_k\rangle]$$

$$+ \Sigma_{t=1,n-1}\, W_{mi,t}\, [\, \Sigma_{j\neq i} B'_{ij,n-t}\, \langle u_{ms}|u_{mj}\rangle + \Sigma_{k\neq m}\, B'_{ik,n-t}\, \langle u_{ms}|u_k\rangle]$$

$$+ W_{mi,n}\, \langle u_{ms}||u_{mi}\rangle$$

Our first round of simplification gives

$$0 =$$

$$- \Sigma_{j\neq i} B'_{ij,n-1}\, \langle u_{ms}| H' |u_{mj}\rangle - \Sigma_{k\neq m}\, B'_{ik,n-1} \langle u_{ms}| H' |u_k\rangle$$

$$+ \Sigma_{t=1,n-1}\, W_{mi,t}\, [\, \Sigma_{j\neq i} B'_{ij,n-t}\, \delta_{s,j} + 0]$$

$$+ W_{mi,n}\, \delta_{s,i}$$

Now use the fact that $\langle u_{ms}| H' |u_{mj}\rangle = \delta_{s,j} \langle u_{ms}| H' |u_{ms}\rangle = \delta_{s,j} W_{ms,1}$. We then have

$$0 = -\Sigma_{j\neq i} B'_{ij,n-1}\ \delta_{s,j}\ W_{ms,1} - \Sigma_{k\neq m} B'_{ik,n-1}\langle u_{ms}| H' |u_k\rangle$$

$$+ \Sigma_{t=1,n-1} W_{mi,t}\ [\Sigma_{j\neq i} B'_{ij,n-t}\ \delta_{s,j} + 0] + W_{mi,n}\ \delta_{s,i}$$

Now we want to claim this general thing

$$\Sigma_{j\neq i}\ F_{ij}\ \delta_{s,j} = F_{is}\ (1 - \delta_{s,i})$$

and then use that idea twice to get, and also use

$$0 = -B'_{is,n-1}\ W_{ms,1}\ (1 - \delta_{s,i}) - \Sigma_{k\neq m} B'_{ik,n-1}\langle u_{ms}| H' |u_k\rangle$$

$$+ \Sigma_{t=1,n-1} W_{mi,t}\ B'_{is,n-t}(1 - \delta_{s,i}) + W_{mi,n}\ \delta_{s,i}$$

Next, break out the t=1 term from the sum to get

$$0 = -B'_{is,n-1}\ W_{ms,1}\ (1 - \delta_{s,i}) - \Sigma_{k\neq m} B'_{ik,n-1}\langle u_{ms}| H' |u_k\rangle \qquad n>1$$

$$+ W_{mi,1}\ B'_{is,n-1}(1 - \delta_{s,i}) + \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t}(1 - \delta_{s,i}) + W_{mi,n}\ \delta_{s,i}$$

This allows us to combine the first and third terms together, and put them on the LHS:

$$B'_{is,n-1}(1 - \delta_{s,i})\ [W_{mi,1} - W_{ms,1}] \qquad n>1$$

$$= + \Sigma_{k\neq m} B'_{ik,n-1}\langle u_{ms}| H' |u_k\rangle - \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t}(1 - \delta_{s,i}) - W_{mi,n}\ \delta_{s,i}$$

This thing is valid for all i,s in the m subspace. As before, let's develop the n = 1 equation separately,

$$(H_0 - E_m)\ \psi_{mi,1} = - H' u_{mi} + W_{mi,1}\ u_{mi} \qquad n = 1$$

Closing with $\langle u_{ms}|$ makes 0 on the left and we get

$$0 = -\langle u_{ms}| H' | u_{mi}\rangle + W_{mi,1}\ \delta_{s,i}$$

This is of course where we first learn that H' must be diagonal in the u_{mi} and then this just gives us the first order energy correction, so the n = 1 equation is not so interesting here, we already "know" everything it has to offer us.

Now go back to the previous n> 1 result

$$B'_{is,n-1}(1 - \delta_{s,i})\ [W_{mi,1} - W_{ms,1}] \qquad n>1$$

$$= + \Sigma_{k\neq m} B'_{ik,n-1} H'_{sk} - \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t}(1 - \delta_{s,i}) - W_{mi,n}\,\delta_{s,i}$$

For i = s, it tells us this:

$$0 = \Sigma_{k\neq m} B'_{ik,n-1} H'_{ik} - W_{mi,n}$$

$$W_{mi,n} = \Sigma_{k\neq m} B'_{ik,n-1} H'_{ik} = (H'Q_{0m}H')_{ii}$$

so this is a result we already knew, and here we have rederived it.

For i ≠ s it tells us this: n>1

$$B'_{is,n-1}\,[W_{mi,1} - W_{ms,1}] = \Sigma_{k\neq m} B'_{ik,n-1} H'_{sk} - \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t}$$

And this equation in general tells us the $\mathcal{H}^{(m)}$ $B'_{is,n-1}$ coefficients in terms of the $B'_{ik,n-1}$ of the same lower, and $B'_{is,n-t}$ of lower order.

Question: What do we do when $W_{ms,1} = W_{mi,1}$ for a pair of states? It seems that this denies us a starting point for the $B'_{is,1}$ coefficients! For n=2 our equation above is

$$B'_{is,1}\,[W_{mi,1} - W_{ms,1}] = \Sigma_{k\neq m} B'_{ik,1} \langle u_{ms}| H' |u_k\rangle$$

C. Summary of what we just did above: A systematic iterative method good to all orders

We took the *general* ladder equation and closed it first with <k| and second with $\langle u_{ms}|$ and got lots of interesting results -- here they are:

$$\psi_{mi,n} = \{\ \Sigma_{j\neq i} B'_{ij,n}\ u_{mj}\ \} \oplus \Sigma_{k\neq m} B'_{ik,n}\ u_k \qquad n = 1,2,3...$$

$$W_{mi,1} = H'_{ii} \qquad (0)$$

Closure with $\langle u_{k'}|$:

$$(E_{k'} - E_m)\ B'_{ik',1} = - H'_{k'i} \qquad n = 1 \qquad (1)$$

$$(E_{k'} - E_m)\ B'_{ik',n} = - \Sigma_{j\neq i} B'_{ij,n-1}\ H'_{k'j} \qquad n > 1$$

$$- \Sigma_{k\neq m} B'_{ik,n-1} H'_{k'k} + \Sigma_{t=1,n-1} W_{mi,t}\ B'_{ik',n-t} \qquad (2)$$

