Chapter 6

1) Time-Independent Perturbation Theory

Perturbation theory deals with getting ~~solu~~ approximate solutions for systems that are PERTURBED to some degree from systems for which known solutions exist. The known solutions may be exact or approximations themselves.

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The <u>perturbation</u> is some relatively small change in <u>Hamiltonian</u> from the Hamiltonian of the unperturbed system.

Usually ~~the perturbation is~~ a ~~change in~~ perturbation potential.

→ But other kinds of perturbations exist. — e.g., fields for which ~~potentials~~ don't exist (i.e., vector potential of E&M), changes to the kinetic energy operator to account for relativistic effects to low order

True
?

Time-independent perturbation Theory

deals with finding the perturbed stationary states.

It's really simple in principle {Actually, there are a few more tricky bits in the derivations than I'd remembered.} but real applications are often tough.

[There is classical perturbation theory too which is similar in concept to QM perturbation theory, but I know little of it — it's been bypassed in my education.]

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2) Non-Degenerate Time-Independent Perturbation Theory

We first introduce the perturbation parameter λ.

It allows us to mathematically control the amount of perturbation and to easily understand and keep track of the order of perturbation.

In real cases, ~~where~~ perturbation cannot be controlled $\lambda = 1$.

But there are many experimental cases where the perturbation can be controlled (e.g., turning up or down a magnetic field), and so ~~it is very useful to have λ around.~~ there is a real λ.

So overall λ is formally and practically useful and I don't set it any particular value in the formalism — but only in particular applications.

Say H_0 is the original unperturbed Hamiltonian

(I lied, I'm not introducing λ first)

and it is assumed that we know complete set of solutions and eigenvalues

We assume an ortho-normal set since if not we can always construct an equivalent set that is.

and there is no degeneracy.

Thus

$$H_0 |\psi_{0i}\rangle = E_{0i} |\psi_{0i}\rangle$$

and we know set $\{|\psi_{0i}\rangle\}$

and all E_{0i} and

$$E_{0i} \neq E_{0j} \text{ if } i \neq j$$

(i.e., no degeneracy).

Since $\{|\psi_{0i}\rangle\}$ is a complete set for the space of the system, ~~and~~ a general state $|\psi_{gen}\rangle$ of that space can be expanded in $\{|\psi_{0i}\rangle\}$: i.e.

$$|\psi_{gen}\rangle = \sum_i c_i |\psi_{0i}\rangle$$

Now say we come along and change the Hamiltonian — i.e., perturb it.

by adding λH_1

where H_1 is the perturbation Hamiltonian an λ is the aforediscussed perturbation parameter. — a pure real.

∴ The new or perturbed ~~Hamiltoxeon~~ Hamiltonian is

$$H = H_0 + \lambda H_1$$

Since $H = H^\dagger$ and $H_0 = H_0^\dagger$, $H = H^\dagger = H_0^\dagger + \lambda H_1^\dagger = H_0 + \lambda H_1$, $H_1 = H_1^\dagger$ and so H_1 is Hermitian

In principle, $\lambda \in (-\infty, \infty)$, but if $|\lambda|$ is too large the perturbation approach fails. Too large depends on the particular case.

What we what is to solve

$$H|\psi_i\rangle = E_i|\psi_i\rangle$$

for the set $\{|\psi_i\rangle\}$ and eigenvalues E_i

Well it's something like Taylor's series.

and ~~we~~ we just can't do that exactly or it's too hard.

Really a Taylor's expansion?? → For any specific ~~constant~~ values it is. But it is an expansion of functions

Then we can Taylor expand ~~both~~ $|\Psi_i\rangle$ and E_i

about, respectively $|\Psi_{0i}\rangle$ and E_{0i}. with respect to λ.

All math tells us this should be possible for sufficient smooth functions of λ.

