Scraps from Degen Pert theory

Well, this first set of "scraps" is from my failed attempts to understand Schiff's 31.6

Plan A: fails.

Here I was hypothesizing that the new adjusted ψ called ψ' (which is what must be appearing in 31.6) was the original ψ minus its projection onto the state $\psi^{(m)}_0$. Now I know this is the wrong relationship between ψ' and ψ. Schiff gave me no advice, so of course this was the first thing I tried. I have moved these notes to the scraps document. Here is a quick review of what happens if you go down this wrong path.

Now let's define new $\psi'^{(m)}_s$ states as follows (for s = 1,2,3...)

$$\psi'^{(m)}_s \equiv \psi^{(m)}_s - \langle \psi^{(m)}_s | \psi^{(m)}_0 \rangle \psi^{(m)}_0 = \psi^{(m)}_s - a^{(m)}_s \psi^{(m)}_0 \qquad \text{// define a}$$

Then we have

$$\langle \psi'^{(m)}_s | \psi^{(m)}_0 \rangle = \langle \psi^{(m)}_s | \psi^{(m)}_0 \rangle - \langle \psi^{(m)}_s | \psi^{(m)}_0 \rangle \langle m|m \rangle = 0$$

where we assume our u_k states are orthonormal so that $\langle m|m \rangle = 1$.

Now let's sub in for $\psi^{(m)}_s$ the value $\psi'^{(m)}_s + a^{(m)}_s \psi^{(m)}_0$ into our all-s equation to get

$$(H_0 - E_0) [\psi'^{(m)}_s + a^{(m)}_s \psi^{(m)}_0]$$

$$= (W^{(m)}_1 - H') [\psi'^{(m)}_{s-1} + a^{(m)}_{s-1} \psi^{(m)}_0] + \Sigma_{j=2,3..s} W^{(m)}_j [\psi'^{(m)}_{s-j} + a^{(m)}_{s-j} \psi^{(m)}_0]$$

But we know that $(H_0 - E_0) \psi^{(m)}_0 = 0$ on the LHS, so we are left with

$$(H_0 - E_0) \psi'^{(m)}_s$$

$$= (W^{(m)}_1 - H') [\psi'^{(m)}_{s-1} + a^{(m)}_{s-1} \psi^{(m)}_0] + \Sigma_{j=2,3..s} W^{(m)}_j [\psi'^{(m)}_{s-j} + a^{(m)}_{s-j} \psi^{(m)}_0]$$

We can now write the RHS as two separate pieces

$$= (W^{(m)}_1 - H') \psi'^{(m)}_{s-1} + \Sigma_{j=2,3..s} W^{(m)}_j \psi'^{(m)}_{s-j}]$$

$$+ \{ (W^{(m)}_1 - H') a^{(m)}_{s-1} + \Sigma_{j=2,3..s} W^{(m)}_j a^{(m)}_{s-j} \} \psi^{(m)}_0$$

Suppose we name this {...} object to be A(m,s). Then we arrive at this result

$$(H_0 - E_0) \psi'^{(m)}_s = (W^{(m)}_1 - H') \psi'^{(m)}_{s-1} + \Sigma_{j=2,3..s} W^{(m)}_j \psi'^{(m)}_{s-j} + A(m,s) \psi^{(m)}_0$$

where of course A depends on H' and lots of other stuff.

I think Schiff has cheated us by pretending this last term does not exist. I am willing now to rename the primed functions to be unprimed, but this extra piece really is present.

$$(H_0 - E_0)\,\psi^{(m)}_s = (W^{(m)}_1 - H')\,\psi^{(m)}_{s-1} + \Sigma_{j=2,3..s} W^{(m)}_j \psi^{(m)}_{s-j} + A(m,s)\,\psi^{(m)}_0$$

$$\langle \psi^{(m)}_s \mid \psi^{(m)}_0 \rangle = 0 \qquad \text{both for s = 1,2,3...}$$

We shall see if this extra piece affects any of his later calculations.