Closure with $\langle u_{ms}|$:

$$(H_0 - E_m)\ \psi_{mi,1} = - H'\ u_{mi} + W_{mi,1}\ u_{mi} \qquad n = 1 \qquad (3)$$

$$B'_{is,n-1}(1 - \delta_{s,i})\,[W_{mi,1} - W_{ms,1}] \qquad n>1$$

$$= + \Sigma_{k\neq m} B'_{ik,n-1}H'_{sk} - \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t}(1 - \delta_{s,i}) - W_{mi,n}\,\delta_{s,i}$$

The last equation (not numbered) can be further broken down as to whether $s \neq i$ or $s = i$:

$$B'_{is,n-1}\,[W_{mi,1} - W_{ms,1}] = \Sigma_{k\neq m} B'_{ik,n-1}H'_{sk} - \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t} \qquad s \neq i \qquad (4)$$

$$W_{mi,n} = \Sigma_{k\neq m} B'_{ik,n-1}\,H'_{ik} \qquad s = i \qquad (5)$$

The very last equation states the famous result $W_{mi,n} = \langle u_{mi} \mid H' \mid \psi_{mi,n-1}\rangle$.

Now what kind of iterative scheme do these equations allow? I am now happy to consider a state "i" which is like the state "n" in our Messiah picture, one that has become a singlet after the first level EV equation. What then can we learn about this singlet state i's coefficients?

- First, we know $B'_{ik',1}$ from equation (1), and we know the $W_{mi,1}$ from (0)

- We set n = 2 in equation (4) to find $B'_{is,1}$ which has only the leading term on the RHS. This equation then says $B'_{is,1}\,[W_{mo,1} - W_{ms,1}] = \Sigma_{k\neq m} B'_{ik,1}\langle u_{ms}| H' |u_k\rangle = (H'Q_{0m}H')_{si}$

- We set n = 2 in equation (2) to get $B'_{ik',2}$ in terms of the $B'_{ik',1}$

- We set n=3 in equation (4) to get $B'_{is,2}$ in terms of $B'_{ik,2}$ and $B'_{is,1}$ and $W_{mi,2}$

And so on. So, for a singlet state "n", this set of equations allows us to compute the corrected state $\psi_{mi,n}$ *to arbitrarily high order*. The iterative process seems totally well defined. There might be some "operator method" to put things into a more compact notation, but eventually we have to do all the calculations at each stage that this iterative method implies.

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12. Digression: Schiff page 249 lower half of the page:

In my current understanding of things, if we have an N = 2 degeneracy, we have to find u_k that will diagonalize H' in order to get started. My usual approach is this

$$S^{-1}H'S = \Lambda \qquad H'\,S = S\Lambda \qquad H'_{ij}S_{jk} = S_{ij}\Lambda_{jk} = S_{ij}\,\delta_{jk}\Lambda_{kk} = \Lambda_{kk}S_{ik}$$

So we have an eigenvalue equation of this form:

$$H'_{ij}S_{jk} = \Lambda_{kk}S_{ik}$$

where notice that the index k denotes the column of S_{ik}. We can denote a column by $[S_k]_i$ where i reads off the components of the column. Then we have

$H'_{ij}\,[S_k]_i = \Lambda_{kk}\,[S_k]_i$ or $H'\,S_k = \Lambda_{kk}\,S_k$

and we see as usual that the columns of S_{ik} are the eigenvectors of H'.

Now let's start with basis column vectors (1 0) and (0 1) and write a general one as (a,b). Once we diagonalize H' in this process, the two diagonal elements which I call Λ_{kk} are really $\langle u_{mk}|\, H'|u_{mk}\rangle$ for the two values of k we can call k = 1,2. In my notation I would call these $W_{mk,1}$ for k = 1,2. Schiff just calls them "the two values of W_1". I expect to find two solutions (a,b) and (a', b'), one for each $W_{mk,1}$ value. So here is one of our eigenvalue equations:

$H\,S_k = W_1\,S_k$ H' = H for short here

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = W_1\begin{pmatrix} a \\ b \end{pmatrix}$$

$H_{11}\,a + H_{12}\,b = W_1\,a$
$H_{21}\,a + H_{22}\,b = W_1\,b$

$(H_{11} - W_1)\,a + H_{12}\,b = 0$ m =1 $\ell = 2$ $a = a_m$ $b = a_\ell$
$H_{21}a + (H_{22}-W_1)b = 0$

And this is **Schiff 31.15** on page 249 (finally). He gets it from the 31.4 second line, but I get it differently. I regard 31.4 second line as saying H' must be diagonal, and then above I find out how to make it be diagonal. Fine.

The two W_1 come from the secular equation which is this

$\det(H - W_1 1) = 0$ $\det\begin{pmatrix} H_{11}-W_1 & H_{12} \\ H_{21} & H_{22}-W_1 \end{pmatrix}$

$(H_{11}-W_1)\,(H_{22}-W_1) - H_{12}H_{21} = 0$

$W_1^2 - (H_{11} + H_{22})W_1 + (H_{11}H_{22} - H_{12}H_{21}) = 0$

$W_1 = (H_{11} + H_{22})/2 \pm [(H_{11} + H_{22})^2 - 4\,(H_{11}H_{22} - H_{12}H_{21})]^{1/2}/2$

$= (H_{11} + H_{22})/2 \pm [\,(H_{11} - H_{22})^2 + 4\,|H_{12}|^2\,)]^{1/2}/2$

And this is **Schiff 31.16** in his notation. The two W_1 solutions will only be equal if both square root terms are 0, which means if $H_{11} = H_{22}$ and $H_{12} = 0$, which is to say, if H' was a multiple of the identity! In this case of course it is already diagonal and we just get W_1 = the equal diagonal elements.

Now recall our result

$$(E_m - E_k)B'_{ik,1} = \langle u_k | H' | u_{mi} \rangle \qquad k \text{ in } \mathcal{H}^{\perp}$$

I suppose we can write $|u_{mi}\rangle = a|1\rangle + b|2\rangle$ in ket notation and then I get

$$(E_m - E_k)B'_{ik,1} = \langle u_k | H' |1\rangle a + \langle u_k | H' |2\rangle b$$

and this is what he means by **equation 31.18.** It is just pulling teeth, his notation just stinks to high heaven. Just as he has no distinguishing index on W_1, he also has none on his $a^{(1)}_k$ which is really my object $B'_{ik,1}$.