A key point. $|\Psi_i\rangle$ is required to stay normalized as λ is varied. This requirement is a key constraint in constructing the $|\Psi_{mi}\rangle$'s. There must be some way to maintain normalization ~~& (a)~~ real $|\Psi_i\rangle$ is a real variation on $|\Psi_{0i}\rangle$

~~$|\Psi_i\rangle = \sum_{m=0}^{\infty} \lambda^m |\Psi_{0im}\rangle$~~

~~0 means~~ unpe

$$|\Psi_i\rangle = \sum_{m=0}^{\infty} \lambda^m |\Psi_{mi}\rangle$$

Note $|\Psi_{0i}\rangle$ is the unperturbed state and also the zeroth order perturbed state

$|\psi_{1i}\rangle$ is the 1st order perturbation correction state

and $|\psi_i^{1st}\rangle = |\psi_{0i}\rangle + \lambda|\psi_{1i}\rangle$

is the 1st order corrected state.

The two are clearly distinct things, but in discussion it's easy to mix them up.

Then there's $|\psi_{2i}\rangle$ and $|\psi_i^{2nd}\rangle$

etc.

Similarly $$E_i = \sum_{\ell=0}^{\infty} \lambda^\ell E_{\ell i}$$

E_{0i} is the ~~zeroth ord~~ unperturbed energy

E_{1i} is the 1st order correction

E_i^{1st} is the 1st order corrected energy

6-10) $|\Psi_{0i}\rangle$ and E_{0i} are the solutions of ~~Substituting~~ the original Hamiltonian H_0, of course.

Both expansions should converge for λ sufficiently small.

Even if one has convergence, if the convergence is slow perturbation theory may be impractical or impracticable

But if λ is too large, they may not — and then perturbation theory fails and one needs a non-perturbative method — like diagonalizing the Hamiltonian H which we've already covered briefly and will reiterate below.

a series is only a solution when converges e.g.: $\frac{1}{1-r} = \sum_{\ell=0}^{\infty} r^{\ell}$ but $|r|>0$ LHS is something but RHS is $\to\infty$

Substituting the expansions into

$$H|\Psi_i\rangle = E_i|\Psi_i\rangle$$

gives

$$H\sum_{m=0}^{\infty}\lambda^m|\Psi_{mi}\rangle = \left(\sum_{\ell=0}^{\infty}\lambda^{\ell}E_{\ell i}\right)\left(\sum_{m=0}^{\infty}\lambda^m|\Psi_{mi}\rangle\right)$$

Now $H = H_0 + \lambda H_1$

but for symmetry I like to use

$$H = \sum_{\ell=0}^{\infty} \lambda^\ell H_\ell$$

~~and~~ with $H_\ell = 0$ ~~for~~ $\ell \geq 2$.

It just makes the formalism clearer I think.

Thus of eigenproblem is

$$\left(\sum_{\ell=0}^{\infty} \lambda^\ell H_\ell\right)\left(\sum_{m=0}^{\infty} \lambda^m |\psi_{mi}\rangle\right) = \left(\sum_{\ell=0}^{\infty} \lambda^\ell E_{\ell i}\right)\left(\sum_{m=0}^{\infty} \lambda^m |\psi_{mi}\rangle\right)$$

$$\sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty} \lambda^{\ell+m} H_\ell |\psi_{mi}\rangle = \sum_{\ell=0}^{\infty}\sum_{m=0}^{\infty} \lambda^{\ell+m} E_{\ell i} |\psi_{mi}\rangle$$

Now what we'd like is separate equations to solve for each order of perturbation. (i.e., 0th, 1st, 2nd etc.)

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So first we'd like to ~~re arrange~~ re-order the double sums to get the λ's with a single index.

We can do this if all the series are <u>absolutely convergent</u> (Arfken - 252)

Products of absolutely convergent series are sum of the products of the terms and are also absolutely convergent

ie. series $\sum_i a_i$ is absolutely convergent if $\sum_i |a_i|$ converges not just $\sum_i a_i$ converges.

We assume our series have this property

Re-ordering is a tricky business, but it's NOT so bad for double summations

Imagine double sum

$$\sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} a_{\ell m} \quad \text{and}$$

we lay the terms out on a table

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$\ell \backslash m$	0	1	2	3	
0	a_{00}	a_{01}	a_{02}	a_{03}	$\cdots$
1	a_{10}	a_{11}	a_{12}	a_{13}	$\cdots$
2	a_{20}	a_{21}	a_{22}	a_{23}	$\cdots$
3	a_{30}	a_{31}	a_{32}	a_{33}	$\cdots$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

Written $\sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} a_{\ell m}$ it looks like you add up the terms infinite row by infinit row,

but with absolute convergence of the double series, we can add up finite diagonal by finite diagonal.