What happens if we close our big equation above from the left with $\psi^{(m)}_0$? It seems to me that we get this result:

$$0 = -\langle \psi^{(m)}_0 \mid H' \mid \psi^{(m)}_{s-1} \rangle + W^{(m)}_s + A(m,s)$$

which then tells us that

$$W^{(m)}_s = -A(m,s) + \langle \psi^{(m)}_0 \mid H' \mid \psi^{(m)}_{s-1} \rangle$$

so <u>right off the bat we have a problem Houston</u>. For each expansion level s, A(m,s) is different, so we cannot treat it as a constant energy offset.

Plan C: fails. This plan made no sense at all, see scraps.

Well, maybe there is a better way out. Suppose you don't impose this condition from the start, and suppose we do our perturbation theory and somehow come up with a convergent series for $\psi^{(m)}$ that solves our problem. Then we certainly can rescale that final result $\psi^{(m)}$ such that $\langle \psi^{(m)}_0 \mid \psi^{(m)} \rangle = 1$. No question about it. In so doing, we are rescaling each term in the series. Suppose we came up with

$$\langle \psi^{(m)}_0 \mid \psi^{(m)} \rangle = \langle \psi^{(m)}_0 \mid \Sigma_{n=0} \lambda^n \psi^{(m)}_n \rangle = 5$$

$$\langle \psi^{(m)}_0 \mid \psi^{(m)}_0 \rangle + \lambda \langle \psi^{(m)}_0 \mid \psi^{(m)}_1 \rangle + \lambda^2 \langle \psi^{(m)}_0 \mid \psi^{(m)}_2 \rangle + ... = 5$$

which says

$$\lambda \langle \psi^{(m)}_0 \mid \psi^{(m)}_1 \rangle + \lambda^2 \langle \psi^{(m)}_0 \mid \psi^{(m)}_2 \rangle + ... = 4$$

But this is not taking me anywhere useful. What do I do next here? I could scale λ to get the RHS = 4, but how do I know I can get each term to be 0, etc etc etc.

In fact, it is useful to express the above state ψ_{mi} in this manner:

$$\psi_{m,i} = \varphi_i \oplus \chi_i \qquad \text{where } \varphi_i \in \mathcal{H}^{(m)} \qquad \text{and } \chi_i \in \mathcal{H}^{\perp}$$

$$\varphi_i = u_{m,i} + \Sigma_j B_{ij}\ u_{m,j} \qquad\qquad \chi_i = \Sigma_{k \neq m} B_{ik}\ u_k$$

Now suppose we form another basis in the m subspace by doing the following linear combinations

$$v_{m,s} = \Sigma_i\ c_{s,i}\ u_{m,i} \qquad\qquad u_{m,s} = \Sigma_i\ c^{-1}{}_{s,i}\ v_{m,i}$$

Now apply the operation $\Sigma_i\ c_{s,i}$ to the φ_i equation shown above to get

$$\Sigma_i\ c_{s,i}\ \varphi_i \ = \ \Sigma_i\ c_{s,i}\ u_{m,i} + \Sigma_i\ c_{s,i}\ \Sigma_j\ B_{ij}\ u_{m,j}$$

$$\varphi_s' \ = \ v_{m,s} + \Sigma_i\ c_{s,i}\ \Sigma_j\ B_{ij}\ u_{m,j}$$

where we have thus created now a new state φ_s' inside $\mathcal{H}^{(m)}$. We would now like to select the coefficients c such that the following is true, where B_s vanishes when $\lambda \rightarrow 0$, just like all the other B things,

$$\varphi_s' \ = \ v_{m,s} + B_s\ v_{m,s} \ = \ (1 + B_s)\ v_{m,s}$$

If we can find some states $v_{m,s}$ that make this be true, then the effect of the perturbation within $\mathcal{H}^{(m)}$ is solely to add a multiple of $v_{m,s}$, and none of the other $v_{m,r}$ are mixed in. Then we will have this situation for our perturbation theory "set up" :

$$\psi'_{m,i} = \ \varphi_i' \oplus \chi_i \ = \ (1 + B_s)\ v_{m,s} \ \oplus \ \Sigma_{k \neq m}\ B_{ik}\ u_k$$

which greatly resembles the non-degenerate perturbation theory starting point.