How can I interpret Schiff's obscure notation?

me	Schiff	me
$W_{mi,1}$	W_1	
$B'_{ik,1}$	$a_k^{(1)}$	
$B'_{ij,1}$	$a_\ell^{(1)}$, $a_m^{(1)}$	$B'_{12,1}$ and $B'_{21,1}$??

Schiff:

$$\psi_1 = \Sigma_n a_n^{(1)} u_n$$

Me:

$$\psi_{mi,1} = \{ \Sigma_{j\neq i} B'_{ij,1} u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,1} u_k$$

If I were to go with an "implied" i = 1,2 index, this last would become

$$\psi_{m,1} = \{ \Sigma_{j\neq i} B'_{j,1} u_{mj} \} \oplus \Sigma_{k\neq m} B'_{k,1} u_k$$

$$= \{ \Sigma_{j\neq i} a_j^{(1)} u_{mj} \} \oplus \Sigma_{k\neq m} a_k^{(1)} u_k$$

which at least looks like his $\psi_1 = \Sigma_n a_n^{(1)} u_n$. I just don't think a symbol $a_\ell^{(1)}$ is well defined in his notation. I am now reminded of this Amazon reviewer's comments"

"Legend tells that Leonard Schiff, while learning quantum mechanics from J. R. Oppenheimer, produced a careful set of notes which eventually became the first edition of this text. Soon followed a second, which was, for a long time, the unanimous choice of QM text-book in English. The third introduced things like group theory, a little of what was then called formal scattering theory (Lippman-Schwinger equation), and other new things. Schiff's text was a minimalist one, in the sense that you found everything, but in a very compact, no frills style. A teacher was required. The ratio of words to formulas was quite small. It entirely dominated the panorama. **I, studying by myself, tried very hard, but could not understand, for instance, his treatment of perturbation of degenerate levels.** Neither could I understand the infamous "box of very large dimensions" where the systems with a continuous spectrum were trapped so that their spectra became discrete. Even less could I acquire the much desired "global view" of quantum mechanics. **I was very unhappy with Schiff.** Someone suggested Bohm's textbook for me, but, at that moment, it seemed too leisurely paced for my impatience. Then I hit upon the newly arrived English translation of Landau, Lifshitz, "and all was Light". Nowadays I think there is no more place for "ole Schiff", but I must confess some of my colleagues still swear by their second edition, with the famous greenish McGraw-Hill cover. Well, I must recognize that the Dirac equation treatment was quite good, and that you could trust the equations as they appeared in the text: almost no typos."

I really do think Schiff has badly dropped the ball here! His notation just cannot handle the problem he is looking at!

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13. Review of the development so far.

So now let's review what I have done on my own with what I regard as adequate notation:

1. My general expansion for ψ is as follows:

$$\psi_{mi,n} = \Sigma_{j\neq i} B'_{ij,n}\, u_{mj} + \Sigma_{k\neq m} B'_{ik,n}\, u_k \qquad n > 0$$
$$\psi_{mi,0} = u_{mi} \qquad n = 0$$

and I assume that H' has been pre-diagonalized within $\mathcal{H}^{(m)}$ so we have "the right" u_{mi} .

2. The general form of equation 31.4 may be written as follows:

$$(H_0 - E_m)\,\psi_{mi,n} = -H'\,\psi_{mi,n-1} + \Sigma_{t=1,n-1} W_{mi,t}\,\psi_{mi,n-t} + W_{mi,n}\,u_{mi} \qquad n>1$$

$$(H_0 - E_m)\,\psi_{mi,1} = -H'\,u_{mi} + W_{mi,0}\,u_{mi} \qquad n=1$$

And if we insert the above expansions into our n>1 formula we get this for our 31.4

$$(H_0 - E_m)\,[\,\Sigma_{j\neq i} B'_{ij,n}\,|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n}\,|u_k\rangle] =$$

$$-H'\,[\,\Sigma_{j\neq i} B'_{ij,n-1}\,|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n-1}\,|u_k\rangle]$$

$$+\,\Sigma_{t=1,n-1} W_{mi,t}\,[\,\Sigma_{j\neq i} B'_{ij,n-t}\,|u_{mj}\rangle + \Sigma_{k\neq m} B'_{ik,n-t}\,|u_k\rangle] + W_{mi,n}\,|u_{mi}\rangle$$

3. If we close item 2 with $\langle u_{k'}|$ in $\mathcal{H}^{\perp}$, we get these results:

$$(E_{k'} - E_m)\,B'_{ik',1} = -\langle u_{k'}|H'|u_{mi}\rangle \qquad n = 1$$

$$(E_{k'} - E_m)\,B'_{ik',n} = -\Sigma_{j\neq i} B'_{ij,n-1}\,\langle u_{k'}|\,H'\,|u_{mj}\rangle \qquad n > 1$$

$$-\,\Sigma_{k\neq m} B'_{ik,n-1}\langle u_{k'}|\,H'\,|u_k\rangle + \Sigma_{t=1,n-1} W_{mi,t}\,B'_{ik',n-t}$$

and this does seem to provide a systematic way to build up B' coefficients from those of lower order.

B. If we close item 2 with $\langle u_{ms}|$ in $\mathcal{H}^{(m)}$, we get these results:

$$0 = -\,\langle u_{ms}|\,H'\,|\,u_{mi}\rangle + W_{mi,1}\,\delta_{s,i} \qquad n = 1$$

$$B'_{is,n-1}(1 - \delta_{s,i})\,[W_{mi,1} - W_{ms,1}] \qquad n>1$$

$$= + \Sigma_{k\neq m} B'_{ik,n-1}H'_{sk} - \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t}(1 - \delta_{s,i}) - W_{mi,n}\,\delta_{s,i}$$

We can then consider the two cases: s = i and s ≠ i.