6-14

$\ell \backslash m$	0	1	2	
0	a_{00}	a_{01}	a_{02}	$\ldots$
1	a_{10}	a_{11}	a_{12}	
2	a_{20}	a_{21}	a_{22}	
	$\vdots$			

Let $n = \ell + m$, $n = 0, 1, 2, \ldots$

$k = 0, 1, \ldots, n$

and $m = k = 0, 1, \ldots, n$

$\ell = n - m = n - k = n, n-1, \ldots, 0$

$$\therefore \sum_{\ell=0}^{\infty} \sum_{m=0}^{\infty} a_{\ell m} = \sum_{n=0}^{\infty} \sum_{k=0}^{n} a_{n-k\,k}$$

(actually written so going down the diagonal)

which in our case (see p. 6-11) gives

$$\sum_{n=0}^{\infty} \lambda^n \sum_{k=0}^{n} H_{n-k} |\psi_{ki}\rangle = \sum_{n=0}^{\infty} \lambda^n \sum_{k=0}^{n} E_{n-k\,i} |\psi_{ki}\rangle$$

We now see we have
a <u>power series in λ</u>
on both sides of equality.

We assume both series
have <u>uniform convergence</u>
over (Arfken - 255)
the relevant region.

Then in that <u>region</u>, the power
series must be <u>unique</u>
(Arfken - 268)

If $f(x) = \sum_{n=0}^{\infty} a_n x^n$

$$= \sum_{n=0}^{\infty} b_n x^n ,$$

then $a_n = b_n$

— uniqueness of power series

6-16

So we now have

$$\sum_{k=0}^{n} H_{n-k} |\Psi_{ki}\rangle = \sum_{k=0}^{n} E_{n-k\,i} |\Psi_{ki}\rangle$$

Recall only H_0 and H_1 are non-zero.

which holds for $n = 0, 1, 2, \dots$

So here we have equation that involves E_{li} for $l = 0, \dots, n$ and $|\Psi_{mi}\rangle$ for $m = 0, \dots, n$.

This suggests we can solve for each order of perturbation n making use of the solutions of lower order $n' = 0, \dots, n-1$

And so we can in principle.
In practice if a 2nd order solution is not good enough, then I think people give up and go on to something else.

The formalism for going to 5th order has been developed (Gr-256)— — but does it ever get used in practice? Maybe there are special applications.

But usually I think people give up on perturbation theory if 2nd order is NOT accurate enough ~~and~~ and do something else — e.g., diagonalize the matrix.

3) An Important Normalization Result that is Often Glossed Over

— Gr-253 glosses over it

— but Cohen-Tannoudji doesn't, of course.

We demand $|\psi_0\rangle$ and $|\chi\rangle$ both be normalized. A physical requirement.

I've suppressed the state index i for simplicity here

6-18

$$\langle \psi_0 | \psi_0 \rangle = 1$$

$$\langle \psi | \psi \rangle = 1$$

But recall $|\psi\rangle = \sum_{k=0}^{\infty} \lambda^k |\psi_k\rangle$

valid as λ varies over the ~~range of~~ region of convergence.

If $|\psi\rangle$ is going to stay normalized as λ varies and the corrections $|\psi_k\rangle$ are to stay fixed, then that imposes constraints on the $|\psi_k\rangle$. { ~~Except for k=0 $|\psi_0\rangle$ they are corrections and~~ NOT states and are NOT normalized

We really believe the expansion should work → So those constraints are necessary and they are NOT overconstraints.

$\langle \psi_k | \psi_k \rangle \neq 1$ in general for $k > 0$

Remember the $|\psi_k\rangle$ for $k>0$ are not full states

They are corrections

$\therefore$ $\langle\psi_k|\psi_k\rangle \neq 1$ for $k>0$ in general.

but $\langle\psi_k|\psi_k\rangle$ are pure real

and $\langle\psi_k|\psi_k\rangle \geq 0$ where the equality ~~unless~~ holds only if $|\psi_k\rangle = 0$ (Gr-439)

We do have some <u>freedom</u> in setting the form of the constraints. — the freedom does change any physical result.