4. Finding the c coefficients and Bs eigenvalues. Now how can we select the c coefficients to make this happen? We need this to be true:

$$\Sigma_i\ c_{s,i}\ \Sigma_j\ B_{ij}\ u_{m,j} \ = B_s\ v_{m,s}$$

Now let's just start processing this thing:

$$\Sigma_i\ c_{s,i}\ \Sigma_j\ B_{ij}\ u_{m,j} \ = B_s\ (\Sigma_j\ c_{s,j}\ u_{m,j})$$

$$\Sigma_j\ \{\ \Sigma_i\ c_{s,i}\ B_{ij}\ \}\ u_{m,j} \ = \Sigma_j\ \{\ B_s\ c_{s,j}\ \}\ u_{m,j}$$

Since the $u_{m,j}$ span the m subspace, the above can only be true if:

$$\Sigma_i\ c_{s,i}\ B_{ij} = B_s\ c_{s,j}$$

$$\Sigma_i\ c_{s,i}\ B_{ij} = \Sigma_{s'}\ [\delta_{s,s'} B_{s'}]\ c_{s',j} \ = \Sigma_{s'} \Lambda_{ss'}\ c_{s',j}$$

where Λ is the diagonal matrix shown. We then have the following matrix equation

$$\Sigma_i\, c_{s,i}\, B_{ij} = \Sigma_{s'} \Lambda_{ss'}\, c_{s',j}$$

$$c\, B = \Lambda\, c \qquad\qquad B\, c^{-1} = c^{-1}\, \Lambda$$

$$c\, B\, c^{-1} = \Lambda$$

Thus, our matrix of coefficients c is seen to be the unitary transformation that diagonalizes B. So our problem of finding the c coefficients boils down to finding this unitary transformation. The first step we know is to find the eigenvalues B_s which are the diagonal elements of Λ. This comes from the secular equation, and to find that equation, we have to write things out as an eigenvector problem:

$$B\, c^{-1} = c^{-1}\, \Lambda$$

$$\Sigma_j\, B_{ij}\, c^{-1}{}_{jk} = \Sigma_j\, c^{-1}{}_{ij}\, \Lambda_{jk} = \Sigma_j\, c^{-1}{}_{ij}\, \delta_{jk} B_k = c^{-1}{}_{ik} B_k = B_k c^{-1}{}_{ik}$$

$$\Sigma_j\, B_{ij}\, c^{-1}{}_{jk} = B_k c^{-1}{}_{ik}$$

$$\Sigma_j\, B_{ij}\, [c^{-1}{}_k]_j = B_k\, [c^{-1}{}_k]_i$$

$$B\, [c^{-1}{}_k] = B_k\, [c^{-1}{}_k]$$

Here our matrix is B, our N eigenvectors are $[c^{-1}{}_k]$ with k as a label, and components $[c^{-1}{}_k]_i = c^{-1}{}_{ik}$, and our eigenvalues are the B_k. So rewrite this as

$$[\, B - B_k\, 1\,]\, [c^{-1}{}_k] = 0$$

and the secular equation is (which allows non-trivial solution vectors $[c^{-1}{}_k]$)

$$\det(B - B_k\, 1) = 0$$

and this determines our N eigenvalues B_k. The rows or columns of c or c^{-1} are then the coefficients we want. So let's assume that we can manually solve that whole problem.

Before continuing, let's just review what we did here. We had within the m subspace:

$$\varphi_s' = v_{m,s} + \Sigma_i\, c_{s,i}\, \Sigma_j\, B_{ij}\, u_{m,j}$$

$$\varphi_s' = v_{m,s} + \Sigma_i\, c_{s,i}\, \Sigma_j\, B_{ij}\, \Sigma_k\, c^{-1}{}_{j,k}\, v_{m,k}$$

$$\varphi_s' = v_{m,s} + \Sigma_k\, [\, \Sigma_i\, \Sigma_j\, c_{s,i}\, B_{ij}\, c^{-1}{}_{j,k}\,]\, v_{m,k}$$

We then sought c coefficients to have this be true

$$[\ \Sigma_i \Sigma_j\ c_{s,i}\ B_{ij}\ c^{-1}{}_{j,k}\ ] = B_s\ \delta_{s,k}$$

$$c\ B\ c^{-1} = \Lambda$$

Then we ended up with

$$\varphi_s' \quad = \quad v_{m,s} + B_s\ v_{m,s} \quad = (1 + B_s)\ v_{m,s}$$

Now let's continue with our perturbation theory.