For s=i:

$$W_{mi,1} = \langle u_{mi}| H' | u_{mi}\rangle \qquad n=1$$

$$W_{mi,n} = \Sigma_{k\neq m} B'_{ik,n-1}\langle u_{mi}| H' |u_k\rangle \qquad n > 1$$

For s≠i:

$$\langle u_{ms}| H' | u_{mi}\rangle = 0 \qquad n=1$$

$$B'_{is,n-1}\,[W_{mi,1} - W_{ms,1}] =$$

$$\Sigma_{k\neq m} B'_{ik,n-1}\langle u_{ms}| H' |u_k\rangle - \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t} \qquad n>1$$

The s=i results tell us how to construct the n^{th} order energy correction if we are given the $(n-1)^{th}$ order coefficients of the perp space only, which I call $B'_{ik,n-1}$.

The s≠i results tell us the values of the m-subspace $B'_{is,n-1}$ in terms of the perp space $B'_{ik,n-1}$ of the same order, and the m-space $B'_{is,n-t}$ of *lower* orders.

14. The special case where $W_{ms,1} = W_{mi,1}$.

However, if it happens that our initially diagonalized H' matrix in the m-subspace has identical diagonal elements for i and s, then we have $W_{ms,1} = W_{mi,1}$ and we have to deal with this as a special case. This is how far I have gotten today, and I don't know how to proceed in this case. Should I regard $B'_{is,n-1}$ as blowing up, or should I regard $B'_{is,n-1}$ as being undetermined? [I think undetermined is correct.]

If we assume this is the case, and if we don't imagine $B'_{is,n-1}$ blowing up, then we have

$$0 = - \Sigma_{k\neq m} B'_{ik,n-1}\langle u_{ms}| H' |u_k\rangle + \Sigma_{t=2,n-1} W_{mi,t}\ B'_{is,n-t} \qquad n>1$$

Let's write this out for n = 2 and n=3 and n=4 (all only valid for i≠s)

$$0 = - \Sigma_{k\neq m} B'_{ik,1}\langle u_{ms}| H' |u_k\rangle \qquad n=2$$

$$0 = - \Sigma_{k\neq m} B'_{ik,2}\langle u_{ms}| H' |u_k\rangle + W_{mi,2}\ B'_{is,1} \qquad n=3$$

$$0 = - \Sigma_{k\neq m} B'_{ik,3}\langle u_{ms}| H' |u_k\rangle + W_{mi,2}\ B'_{is,2} + \Sigma_{t=2,3} W_{mi,3}\ B'_{is,1} \qquad n=4$$

I think we may be getting somewhere. The n=2 equation is a peculiar fact I guess, only true when i≠s. What happens if I install into it the known coefficients

$$B'_{ik,1} = \langle u_k | H' | u_{mi} \rangle / (E_m - E_k) = H'_{ki} / (E_m - E_k)$$

Then the n=2 equation seems to say

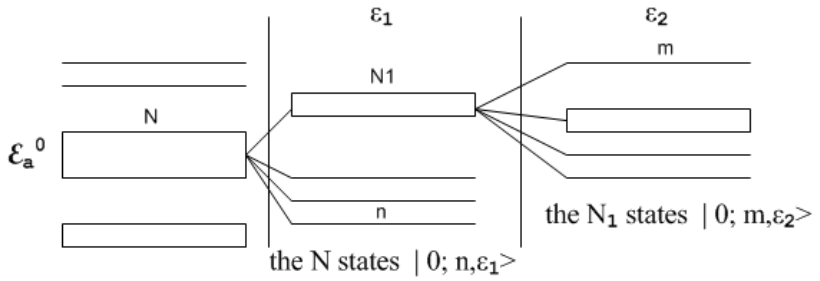
$$0 = - \Sigma_{k \neq m} \langle u_{ms} | H' | u_k \rangle \langle u_k | H' | u_{mi} \rangle / (E_m - E_k) \qquad s \neq i$$

$$0 = - \Sigma_{k \neq m} H'_{sk} H'_{ki} / (E_m - E_k) = - (H' Q_{om} H')_{si} \qquad s \neq i$$

$(H'Q_{om}H')_{si} = 0$ when $s \neq i$ // 2.9.09 Ie, we have to diagonalize $VQ_{0a}V$!!

This is a fascinating fact now that I have done some Messiah work. At first I thought it was some useless sum rule, but now I see it is the solution to our whole problem!! We have now quietly exposed new conditions (from the perturbation equations) on our states "i" and "s" that they must be certain linear combinations of the basic states which already diagonalized H' and which now must diagonalize the operator $H'Q_{om}H'$ within the N_1 subspace! These new linear combinations continue to diagonalize H' because $W_{mi,1}$ is the same for all the eigenstates of our N state level 1 EV problem. These states i and s are the ones I called $|0; m,\varepsilon_2\rangle$ in my Messiah notes. So from now on, we have to think of the states i and s as being these special states. Also, we already showed earlier in these notes that the diagonal elements are $(H'Q_{om}H')_{ii} = W_{mi,2}$. So right at this point we have found that:

" The states in the N_1 subspace which are degenerate and which I label with letters like i and s, are in fact eigenvectors of the EV problem $H'Q_{om}H' |i,1\rangle = W_{mi,2}|i,1\rangle$. "



So we have stumbled upon the level 2 EV problem by doing our "general treatment", very good. Of course this is confirmed in Messiah.

Now consider that $|i,1\rangle = \Sigma_{j \neq i} B'_{ij,1} |u_{mj}\rangle$ = the portion of our first order state correction that lies in the space $\mathcal{E}_a^0$. Our "solution for the $B'_{ij,1}$" is the same as our solution for the eigenstates to the above EV problem, so we are suddenly done! We start with some starting states and diagonalize $H'Q_{om}H'$ and then we know the $B'_{ij,1}$. There is no need for more elaborate equations here!

(old comment retained) Wow! I wonder if it really is this complicated? This is far beyond Schiff, but perhaps one of my other books has some comments. This is just too messy for me to pursue without

having a source to check things against. I think in practice one "ignores far away levels" and maybe things simplify.

15. Comments on Saxon's Approach.

I have now read Saxon's "take" on this subject, and it is different from that of Schiff. I quote my own notes in my Saxon doc on some of the key differences:

- There are no explicit power series expansions, but we are given a successive approximations rule.
- He does not normalize ψ in the special way that makes $\langle u_{mi} | \psi_{mi} - u_{mi} \rangle = 0$.
- He does not "require" that H' must start off being diagonal in the u_{mi}, though he does end up with a result that gives the required linear combinations.
- He tends to work with objects "to all orders" rather than "in particular orders"
- He uses what I call D_{ij} coefficients in place of Schiff's B'_{ik} coefficients.