There is a <u>conventional</u> ~~cho~~ way to use the freedom.

<u>Freedom of Conventional Choice</u>

$\langle\psi_0|\psi\rangle =$ a complex number in general

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$\langle \chi_0 | \chi \rangle = re^{i\theta}$ is the number in polar form

r is magnitude
θ is phase.

Say we demand the global phase of $|\chi\rangle$ to be such that $\theta = 0$

— The global phase of a state is physically arbitrary and so we are free to make this demand.

[The results we derive having made this demand enforce that the demand is satisfied]

Having made the demand

$\langle \chi_0 | \chi \rangle$ = a pure real number

$$\langle\psi_0|\psi\rangle = \sum_{k=0}^{\infty} \lambda^k \langle\psi_0|\psi_k\rangle$$

pure real

λ are pure real by the Taylor expansion assumption

corrections are λ independent by our Taylor's series expansion assumption

If we vary λ over the whole range of convergence, it seems that all $\langle\psi_0|\psi_k\rangle$ must be pure real too, to keep $\langle\psi_0|\psi\rangle$ pure real.

We can prove this:

$$\frac{\partial^{\ell}}{\partial\lambda^{\ell}}\langle\psi_0|\psi\rangle\Big|_{\lambda=0} = \ell!\,\langle\psi_0|\psi_\ell\rangle$$

- pure real by our demand.

$\therefore$ this is pure real where ℓ is general.

$\therefore$ $\langle\psi_0|\psi\rangle$

and all $\langle\psi_0|\psi_k\rangle$ are pure real.

Having used our freedom of setting the global phase factor of $|\psi\rangle$ to make the ~~our~~ conventional choice, let us now see what the <u>normalization</u> constraint imposes.

$$1 = \langle \psi | \psi \rangle = \sum_{k=0}^{\infty} \sum_{\ell=0}^{\infty} \lambda^{k+\ell} \langle \psi_k | \psi_\ell \rangle$$

$$= \sum_{n=0}^{\infty} \lambda^n \sum_{m=0}^{n} \langle \psi_{n-m} | \psi_m \rangle$$

We use exactly the same re-ordering as on p. 6-14

The $n=0$ term is just $\lambda^0 \langle \psi_0 | \psi_0 \rangle = 1$.

We cancel 1 from both sides

$$0 = \sum_{n=1}^{\infty} \lambda^n \sum_{m=0}^{n} \langle \psi_{n-m} | \psi_m \rangle$$

This is a power series.

On the left-hand side is a power series where all coefficients are zero.

By the uniqueness of power series (Art-268) (assuming uniform convergence; Art-255 — which we have anywhere in the ~~radius~~ region defined by the radius of convergence),

we ~~have that~~ all coefficients on the right-hand side must be zero too.

$\therefore$ for $n \geq 1$, $\sum_{m=0}^{\infty} \langle \psi_{n-m} | \psi_m \rangle = 0$

$n=1$, $\langle \psi_1 | \psi_0 \rangle + \langle \psi_0 | \psi_1 \rangle = 0$

$n=2$, $\langle \psi_2 | \psi_0 \rangle + \langle \psi_1 | \psi_1 \rangle + \langle \psi_0 | \psi_2 \rangle = 0$

and so on.

But $\langle \psi_0 | \psi_k \rangle$ is pure real for all k (see p. 6-22)

$\therefore$ $n=1$, $0 = 2\langle \psi_0 | \psi_1 \rangle$

$0 = \langle \psi_0 | \psi_1 \rangle$

and boy it took a lot of machinery to ~~proof~~ prove this simple but essential little result.

$n=2$, $0 = \underbrace{\langle \psi_1 | \psi_1 \rangle}_{} + 2\underbrace{\langle \psi_0 | \psi_2 \rangle}_{}$

~~Not =1~~ since the $|\psi_k\rangle$ for $k \geq 1$ are not states but only state corrections recall

pure real since a vector inner product with itself and ≥ 0

pure real by p. 6-21

$\therefore$ $\langle \psi_0 | \psi_2 \rangle = -\frac{1}{2}\langle \psi_1 | \psi_1 \rangle \leq 0$

(CT-1097)

We don't need the $n = 2, 3, 4, \ldots$ inner product relations, but they are needed for high order perturbation corrections than we will do.