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We select our states $v_{m,s}$ carefully as discussed above and we then have the following starting point for doing perturbation theory,

$$\psi'_{mi} = \varphi_i' \oplus \chi_i \ = \ (1 + B_i)\ v_{m,i} \ \oplus \ \Sigma_{k\neq m}\ B_{ik}\ u_k$$

where we now simplify by writing m,i = mi, ie, we remove this baggage comma.

We now want to follow our Plan D over Schiff Chapter 8 notes. First, rescale the solution as follows

$$\psi''_{mi} = \psi'_{mi} / (1 + B_s)$$

$$= \ v_{mi} \ \oplus \ \Sigma_{k\neq m}\ a_{ik}\ u_k \qquad\qquad \text{where} \quad a_{ik} = B_{ik}/ (1 + B_s)$$

Let's now drop the double-prime on ψ since this is the thing we will be "working with" ,

$$\psi_{mi} \ = \ v_{mi} \ \oplus \ \Sigma_{k\neq m}\ a_{ik}\ u_k$$

where remember that these u_k shown on the right are all in $\mathcal{H}^{\perp}$. Consider then

$$< v_{mi} \mid \psi_{mi} > \ = \ 1$$

$$< v_{mj} \mid \psi_{mi} > \ = \ 0 \quad j \neq i$$

$$< u_k \ \mid \psi_{mi} > \ = \ a_{ik}$$

$$< \psi_{mi} \mid \psi_{mi} > \ = \text{some positive number that is most probably } \textit{not} \text{ unity!}$$

$$< v_{mi} \mid \Sigma_{k\neq m}\ a_{ik}\ u_k > = 0$$

The trick now is to expand the *correction coefficients* in λ :

$$a_{ik} = \Sigma_{n=0}\ \lambda^n\ a_{ik,n}$$

Since we know that $\psi_{mi} = v_{mi}$ when $\lambda = 0$, we know that

$$a_{ik,0} = 0$$

so we could write

$$a_{ik} = \Sigma_{n=1} \lambda^n a_{ik,n}$$

Now go way back to our original perturbation problem which is summarized in these statements:

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Derive a new (31.6). Above we had

$$a_{ik} = \Sigma_{n=1} \lambda^n a_{ik,n}$$

$$\psi_{mi} = v_{mi} \oplus \Sigma_{k \neq m} a_{ik} u_k$$

$$\Sigma_{n=0} \lambda^n \psi_{mi,n} = v_{mi} \oplus \Sigma_{k \neq m} (\Sigma_{n=1} \lambda^n a_{ik,n}) u_k$$

$$\Sigma_{n=1} \lambda^n \psi_{mi,n} = \Sigma_{k \neq m} (\Sigma_{n=1} \lambda^n a_{ik,n}) u_k = \Sigma_{n=1} \lambda^n \{ \Sigma_{k \neq m} a_{ik,n} u_k \}$$

$$\Rightarrow \quad \psi_{mi,n} = \Sigma_{k \neq m} a_{ik,n} u_k \qquad n = 1,2,3....$$

Therefore we have

$$< v_{mj} | \psi_{mi,n} > = 0 \qquad n = 1,2,3... \qquad \text{which is our new 31.6}$$

This was the thing that got me so mystified in the Chap 8 notes but which now makes sense. All the corrections $\psi_{mi,n}$ lie in $\mathcal{H}^{\perp}$, so the corrections are orthogonal to anything in $\mathcal{H}^{(m)}$. Notice that our new version of 31.6 now applies for any i,j in $\mathcal{H}^{(m)}$, so the result is a little different that the old 31.6.