My other sources on this subject are Messiah and, I see, Pauling & Wilson.

16. Comments on my Theorem A and a way to think of the Saxon approach.

(1) Possible Saxon method. This is the theorem that says H' must be diagonal within $\mathcal{H}^{(m)}$. It results from balancing the λ^1 terms on both sides of the power-series-expanded full SE. Now consider this

$$f(\lambda) = f_0 + f_1\lambda + f_2\lambda^2 + f_3\lambda^3 +$$

$$g(\lambda) = g_0 + g_1\lambda + g_2\lambda^2 + g_3\lambda^3 +$$

Such a balance would say that $f_i = g_i$. But suppose you were to write these in a different way:

$$f(\lambda) = f_0 + f_1\lambda + F_2\lambda^2 \qquad F_2 = f_2 + f_3\lambda + f_4\lambda^2 + \ldots$$
$$g(\lambda) = g_0 + g_1\lambda + G_2\lambda^2 \qquad G_2 = g_2 + g_3\lambda + g_4\lambda^2 + \ldots$$

where now we include in F_2 and G_2 "the λ^2 term and all higher orders". Now if someone says $f(\lambda) = g(\lambda)$, you then have $F_2 = G_2$. But we would only say $F_2 = f_2$ to zeroth order. Also, the equation $F_2 = G_2$ would not be the same as the equation $f_2 = g_2$, though both equations are true.

I think maybe Saxon works with things like F_2 because he subtracts out first order results. Look for example at Saxon page 191 equations 28 and 29. These both have the form I show above :

$$f(\lambda) = f_0 + f_1\lambda + F_2\lambda^2$$

In the case of the coefficients, it happens that $f_0 = 0$.

Let's see what happens if we take the Saxon approach relative to our Theorem A. Consider this:

$$\psi_{mi} = u_{mi} + \lambda\, \psi_{mi,rest} \qquad \psi_{mi,0} = u_{mi}$$

$W_{mi} = E_m + \lambda W_{mi,1} + \lambda^2 W_{mi,rest}$ $\quad W_{mi,0} = E_m$ // I could have used $\lambda W_{mi,rest}$

where "rest" means "all the rest of the terms packed into one term". What happens if we plug this into our SE and just separate out the λ^0 terms from the rest: (there are 4+6 = 10 terms)

$(H_0 + \lambda H')\{ u_{mi} + \lambda \psi_{mi,rest}\} = (E_m + \lambda W_{mi,1} + \lambda^2 W_{mi,rest})\{ u_{mi} + \lambda \psi_{mi,rest}\}$

$H_0 u_{mi} = E_m u_{mi}$ $\quad \lambda^0$

$\lambda H' u_{mi} + \lambda H_0 \psi_{mi,rest} + \lambda^2 H' \psi_{mi,rest}$

$= \lambda W_{mi,1} u_{mi} + \lambda E_m \psi_{mi,rest} + \lambda^2 W_{mi,rest} u_{mi} +$

$+ \lambda^2 W_{mi,1} \psi_{mi,rest} + \lambda^3 W_{mi,rest} \psi_{mi,rest}$ $\quad \lambda^1$ and higher

Now cancel one λ to get (note there really are 10 terms above and below)

$H' u_{mi} + H_0 \psi_{mi,rest} + \lambda H' \psi_{mi,rest}$

$= W_{mi,1} u_{mi} + E_m \psi_{mi,rest} + \lambda W_{mi,rest} u_{mi} +$

$+ \lambda W_{mi,1} \psi_{mi,rest} + \lambda^2 W_{mi,rest} \psi_{mi,rest}$ $\quad \lambda^1$ and higher

or

$(H_0 - E_m) \psi_{mi,rest} = (W_{mi,1} - H') u_{mi}$

$+ \lambda W_{mi,rest} u_{mi} + \lambda (W_{mi,1} + \lambda W_{mi,rest}) \psi_{mi,rest}$

Now close with mj ≠ mi and get

$0 = - H'_{mj,mi} + \lambda (W_{mi,1} + \lambda W_{mi,rest}) < u_{mj} | \psi_{mi,rest}>$

NOW we would claim this:

$H'_{mj,mi} = \lambda (W_{mi,1} + \lambda W_{mi,rest}) < u_{mj} | \psi_{mi,rest}>$

and then we would say "Oh, $H'_{mj,mi} = 0$ only in zeroth order" but when higher orders are included, we do not get $H'_{mj,mi} = 0$."

Everything done above is EXACT! No approximations were made. $H'_{mj,mi}$ is not zero!

$\psi_{mi} = u_{mi} + \lambda \psi_{mi,rest}$

In general we don't know much about the component of $\psi_{mi,rest}$ on u_{mj} for j≠i, but it is likely non-zero for a general H'.

So now I have two conflicting facts:

[1] my Schiff argument says $H'_{mj,mi} = 0$
[2] my Saxon argument says $H'_{mj,mi} \neq 0$

Which argument is correct??? I could try a sample problem I suppose.

Does this contradiction have anything to do with degeneracy? YES! In both cases, I have to "close" with some mj ≠mi, so I am assuming there are at least two states with energy E_m. So this contradiction is specific to perturbation theory of *degenerate* states.

Here is one possible resolution: "If the power series expansions exist, meaning they converge, then $H'_{mj,mi} = 0$ in $\mathcal{H}^{(m)}$ and it will then magically turn out that $< u_{mj} \mid \psi_{mi,rest} > = 0$, and there will be no contradiction".

(2) The 2x2 diagonalization of H' in Schiff. Now, any text author who does the Schiff "series thing" is going to run into this $H'_{mj,mi} = 0$ requirement, I think. I certainly did right away. I am amazed that Schiff does not seem to mention it. On the other hand, on page 249 when Schiff is faced with actually *doing* a degeneracy analysis with N=2, the first thing he does is he finds basis functions that diagonalize H' !! Recall from notes above that he does this:

$$\begin{pmatrix} H'_{11} & H'_{12} \\ H'_{21} & H'_{22} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = W_1 \begin{pmatrix} a \\ b \end{pmatrix} \qquad m=1 \quad \ell = 2 \qquad a = a_m \qquad b = a_\ell$$

$H' S_k = \Lambda_{kk} S_k$ // my notation.