So all the derivation from

$p^{6\text{-}17}$ $\cancel{\langle \Psi_0 | \Psi_1 \rangle = 0}$

is to prove $\langle \Psi_0 | \Psi_1 \rangle = 0$

or to restore the state index

$$\langle \Psi_{0i} | \Psi_{1i} \rangle = 0$$

Note $|\Psi_{1i}\rangle = \sum_m c_{1im} |\Psi_{0m}\rangle$ an expansion in the complete set of $\{|\Psi_{0i}\rangle\}$ which we can always assume is orthonormal

Now $0 = \langle \Psi_{0i} | \Psi_{1i} \rangle = \sum_m c_{1im} \underbrace{\langle \Psi_{0i} | \Psi_{0m} \rangle}_{\delta_{im}}$

$= c_{1ii}$

So $c_{1ii} = 0$. $\Big\{$ A lot of work to prove this but it had to be done.

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4) Now expansion in the Complete set $\{|\Psi_{oi}\rangle\}$

Omit from ~~[illegible]~~ vocal lecturing. Just following up a detail. Skip to p. 6-29

Recall $\{|\Psi_{oi}\rangle\}$ is a complete set for the space of the system of interest.

We assume $\{|\Psi_{oi}\rangle\}$ is orthonormal since a complete can be always made orthonormal if it is not originally.

We can expand the state corrections in the complete set.

$$|\Psi_{ki}\rangle = \sum_m c_{kim} |\Psi_{om}\rangle$$

correction k

for state i

The corrections can be viewed as mixtures of the unperturbed states
$\therefore$ the ~~whole~~ perturbed states themselves can be viewed as mixtures of the unperturbed states.
— This is a clue for the common non-perturbative solution in terms of a complete set of non-solutions.
→ Diagonalization of the Hamiltonian — which we've covered before, but will reiterate below.

If we knew the expansion coefficients c_{nim}, we'd know the whole perturbation solution

6-28

to any order we like:

$$|\psi_i\rangle = \sum_{k=0}^{\infty} \lambda^k \left(\sum_m c_{kim} |\psi_{0m}\rangle \right)$$

but we don't know all c_{kim}, (except $c_{1ii} = 0$)

~~But we can make some progress in finding them by using inner products to isolate values.~~

If we knew $|\psi_{ki}\rangle$ we could find them from

$$\langle \psi_{0j} | \psi_{ki} \rangle = \sum_m c_{kim} \underbrace{\langle \psi_{0j} | \psi_{0m} \rangle}_{\delta_{jm}}$$

δ_{jm} by orthonormality of set $\{|\psi_{0i}\rangle\}$

$$\langle \psi_{0j} | \psi_{ki} \rangle = c_{kij}$$

But we can't do it this straightforward ~~way~~ way since we don't know $|\psi_{ki}\rangle$ apriori.

5) 1st Order Perturbation

Recall from p 6-16

$$\sum_{k=0}^{n} H_{n-k} |\chi_{ki}\rangle = \sum_{k=0}^{n} E_{n-k\,i} |\chi_{ki}\rangle$$

Recall on H_0 and H_1 are non-zero, and so the sum could start from $k=n-1$

$n-k$ and k are perturbation orders.

i is the state label of the perturbed state.

$n = 0, 1, 2, 3, \ldots$

So we have one such equation for each order of perturbation

— but each such equation involves all lower orders than n, and so one can't solve

6-30

for nth order correction without knowing the $n = 0, 1, \ldots n-1$ order corrections.

0^{th} order

$$H_0 |\psi_{0i}\rangle = E_{0i} |\psi_{i0}\rangle$$

but this is just the eigenproblem for the unperturbed system which we assume is a known.