Derive a new (31.7). Start with our "big equation",

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

Let's rewrite this now like so

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

Close from the left with $< v_{mj}| = < \psi_{mj,0}|$. The LHS gives 0 due to the left-action of $(H_0 - E_m)$. We pick up an H' term, and then we pick up a hit from the term on the right which has s-j=0 or j = s. Thus

$$0 = - < v_{mj}| H' \ |\psi_{mi,s-1}> + W_{mi,s} < v_{mj} \mid v_{mi}>$$

=> (1)	$W_{mi,s} = < v_{mi}\| H' \ \|\psi_{mi,s-1}>$	$j = i$	31.7 A	$s = 1,2,3...$
(2)	$0 = < v_{mj}\| H' \ \|\psi_{mi,s-1}>$	$j \neq i$	31.7 B	$s = 1,2,3...$

Is this item (2) new, or is it already expected? It seems new to me. It implies several things:

$< v_{mj}\| H' \ \| v_{mi} > = 0$	$j \neq i$	if $s = 1$
$< v_{mj}\| H' \ \|\psi_{mi,s-1}> = 0$	$j \neq i$	if $s > 1$

If this is really true, it seems to me that this must be true:

$$< v_{mj}| H' \ |\psi_{mi}> = 0 \qquad j \neq i$$

because it is true in each λ order. Recall that $\psi_{mi} = v_{mi} \oplus \Sigma_{k\neq m} a_{ik} u_k$. The implication then is that

$$< v_{mj}| H' \ | \Sigma_{k\neq m} a_{ik} u_k > = 0 \qquad j \neq i$$

$$\Sigma_{k\neq m} a_{ik} < v_{mj}| H' \ | u_k > = 0 \qquad j \neq i$$

This really does seem new to me and I am not sure whether or not it is true. We expect that H' can cross between the two spaces $\mathcal{H}^{(m)}$ and $\mathcal{H}^{\perp}$. Let's let this ride for the time being. We have successfully arrived at a new 31.7 which is this

$$W_{mi,s} = < v_{mi}| H' \ |\psi_{mi,s-1}> \qquad s = 1,2,3...$$

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$$\psi_{mi,1} = \Sigma_{k\neq m} a_{ik,1} u_k$$

so the above says

$$(H_0 - E_m) \Sigma_{k\neq m} a_{ik,1} u_k = (W_{mi,1} - H') v_{mi}$$

Close this from the left with some $u_{k'}$ in $\mathcal{H}^{\perp}$ to get

$$\Sigma_{k\neq m}\, a_{ik,1} \langle u_{k'}| (H_0 - E_m) |u_k\rangle = \langle u_{k'}| (W_{mi,1} - H') |v_{mi}\rangle = - \langle u_{k'}| H' |v_{mi}\rangle$$

The LHS allows H_o to be replaced by $E_{k'}$ and then $\langle k' |k\rangle = \delta_{k',k}$ which kills off the sum, so

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

$$(E_k - E_m)\, a_{ik,1} = - \langle u_k| H' |v_{mi}\rangle \qquad k \neq m$$

$$a_{ik,1} = \langle u_k| H' |v_{mi}\rangle /(E_m - E_k) \qquad k \neq m$$ which is 31.10.

So there we have it. We have computed the first order energy correction, and the first order wavefunction correction. Recall that

$$\psi_{mi,1} = \Sigma_{k\neq m}\, a_{ik,1}\, u_k = \Sigma_{k\neq m} \{ \langle u_k| H' |v_{mi}\rangle /(E_m - E_k) \}\, u_k$$

$$\psi_{mi} \approx v_{mi} + \lambda\, \psi_{mi,1}$$

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

Happily, we know that $\Sigma_{k\neq m}$ is only over k in $\mathcal{H}^{\perp}$ so we don't get any denominator blow ups. Again, it depends on the nature of H' whether or not degeneracy is lifted for a state |mi> in first order.

Note also that we have to know what the v_{mi} are in order to compute this matrix element. We looked into that issue in a general way above, but now how would be actually do it in practice?

7. Comment on the invalidity of our first starting point.

That starting point was this:

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

Our fundamental equations 31.4 come only from the SE and don't depend on "starting point" and the s=1 equation says this:

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Schiff page 245 equation 31.4 second line says this:

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

Now given our u_{mi} starting point, this says that

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

Now suppose we close this with u_{mj} where $j \neq i$. The $(H_0 - E_m)$ kills to the left giving 0. We get

$$0 = - < u_{mj} | H' | u_{mi} >$$

But WHY should this be true?? It seems very likely it would NOT be true.