(3) Question: $<u_{mj}| \psi'_{mi,rest}> = 0$ for i≠j ? No!

In Theorem B above I show this fact

$<u_{mi}| \psi'_{mi,n}> = 0$ n>0 which is 31.6

Now compare:

$\psi_{mi} = u_{mi} + \lambda \psi_{mi,rest}$

$\psi_{mi} = u_{mi} + \lambda \psi_{mi,1} + \lambda^2 \psi_{mi,2} + \ldots$

I have clearly proven that

$<u_{mi}| \psi'_{mi,rest}> = 0$

Here is the question: is there some equivalent theorem that says $<u_{mj}| \psi'_{mi,rest}> = 0$ for $j \neq i$? If so, this would quickly resolve our contradiction above. Let's copy the previous proof and edit as needed:

6. Theorem B': { show 31.6: $<u_{mj}| \psi_{mi,n}> = 0$ for $n > 0$ and $j \neq i$ }

Proof. Renormalize as before to get

$$\psi'_{mi} = \{\ u_{mi} + \Sigma_{j\neq i} B'_{ij}\ u_{mj}\ \} \oplus \Sigma_{k\neq m} B'_{ik}\, u_k$$

We know that $\psi'_{mi,0} = u_{mi}$. For any higher order component we have

$$\psi'_{mi,n} = \{\ \Sigma_{j\neq i} B'_{ij,n}\ u_{mj}\ \} \oplus \Sigma_{k\neq m} B'_{ik,n}\, u_k \qquad n > 0$$

where we imagine expanding the B' just as we expand ψ' or W. Then we have for j' ≠ i

$$\langle u_{mj'} |\ \psi'_{mi,n}\rangle = \langle u_{mj'} |\ \Sigma_{j\neq i} B'_{ij,n}\ u_{mj}\rangle = \Sigma_{j\neq i} B'_{ij,n}\, \delta_{j'j} = B'_{ij',n}$$

Therefore

$$\langle u_{mj} |\ \psi'_{mi,n}\rangle = B'_{ij,n} \qquad\qquad B'_{ij,n}$$

We know that $B'_{ij,0} = 0$ because there is it starts at the λ = 1 level. Thus we have shown that

$$\langle u_{mj} |\ \psi'_{mi,rest}\rangle = B'_{ij}$$

and this is not necessarily 0 !

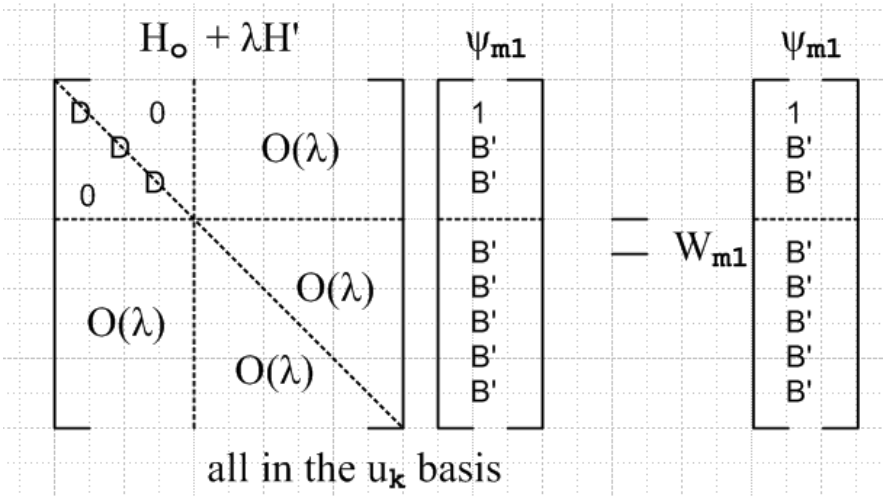
Therefore, here is what the Saxon argument is saying:

$$H'_{mj,mi} = \lambda\,(\,W_{mi,1} + \lambda W_{mi,rest})\, B'_{ij}$$

Well, what about the first factor $(\,W_{mi,1} + \lambda W_{mi,rest})$. Could it be zero somehow? If H' were diagonal in $\mathcal{H}^{(m)}$, then you might argue that there will be no energy corrections ever and so this factor should vanish.

(4) Pause to consider a new (and bogus!) Theorem D.

Here is the full $H\psi_{m1}=W_{m1}\psi_{m1}$ equation written *in the unperturbed u_k basis*:



First of all, recall that in this basis, the matrix H_0 is completely diagonal. Now here I am *assuming* that we "prediagonalize" H'. I have positioned H' in the upper left of the H matrix for convenience. In that NxN square, *both* H_0 and H' are diagonal in the u_k basis. Outside of this NxN square, we have H elements everywhere. The diagonal elements along the dotted line are order $1 = \lambda^0$ but the off-diagonal elements all arise from λH' and are therefore O(λ). We are NOT in block diagonal form, which means we still have mixing between $\mathcal{H}^{(m)}$ and $\mathcal{H}^{\perp}$: we cannot pretend we can isolate the $\mathcal{H}^{(m)}$ problem. For our eigenstate, we have chosen ψ_{m1} and that is why there is a 1 at the top of the state vector. This column vector is a representation of this fact used often above:

$$\psi_{m1} = \{ \; u_{m1} + \Sigma_{j\neq i} B'_{1j} \; u_{mj} \; \} \oplus \Sigma_{k\neq m} \, B'_{1k} \, u_k$$

so the "1" here really stands for the leading u_{m1} state, and the first few B' stand for $B'_{1j}u_m$ j = 2..N and then all the later B' below the line stand for $B'_{1k}u_k$ for k > N. The diagonal elements marked D are really these

$$D_{ii} = (H_0)_{ii} + \lambda\,(H')_{ii} = E_{m1} + \lambda H'_{mi,mi} \qquad i = 1...N \qquad D_{ij} = 0 \text{ for } i \neq j$$

where we put E_{m1} for all of $\mathcal{H}^{(m)}$ since these states were degenerate before H' was applied

Now let's write out the first N lines of the above matrix equation:

$$(E_{m1} + \lambda H'_{m1,m1}) \; u_{m1} + \Sigma_{k\neq m} \, H_{1,k} \; B'_{1k} \, u_k = W_{m1} \, u_{m1}$$
$$(E_{m1} + \lambda H'_{m2,m2}) \; B'_{12} u_{m2} + \Sigma_{k\neq m} \, H_{2,k} \; B'_{2k} \, u_k = W_{m1} \, B'_{12} u_{m2}$$
etc