1^{st} order

$$H_1 |\psi_{0i}\rangle + H_0 |\psi_{1i}\rangle = E_{1i} |\psi_{0i}\rangle + E_{0i} |\psi_{1i}\rangle$$

The trick motivated by clairvoyance is to take the <u>inner product</u> of this equation with state $|\psi_{0j}\rangle$

$$\langle \psi_{0j} | H_1 | \psi_{0i} \rangle + \langle \psi_{0j} | H_0 | \psi_{1i} \rangle$$

$$= E_{1i} \underbrace{\langle \psi_{0j} | \psi_{0i} \rangle}_{\delta_{ij}}$$

$$+ E_{0i} \langle \psi_{0j} | \psi_{1i} \rangle$$

Say Q is an observable (thus $Q = Q^\dagger$).

$$Q | q \rangle = q | q \rangle$$

where q is an eigenvalue of Q

Say $| \alpha \rangle$ is general

$$\langle \alpha | Q | q \rangle = q \langle \alpha | q \rangle$$

by definition of Hermitian conjugate

$$\langle q | Q^\dagger | \alpha \rangle^* = q \langle q | \alpha \rangle^*$$

Take the complex conjugate

6-32

of both sides

$$\langle q | Q^\dagger | \alpha \rangle = q^* \langle q | \alpha \rangle$$

$= Q$ since Q is an observable

$= q$ since eigenvalues are pure real.

$$\langle q | Q | \alpha \rangle = q \langle q | \alpha \rangle$$

$\therefore$ Since $|\alpha\rangle$ is general

$$\boxed{\langle q | Q = q \langle q | = \langle q | q}$$

So $\langle \psi_{0j} | H_0 = \langle \psi_{0j} | E_{0j}$

$$\therefore \langle \psi_{0j} | H_1 | \psi_{0i} \rangle + E_{0j} \langle \psi_{0j} | \psi_{1i} \rangle$$

$$= E_{1i} \delta_{ij} + E_{0i} \langle \psi_{0j} | \psi_{1i} \rangle$$

If $i = j$, we get $E_{1i} = \langle \psi_{0i} | H_1 | \psi_{0i} \rangle$

which is a pretty reasonable result.

The 1^{st} order correction to the energy is given by the diagonal matrix element of H_1 with the unperturbed states.

You might even have guessed this.

If $i \neq j$, $\langle \psi_{0j} | H_1 | \psi_{0i} \rangle = (E_{0i} - E_{0j}) \langle \psi_{0j} | \psi_{1i} \rangle$

$$\cancel{\langle \psi_{0j} | \psi_{1i} \rangle = \frac{\langle \psi_{0j} | H_1 | \psi_{0i} \rangle}{E_{0i} - E_{0j}}}$$

$$\langle \psi_{0j} | \psi_{1i} \rangle = \frac{\langle \psi_{0j} | H_1 | \psi_{0i} \rangle}{E_{0i} - E_{0j}}$$

But since $\{|\psi_{0i}\rangle\}$ is a complete set, we can expand

$$|\psi_{1i}\rangle = \sum_m c_{1im}|\psi_{0m}\rangle$$

$$\therefore \langle\psi_{0j}|\psi_{1i}\rangle = \sum_m c_{1im} \underbrace{\langle\psi_{0j}|\psi_{0m}\rangle}_{\delta_{jm}}$$

$$= c_{1ij}$$

$$\therefore c_{1ij} = \langle\psi_{0j}|\psi_{1i}\rangle = \frac{\langle\psi_{0j}|H_1|\psi_{0i}\rangle}{E_{0i} - E_{0j}}$$

We assumed non-degeneracy and so $E_{0i} \neq E_{0j}$ for $i \neq j$ so no catastrophe

<u>but</u> we have this catastrophe,

$$c_{1ii} = \text{undefined} = \frac{\langle\psi_{0j}|H_1|\psi_{0i}\rangle}{0}$$

but $i \neq j$ by our assumption on p. 6-33

So $c_{1ij} = \dfrac{\langle \psi_{0j} | H_1 | \psi_{0i} \rangle}{E_{0i} - E_{0j}}$

is only for $i \neq j$

But what is c_{1ii} then?

All the labor on p. 6-17 – 6-25 was to show that normalization of the full perturbed solution requires $c_{1ii} = 0$.

In my view Gr-253 muffs this. He shows that you can choose $c_{1ii} = 0$, but NOT that it must be to preserve normalization — Not obviously anyway.