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We can then evaluate (where $X_{xxx,n}$ represents the λ order n of something)

$$\psi_{mi,1} = \Sigma_j B_{ij,1}\ u_{mj} \ \oplus\ \Sigma_{k \neq m} B_{ik,1}\ u_k$$

If we insert this into our s=1 31.4 we get

$$(H_0 - E_m)\ \{ \Sigma_j B_{ij,1}\ u_{mj} \ \oplus\ \Sigma_{k \neq m} B_{ik,1}\ u_k \} = (W_{mi,1} - H')\ u_{mi}$$

$$0 \ \oplus\ \Sigma_{k \neq m} B_{ik,1}\ (E_k - E_m)\ u_k \ = \ (W_{mi,1} - H')\ u_{mi}$$

Close this equation with <mj| where $j \neq i$. We get

$$0 \oplus 0 \ = \ < u_{mj} |H' | u_{mi} > \ = 0$$

I am having a LOT of trouble understanding this result. Why should H' be diagonal inside the m subpace??

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Now close this first with some $u_{k'}$ in $\mathcal{H}^{\perp}$

$$B_{ik',1}\ (E_{k'} - E_m) \ = \ - < k' | H' | mi>$$

and this seems a reasonable thing and lets us compute

$$B_{ik,1} \ = < k | H' | mi> / (E_m - E_k)$$

But now close the same equation with some u_{mj} in $\mathcal{H}^{(m)}$

$$0 \oplus 0 \ = \ <mj| \ (W_{mi,1} - H')\ mi>$$

In the case that j = i, we get this reasonable result:

$$W_{mi,1} \ = <mi | H' | mi >$$

In the case that $j \neq i$, we get instead this result

$$<mj \mid H' \mid mi> = 0 \qquad i \neq j$$

BUT: this is a contradiction because in general there is no reason for some H' not to link different states within the m subspace. Therefore, our "starting position" is inconsistent with doing perturbation theory except maybe in special cases where H'_{ji} just happens to be 0 for all unequal state pairs in the subspace.

Now for comparison, let's examine our *second* starting point which is this:

$$\psi_{mi} = \varphi_i \oplus \chi_i = v_{mi} + B_i\, v_{mi} \oplus \Sigma_{k\neq m} B_{ik}\, u_k$$

and let's again look at our s=1 version of 31.4

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

where now we have $\psi_{mi,0} = v_{mi}$. Then we find:

$$\psi_{mi,1} = B_{i,1}\, v_{mi} \oplus \Sigma_{k\neq m} B_{ik,1}\, u_k$$

So insert this into the previous equation to get

$$0 \oplus \Sigma_{k\neq m} B_{ik,1} (E_k - E_m)\, u_k = (W_{mi,1} - H')\, v_{mi}$$

Close with <k'| and get the same result as before. Close with v_{mj} and also get same results as before. In particular we will still get

$$0 = <v_{mj} \mid H' \mid v_{mi}> \qquad \text{when } j \neq i$$

Now is THIS more reasonable than before for some reason? Is it possible to shuffle the u_{mi} states into v_{mi} states such that there are no off diagonal elements of H' ? Aha!! So this transformation must be the one which diagonalizes H' ! Light bulb goes off. Only if you use states $|v_{mi}>$ which diagonalize H' is your perturbation theory self-consistent!

Theorem 1: The states $v_{mj} = \Sigma_i\, c_{ji}\, u_{mi}$ must be chosen to diagonalize H' . Then perturbation theory can be done.

Proof: if H' is not diagonal, we get the inconsistency noted above.

Question: is the diagonality of H' in the v basis connected with our "second starting point" somehow?

Go back again to the "first" starting point:

$$\psi_{mi} = \{ u_{mi} + \Sigma_j B_{ij} u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} u_k$$

Does this form really cause any problems other than the inconsistency above if H' is non-diagonal? Maybe it is OK. What happens if we just try this thing in our $H\psi_{mi} = W_{mi}\psi_{mi}$ equation. Does anything bad happen? Let's write it out:

$(H_0 + H')\ \psi_{mi} = W_{mi}\psi_{mi}$ for ψ_{mi} which "starts out" in $\mathcal{H}^{(m)}$

$(H_0 + H')\ \psi_k = W_k\psi_k$ for ψ_k which "starts out" in $\mathcal{H}^{\perp}$