My entire motivation here was to try to *isolate* coefficients like B'_{12} to learn something about them , so let's see if that has worked. Close the second equation above with u_{m2} and we get

$$(E_{m1} + \lambda H'_{m2,m2}) \; B'_{12} = W_{m1} \, B'_{12} \qquad \text{// since } u_{m2}.u_k = 0$$

$$(W_{m1} - E_{m1} - \lambda H'_{m2,m2}) \, B'_{12} = 0$$

This is interesting. First of all, **if** it just *happens* that $H'_{m2,m2} = H'_{m1,m1}$ (ie, after we prediagonalize H', we find that the 11 and 22 elements are degenerate, sort of a second level of degeneracy in our problem), then the paren above is really $W_{m1,2}$ and higher which is order λ^2. But this should not in general be 0. And if 11 ≠ 22, then again, no reason for it to be 0. So this does seem to imply that $B'_{12} = 0$ to all orders!!! This is a fact I have been long looking for, but I cannot see a simple reason why it should be true apart from the above derivation. For example, suppose paren = $5\lambda^2$, then $5\lambda^2 B'_{12} = 0$ and this says $B'_{12} = 0$ to all orders. Notice that in this entire Theorem D development, we have made NO approximations. Every single equation we have written above is exact to all orders of λ.

This seems to tell us that if we prediagonalize H', then we shall get no mixing within $\mathcal{H}^{(m)}$ to all orders, and we can then claim that really

$$\psi_{mi} = \{ \; u_{mi} + \Sigma_{j\neq i} B'_{ij} \; u_{mj} \; \} \oplus \Sigma_{k\neq m} \, B'_{ik} \, u_k$$

$= \quad u_{m1} \ \oplus \ \Sigma_{k \neq m} B'_{1k} u_k$

Is this really true? I have this sinking feeling that it is "too good to be true".

Contradiction noted: Restate this again: Our Theorem D purports to show that $B'_{ij} = 0$ to all orders for $i \neq j$. Is this really true? If we look back earlier in these notes, I obtained using Schiff's power series approach this equation:

$$B'_{is,1} = [\Sigma_{k \neq m} B'_{ik,1} \langle u_{ms}| H' |u_k\rangle] / (W_{mi,1} - W_{ms,1}) \qquad i \neq s \quad W_{mi,1} \neq W_{ms,1}$$

This certainly does NOT seem to be zero. So I just said that $B'_{ij} = 0$ to all orders, but Schiff's approach tells us right here that $B'_{ij,1} \neq 0$. How can something be 0 to all orders, but be non-zero right in the very first order? Another contradiction in our 6 day saga! I seem to be stuck in a Dr. Who time loop, around and around we go with endless contradictions.

Perhaps the time has come to look at Messiah. Maybe he will point out some little detail (or some large fact) that I am blinded to which is causing these contradictions. The biggest contradiction really is that my theory says you cannot do perturbation theory without prediagonalizing your states, but Saxon and Schiff happily do their theories *without* prediagonalizing. I can also look at Pauling and Wilson.

// I carefully reread all of the above on 1.19.09 after doing a long tour of Stakgold Chap 2. Everything still makes sense, and the confusions still exist. I have gained the suspicion that projection operators can be useful in place of constantly "closing" things from the left all the time.

Resolution of the above Theorem D mystery:

$H|\psi_{m1}\rangle = W_{m1}|\psi_{m1}\rangle$

$|\psi_{m1}\rangle = \{ \ |u_{m1}\rangle + \Sigma_{j \neq 1} B'_{1j} \ |u_{mj}\rangle \ \} \oplus \Sigma_{k \neq m} B'_{1k} |u_k\rangle$

$H [\{ \ |u_{m1}\rangle + \Sigma_{j \neq 1} B'_{1j} \ |u_{mj}\rangle \ \} \oplus \Sigma_{k \neq m} B'_{1k} |u_k\rangle]$

$= W_{m1}[\{ \ |u_{m1}\rangle + \Sigma_{j \neq 1} B'_{1j} \ |u_{mj}\rangle \ \} \oplus \Sigma_{k \neq m} B'_{1k} |u_k\rangle \ ]$

Now insert $1 = \{\Sigma_s |u_{ms}\rangle\langle u_{ms}| + \Sigma_k |k\rangle\langle k|\}$ for subspace plus perp space:

$H \ \{\Sigma_s |u_{ms}\rangle\langle u_{ms}| + \Sigma_k |k\rangle\langle k|\} [\{ \ |u_{m1}\rangle + \Sigma_{j \neq 1} B'_{1j} \ |u_{mj}\rangle \ \} \oplus \Sigma_{k \neq m} B'_{1k} |u_k\rangle]$

$= W_{m1}[\{ \ |u_{m1}\rangle + \Sigma_{j \neq 1} B'_{1j} \ |u_{mj}\rangle \ \} \oplus \Sigma_{k \neq m} B'_{1k} |u_k\rangle \ ]$

now close with some $\langle u_r|$ which could be a u_{ms} or could be a k state.

$\langle u_r| H \{\Sigma_s |u_{ms}\rangle\langle u_{ms}| + \Sigma_k |k\rangle\langle k|\} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle]$

$= \langle u_r| W_{m1} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle]$

Suppose I just combine all into a uniform "unity"

$\langle u_r| H \{\Sigma_{r'} |u_{r'}\rangle\langle u_{r'}| \} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle]$

$= \langle u_r| W_{m1} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle]$

$\Sigma_{r'} \langle u_r| H |u_{r'}\rangle \langle u_{r'}| \} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle]$

$= \langle u_r| W_{m1} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle]$

$\Sigma_{r'} H_{rr'} \langle u_{r'}| \psi_{1m}\rangle = W_{m1} \langle u_r| \psi_{1m}\rangle$

$\Sigma_{r'} H_{rr'} (\psi_{1m})_{r'} = W_{m1} (\psi_{1m})_r$

So here finally is our "matrix equation". I can write the matrix as I wrote it above. But what do the column vectors really look like?