So Now we have the complete 1st order perturbation correction and 1st order corrected quantities

6-36

$$E_{1i} = \langle \chi_{0i} | H_1 | \chi_{0i} \rangle$$

$$E_i^{1st} = E_0 + \lambda \langle \chi_{0i} | H_1 | \chi_{0i} \rangle$$

mixtures of unperturbed states

$$|\chi_{1i}\rangle = \sum_{\substack{j \\ j \neq i}} \frac{\langle \chi_{0j} | H_1 | \chi_{0i} \rangle}{E_{0i} - E_{0j}} |\chi_{0j}\rangle$$

$$|\chi_i^{1st}\rangle = |\chi_{0i}\rangle + \lambda \sum_{j \neq i} \frac{\langle \chi_{0j} | H_1 | \chi_{0i} \rangle}{E_{0i} - E_{0j}} |\chi_{0j}\rangle$$

Note $|\chi_i^{1st}\rangle$ is NOT exactly normalized. It's only normalized to 1st order. The imposed normalization constraint is for $|\chi_i\rangle$ normalized — The exact perturbed state.

Note i comes first in denominator and second in numerator.

We assumed non-degeneracy and so our corrections are NOT undefined.

But what if E_{0i} and E_{0j} get very close?

Then the corrections get very big and ~~that hints~~ ~~our~~ ~~that other~~ high orders are needed for accuracy

OR

the series may not converge (in which case perturbation theory is not adequate).

One could say ~~that~~ as $E_{0j} \rightarrow E_{0i}$ mixing of the unperturbed states becomes strong and eventually too strong.

That's when the diagonalization approach is Needed (see below)

6) 2nd Order Perturbation

— We only do the 2nd order energy.

— the 2nd order state correction is beyond us.

From p. 6-29 with n = 2

$$\sum_{k=1}^{2} H_{2-k} |\psi_{ki}\rangle = \sum_{k=0}^{2} E_{2-k\,i} |\psi_{ki}\rangle$$

$$H_1 |\psi_{1i}\rangle + H_0 |\psi_{2i}\rangle = E_{2i} |\psi_{0i}\rangle + E_{1i} |\psi_{1i}\rangle + E_{0i} |\psi_{2i}\rangle$$

~~We~~ we don't know $|\psi_{2i}\rangle$,

but we can eliminate it by inner producted with $|\psi_{0i}\rangle$

$$\langle \psi_{0i}|H_1|\psi_{1i}\rangle + E_{0i}\langle \psi_{0i}|\psi_{2i}\rangle$$

$$= E_{2i} + E_{1i}\langle \psi_{0i}|\psi_{1i}\rangle$$

$$+ E_{0i}\langle \psi_{0i}|\psi_{2i}\rangle$$

These two cancel

E_{2i} and $\langle \psi_{0i}|\psi_{1i}\rangle = 0$

by p. 6-25

$$E_{2i} = \langle \psi_{0i}|H_1|\psi_{1i}\rangle$$

But we know this from p. 6-36

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So

$$E_{2i} = \langle \chi_{0i} | H_1 | \sum_{\substack{j \\ j \neq i}} \frac{\langle \chi_{0j} | H_1 | \chi_{0i} \rangle}{E_{0i} - E_{0j}} | \chi_{0j} \rangle$$

Note $\langle \chi_{0i} | H_1 | \chi_{0j} \rangle$

$= \langle \chi_{0j} | H_1^{+} | \chi_{0i} \rangle^{*}$ defn. of Hermitian conjugate

$= \langle \chi_{0j} | H_1 | \chi_{0i} \rangle^{*}$ since $H_1 = H_1^{+}$

$$E_{2i} = \sum_{\substack{j \\ j \neq i}} \frac{|\langle \chi_{0j} | H_1 | \chi_{0i} \rangle|^2}{E_{0i} - E_{0j}}$$

Note as $E_{0j} \to E_{0i}$ we again have an explosion. This suggests that approaching degeneracy ~~is~~ causes ~~diverges~~ infinities in all order corrections

$$E_i^{2nd} = E_{0i} + \lambda \langle \chi_{0i} | H_1 | \chi_{0i} \rangle + \lambda^2 \sum_{\substack{j \\ j \neq i}} \frac{|\langle \chi_{0j} | H_1 | \chi_{0i} \rangle|^2}{E_{0i} - E_{0j}}$$