Now consider only the first equation above and insert our expansions

$$(H_0 + H') [\{ u_{mi} + \Sigma_j B_{ij} u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} u_k] = W_{mi} [\{ u_{mi} + \Sigma_j B_{ij} u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} u_k]$$

There are two terms to consider on the LHS, the H_0 term and the H' term:

$$\text{LHS } H_o \text{ term} = E_m \{ u_{mi} + \Sigma_j B_{ij} u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} E_k u_k$$

$$\text{LHS H' term} = H' [\{ u_{mi} + \Sigma_j B_{ij} u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} u_k]$$

$$\text{RHS} = \{W_{mi} u_{mi} + \Sigma_j B_{ij} W_{mi} u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} W_{mi} u_k]$$

Notice that the " LHS H' term" is going to "break" the a ⊕ b structure. That is to say, probably H' applied to some u_{mj} is going to result in components in both $\mathcal{H}^{(m)}$ and $\mathcal{H}^{\perp}$. Thus it would be *wrong* to attempt a naive separate subspace equality. Let's write our equation this way:

$$\text{LHS H' term} = \text{RHS} - \text{LHS } H_o \text{ term}$$

Then we have

$$\text{RHS} - \text{LHS } H_o \text{ term}$$

$$= \{[W_{mi}-E_m] u_{mi} + \Sigma_j B_{ij} [W_{mi}-E_m] u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} [W_{mi}-E_k] u_k$$

where we do have subspace decomposition here. But then

$$\text{LHS H' term} = \{ H'u_{mi} + \Sigma_j B_{ij} H' u_{mj} \} + \Sigma_{k \neq m} B_{ik} H'u_k$$

and here there is no longer a separation, so we se use a regular + to indicate this fact. So we end up with this huge equation that I don't know if we can even make use of (I am looking for inconsistency right now)

$$\{ H'u_{mi} + \Sigma_j B_{ij} H' u_{mj} \} + \Sigma_{k \neq m} B_{ik} H'u_k =$$

$$\{[W_{mi}-E_m] u_{mi} + \Sigma_j B_{ij} [W_{mi}-E_m] u_{mj} \} \oplus \Sigma_{k \neq m} B_{ik} [W_{mi}-E_k] u_k$$

All I know how to do is close this with states from the left.

(1) So let's first close with $u_{k'}$ in $\mathcal{H}^{\perp}$ to get

$$\{ \langle k'|H'|mi\rangle + \Sigma_j B_{ij} \langle k'|H'|mj\rangle \} + \Sigma_{k\neq m} B_{ik} \langle k'|H'|k\rangle = B_{ik'} [W_{mi}-E_{k'}]$$

This messy result links together lots of H' matrix elements and W_{mi} and $E_{k'}$ and all the B_{ij} and B_{ik}. You might ask: why not just diagonalize H' in the entire Hilbert Space $\mathcal{H}^{(m)} \oplus \mathcal{H}^{\perp}$. But if we knew how to do that, we would not be doing perturbation theory. So I guess all I can say about the above messy equation is this: I see no glaring inconsistencies.

(2) Next, let's close with $u_{m\ell}$ in $\mathcal{H}^{(m)}$ and see what happens in that case: $m\ell$

$$\{ \langle m\ell|H'|mi\rangle + \Sigma_j B_{ij} \langle m\ell|H'|mj\rangle \} + \Sigma_{k\neq m} B_{ik} \langle m\ell|H'|k\rangle = [W_{mi}-E_m] \{ \delta_{\ell i} + B_{i\ell} \}$$

I see nothing glaringly inconsistent at this point. But now let's assume we have chosen a basis that diagonalizes H' within $\mathcal{H}^{(m)}$. Then this says

$$\delta_{\ell i} \langle mi|H'|mi\rangle + B_{i\ell} \langle m\ell|H'|m\ell\rangle + \Sigma_{k\neq m} B_{ik} \langle m\ell|H'|k\rangle = [W_{mi}-E_m] \{ \delta_{\ell i} + B_{i\ell} \}$$

which we write out in the two cases.