$(\psi_{1m})_1 = \langle u_{m1}| \} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle] = 1$

$(\psi_{1m})_2 = \langle u_{m2}| \} [\{ |u_{m1}\rangle + \Sigma_{j\neq 1} B'_{1j} |u_{mj}\rangle \} \oplus \Sigma_{k\neq m} B'_{1k} |u_k\rangle] = B'_{12}$

and so on. So our matrix equation drawn above is accurate *exactly as it is written*! There are no extra factors u_{mj} that you "add to it". So our "first few equations" are really these:

$(E_{m1} + \lambda H'_{m1,m1}) + \Sigma_{k\neq m} H_{1,k} B'_{1k} = W_{m1}$
$(E_{m1} + \lambda H'_{m2,m2}) B'_{12} + \Sigma_{k\neq m} H_{2,k} B'_{2k} = W_{m1} B'_{12}$
etc

So now this second equation says:

$(W_{m1} - E_{m1} - \lambda H'_{m2,m2}) B'_{12} = -\Sigma_{k\neq m} H_{2,k} B'_{2k}$

$(W_{m1} - E_{m1} - W_{m2,1}) B'_{12} = -\Sigma_{k\neq m} H_{2,k} B'_{2k}$

and now there is no longer an "argument" that says we have proven that $B'_{12} = 0$. On the contrary, this seems to give us an expression for our B'_{12} to all orders:

$B'_{12} = -(W_{m1} - E_{m1} - \lambda H'_{m2,m2})^{-1} \Sigma_{k\neq m} H_{2,k} B'_{2k}$

Of course we don't know what W_{m1} is nor do we know what B'_{2k} is (both needed to all orders), but this is nonetheless a relationship between the various coefficients to all orders that is just a result of our matrix equation shown above graphically. We could expand both sides in orders of λ, but of course this will just give us our usual "perturbation equation".

17. Relation between Kato Method and Phil Method for Degeneracy [2.9.09]

In my "personal" approach above, I think of the "renormalized" expansion for ψ in $\mathcal{E}_a$,

$\psi_{mi} = \{ u_{mi} + \Sigma_{j\neq i} B'_{ij} u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik} u_k$ // all orders

$\langle u_{mj}|\psi_{mi}\rangle = B'_{ij}$ $\langle k|\psi_{mi}\rangle = B'_{ik}$

$\psi_{mi,n} = \{ \Sigma_{j\neq i} B'_{ij,n} u_{mj} \} \oplus \Sigma_{k\neq m} B'_{ik,n} u_k$ // some order n > 0

$\langle u_{mj}|\psi_{mi,n}\rangle = B'_{ij,n}$ $\langle k|\psi_{mi,n}\rangle = B'_{ik,n}$

and then I write down the "perturbation equations" and try to solve them for the B'. I end up with a viable iterative scheme which handles degeneracy.

In the Kato approach, we end up with an EV problem at some level, for example,

$V|\varphi_\alpha : 1\rangle = \varepsilon_1 |\varphi_\alpha : 1\rangle$ // The 1 means eigenket computed through level 1

Once we solve this EV problem for the kets $|\varphi_i : 1\rangle$ which lie in $\mathcal{E}_a{}^0$, in order to get the kets in $\mathcal{E}_a$ we have to do this

$|\psi_i : 1\rangle = P|\varphi_i : 1\rangle$

Then at that point, we could find our coefficients:

$\langle\varphi_j|\psi_i : 1\rangle = \langle\varphi_j|P|\varphi_i : 1\rangle = B'_{ij,1}$ i,j in 1..N range

and similarly for <k|. At level 2 we would say the following, for any degenerate subspace of N

$VQ_{a0}V|\varphi_i : 2\rangle = \varepsilon_2 |\varphi_i : 2\rangle$ i = 1..M // OK M=1 too

$\langle\varphi_j|\psi_i : 2\rangle = \langle\varphi_j|P|\varphi_i : 2\rangle = (B'_{ij,1} + B'_{ij,2})$ i,j in 1..M range

So that is how we can relate the Kato method to our coefficients.

So even with Kato, we don't have any fancy formula for the $B'_{ij,n}$ in the degeneracy case. You cannot avoid doing the work in either notation.

In the non-degenerate case, we do have a formula of sorts.

$|\psi ;n\rangle$ = coefficient of λ^n in $\{ \langle\varphi| \Sigma_{m=1} \lambda^m P^{(m)}|\varphi\rangle^{-1} [\Sigma_{k=1} \lambda^k P'^{(k)}|\varphi\rangle] \}$

$B'_{1k,n} = \langle k|\psi ;n\rangle$ = coefficient of λ^n in $\{ \langle\varphi| \Sigma_{m=1} \lambda^m P^{(m)}|\varphi\rangle^{-1} \langle k| [\Sigma_{k=1} \lambda^k P'^{(k)}|\varphi\rangle] \}$

18. Comparison to Messiah in General [2.9.09]

Messiah's great contribution is his introduction of the projection operators. In his pre-Kato notes, he deals with P_0 and $Q_0 = 1 - P_0$ in both non-degenerate and then degenerate cases. Then we get the Q_{0a} operator which causes everything to get very compact, no energy denominator sums needed. [Messiah does not credit anyone for this Q_{0a} thing, maybe Kato invented it or some earlier person.] Of course H' = V in Messiah, so in the end, everything we do can be written in terms of P_0 and Q_{0a} and V.

When we get into the Kato approach, we end up with a perturbation theory that looks a lot like scattering theory although Messiah never draws Feynman graphs (Bloch does, he says). In such graphs, each vertex would get a factor of λV, and each line would be a propagator $(z\text{-}H_0)^{-1}$. These things are not spacetime propagators, but are time-independent energy-space propagators.

$$(z\text{-}H)^{-1} = (z\text{-}H_0)^{-1} + (z\text{-}H_0)^{-1}\lambda V(z\text{-}H_0)^{-1} + (z\text{-}H_0)^{-1}\lambda V(z\text{-}H_0)^{-1}\lambda V(z\text{-}H_0)^{-1}$$

When this expansion is put into the formula for projector objects P and B, we get similar expansions for these objects, but now the propagators" are replaced either by P_0 or Q_{0a}. Using these expansions for P and B, we are able to discover the "generalized EV equations" $P_0BP_0\,|\varphi_\alpha\rangle = (E_\alpha - E_a^0)\,P_0PP_0|\varphi_\alpha\rangle$ and these lead us to a solution of any degeneracy problem, albeit lots of work is still needed once the EV problem has been identified.