(2: ℓ=i) First, here is the ℓ = i case:

$$\langle mi|H'|mi\rangle + B_{ii} \langle mi|H'|mi\rangle + \Sigma_{k\neq m} B_{ik} \langle mi|H'|k\rangle = [W_{mi}-E_m] \{ 1 + B_{ii} \}$$

$$(1 + B_{ii}) \langle mi|H'|mi\rangle + \Sigma_{k\neq m} B_{ik} \langle mi|H'|k\rangle = [W_{mi}-E_m] (1 + B_{ii})$$

$$[W_{mi} - E_m - \langle mi|H'|mi\rangle] (1 + B_{ii}) = \Sigma_{k\neq m} B_{ik} \langle mi|H'|k\rangle$$

This looks OK. The bracket on the LHS is probably the corrected energy 2nd order and beyond. Notice that the $\mathcal{H}^{(m)}$ numbers B_{ij} for i≠j don't even enter here, so would not matter whether you used the u or the v function basis, so either starting point seems OK in the case that H' is diagonal in $\mathcal{H}^{(m)}$. We could rewrite that above in this way

$$(1 + B_{ii}) = \Sigma_{k\neq m} B_{ik} \langle mi|H'|k\rangle / [W_{mi} - E_m - \langle mi|H'|mi\rangle]$$

(2: $\ell \neq$ i) Now the $\ell \neq$ i case says this

$$B_{i\ell} \langle m\ell|H'|m\ell\rangle + \Sigma_{k\neq m} B_{ik} \langle m\ell|H'|k\rangle = [W_{mi}-E_m] B_{i\ell}$$

$$[W_{mi}-E_m - \langle m\ell|H'|m\ell\rangle] B_{i\ell} = \Sigma_{k\neq m} B_{ik} \langle m\ell|H'|k\rangle$$

This seems to give an expression for the $B_{i\ell}$ as follows:

$$B_{i\ell} = \Sigma_{k\neq m} B_{ik} \langle m\ell|H'|k\rangle [W_{mi} - E_m - \langle m\ell|H'|m\ell\rangle] \qquad i \neq \ell$$

Theorem 2: Diagonalizing H' does not in general require that $B_{i\ell}$ be diagonal within $\mathcal{H}^{(m)}$.

Proof: above we have a formula for Bi_ℓ and it certainly does not seem to vanish.

Conclusion: My "second starting point" with the v basis is no better than my "first starting point" with the u basis, so all that effort of getting to this second starting point was a complete waste. So here I sit, having gotten nowhere at all in my private effort to do degenerate perturbation theory. Too bad, nice try.
I did seem to obtain two theorems however. The first says you have to diagonalize H' in the m subspace if you expect to do perturbation theory. The second says the first starting point is OK provided you diagonalize H' with your basis in the m subspace.

7. Review the question of how the $|\, v_{mi} >$ are actually computed.

It took me a whole day to just write down all of the above, after getting totally confused in the morning. The Hilbert Space idea helped a lot. But now I don't really see how you would actually solve a problem. I need to somehow relate things like B_{ik} to H' which I have not done at all. This will be where I continue next time.

Recall from above that

$$a_{ik} = B_{ik}/(1 + B_s) \qquad k \text{ in } \mathcal{H}^{\perp}$$

where B_s are the eigenvalues of B_{ij} within the m subspace.

Theorem A: 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 $H_0 u_{mi} = E_m u_m$ 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. In particular, the equation which equates λ^1 on both sides says this:

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

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:

$$0 = \langle u_{mj} \,|\, H' \,|\, u_{mi} \rangle \qquad \text{for any } j \neq i$$

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.

Theorem B: It is possible to normalize ψ_{mi} such that $\langle u_{mi}|\, \psi_{mi,n}\rangle = 0$ 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},

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

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

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

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

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

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), since u_{mi} is presumed normalized, the normalization of ψ'_{mi} is fixed by the above choice, and we cannot then further 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 change the normalization of ψ'_{mi} to get unity.

Theorem C: $W_{mi,s} = \langle u_{mi}|\, H' \,|\, \psi_{mi,s-1}\rangle$ (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 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)

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

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. This, 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

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

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

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

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

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

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

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

This last says

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

which is like the corresponding Schiff equation but we have "rest" in here now. Now close with mj ≠ mi:

$$0 = - \langle u_{mj} | H' | u_{mi} \rangle$$

We STILL seem to have this diagonal H' appearing, I cannot make it go away!

But suppose I go back and try it this way: