Schiff Chap 8 : Bound State Approximation Methods PhL 1.2.09

This is a thick, heavy-duty chapter, crammed into a dense 51 pages (p244-295), 10% of the book.

31. Stationary Perturbation Theory. 2

Nondegenerate Case. 2

Comment regarding differential operators. 3

Derive 31.4. 3

Derive 31.6. 5

Plan A: fails. 5

What does Messiah do? 6

Plan C: fails. 7

Plan D: succeeds. We learn the correct meaning of ψ' and 31.6 is explained. 7

Derive 31.7. 9

First-order Perturbation (246) [non-degenerate case] 9

Second-order Perturbation (247) [non-degenerate case] 10

Pause to comment: 11

Example of non-degenerate 2nd order perturbation theory: the 1D HO (248) 13

Side Problem: what is $\langle m| x^2 |n\rangle$ for a HO? 13

Resume the solution: 15

Degenerate Case. 17

Removal of Degeneracy in Second Order. (250) 18

Zeeman Effect without Electron Spin (251) 18

First order Stark Effect in Hydrogen n = 2 (252). 19

Perturbed Energy Levels (253). 19

Occurrence of Permanent Electric Dipole Moments (253) 19

32. The Variation Method. 20

Expectation value of the energy. 20

Application to excited states. 20

Ground State of Helium. 20

Electron Interaction Energy 21

Variation of the parameter Z. 21

Van der Waals Interaction between two H atoms. 21

Perturbation Calculation -- puts a lower bound on ε_2 21

Variation Calculation -- puts an upper bound on ε_2 21

33. Alternative Treatment of the Perturbation Series (263) 22

Second order Stark Effect in Hydrogen (how Stark moves the ground state energy) 22

Polarizability of Hydrogen 23

Method of Dalgarno and Lewis 23

Third Order Perturbed Energy 23

Interaction of Hydrogen with a Point Charge. 23

34. The WKB Approximation (268) 24

The Goldstein Connection 24

Approximate Solutions 24
Derivation of 34.6 and 271B and 271D and 271E and 34.7 26
Asymptotic Nature of the Solutions (271) 28
Solution near a Turning Point (272) 29
Problem 1: Convert the ODE 34.3 from variable x to variable ξ. 29
Problem 2: Show that the following form solves this ODE 30
Problem 3: Find the large x behavior of this u(x), ... 31
Linear Turning Point (273) 33
Connection at the Turning Point (274) 34
Asymptotic Connection Formulas (275): Derive 34.17. 35
Energy Levels of a Potential Well (276). 36
A quantization Rule (277) 37
Special Boundary Conditions (277) 38
Tunneling Through a Barrier (278). 38
35. Methods for Time-dependent Problems (279) 39
Time Dependent Perturbation Theory(280). 39
Interaction Picture (281) 40
First Order Perturbation (282). 40
Harmonic Perturbation (282). 40
Transition Probability and the Golden Rule (283) 40
Example: Ionization of Hydrogen (285) 41
Density of Final States (186) 41
Ionization Probability (287) 41
Second Order Perturbation -- two-photon processes (288) 42
Adiabatic Approximation (289). Choice of Phases. 42
Connection with TDPT. 43
The Sudden Approximation. (292) 44
HO Example of Adiabatic Approximation (294 top) 46
HO Example of Sudden Approximation (294 bottom) 46

---

31. Stationary Perturbation Theory.

I don't think one can stress enough how important this method is. Only toy problems have exact solutions, all real problems require approximation. This section talks about time-independent perturbation theory that I usually call SSPT (stationary-state).

Nondegenerate Case.

Time to look lively and not get lost in this immensely compact presentation. We think of $H = H_0 + \lambda H'$ where λ is a smallness parameter. We have some linear equation $H\psi=W\psi$ where ψ is a single unknown eigenfunction of operator H, and W is its eigenvalue. Here H is meant to be the Hamiltonian, but it could be any operator you want. We usually think of it as a second-order differential operator (called L in Stakgold), but I think it could be any linear operator, modeled so to speak by any "matrix".

Comment regarding differential operators. Consider $\langle x| p^n|x'\rangle \sim \partial^n_x \delta(x-x')$ in the 1D coordinate representation. If L is an operator L(p,x) of any order, then we can see that the matrix $\langle x| L| x'\rangle$ is entirely concentrated within an infinitesimal distance of the main diagonal. We can think of $\delta(x-x')$ as being exactly "on the diagonal", and perhaps $\delta'(x-x')$ as being antisymmetric on the first off-diagonal, and so on. In general, $\partial^n_x \delta(x-x') = 0$ if x-x' = any finite value!

Now, here is our perturbation theory game plan. We assume we know the solutions of $H_o\psi=E\psi$ and we denote these solutions this way: $H_o u_k=E_k u_k$. We are going to focus on a particular one of these solutions u_m so the letter "m" has that meaning in this section. When we "turn on" the perturbation, we expect so see $u_m \rightarrow \psi^{(m)}$. In the degenerate case treated later, where we might be starting with a set of states $u_m^{[i]}$ where i = 1,2,3....N, say, all with energy E_m, we have to find the right linear combinations of the starting states which move off into the perturbed states, but for now we ignore that problem.

Derive 31.4.

So, a standard method of doing perturbation theory with a linear eigenvalue problem is to assume a power series in λ for "everything" and then match powers. If it can be done, and if the result converges at least in some useful sense, then your assumption was justified.

So here we go. We expand the energy and eigenfunctions in λ:

$$W^{(m)} = \Sigma_{n=0} \lambda^n W^{(m)}_n$$

$$\psi^{(m)} = \Sigma_{n=0} \lambda^n \psi^{(m)}_n$$

$$H = H_0 + \lambda H' \qquad H_o u_k=E_k u_k \qquad H \psi^{(m)} = W^{(m)} \psi^{(m)}$$

Notice the following facts for the λ=0 order:

$$W^{(m)}_0 = E_m \quad \text{and} \quad \psi^{(m)}_0 = u_m = |m\rangle \quad \text{loosely speaking}$$

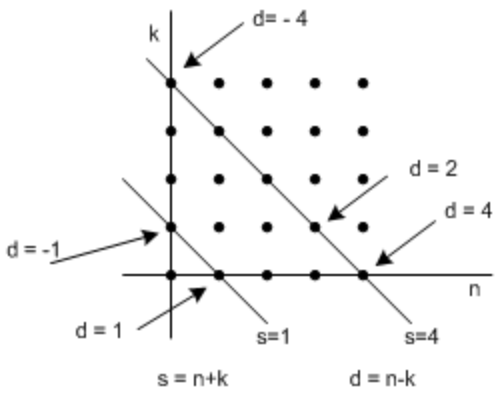
In our notation, we are keeping track of the fact that we started with some specific state "m" by using an upper index. Schiff does not show this index to make things simpler. The subscript on W or ψ refers to the ORDER of that coefficient. So let's now throw these expansions into the SE:

$$(H_0 + \lambda H')\psi^{(m)} = W^{(m)} \psi^{(m)}$$

$$(H_0 + \lambda H') \Sigma_{n=0} \lambda^n \psi^{(m)}_n = \Sigma_{k=0} \lambda^k W^{(m)}_k \Sigma_{n=0} \lambda^n \psi^{(m)}_n$$

$$= \Sigma_{k=0} \Sigma_{n=0} \lambda^{k+n} W^{(m)}_k \psi^{(m)}_n$$

As usual, we think of this double sum as being over a square grid, and we change the summation indices in this manner: (I always have to show this picture to keep track of things:



s = n+k the "sum" index s+d = 2n s-d = 2k
d = n-k the "difference" index

$$RHS = \Sigma_{s=0,1,2} \lambda^s \left[\Sigma_{d=s,s-2\ldots-s} W^{(m)}{}_{(s-d)/2} \psi^{(m)}{}_{(s+d)/2} \right]$$

The Σ_d steps from d = s down to d = -s, decrementing by 2 in each step. We can break out the s=0 term in this sum (which of course has only d = 0)

$$RHS = W^{(m)}{}_0 \psi^{(m)}{}_0 + \Sigma_{s=1,1,2} \lambda^s \left[\Sigma_{d=s,s-2\ldots-s} W^{(m)}{}_{(s-d)/2} \psi^{(m)}{}_{(s+d)/2} \right]$$

$$= E_m u_m + \Sigma_{s=1,2,} \lambda^s \left[\Sigma_{d=s,s-2\ldots-s} W^{(m)}{}_{(s-d)/2} \psi^{(m)}{}_{(s+d)/2} \right]$$

Now we want to process the LHS of our expansion equation in this way, using s = n+1

$$(\lambda H') \Sigma_{n=0} \lambda^n \psi^{(m)}{}_n = H' \Sigma_{n=0} \lambda^{n+1} \psi^{(m)}{}_n = H' \Sigma_{s=1} \lambda^s \psi^{(m)}{}_{s-1}$$

$$\Rightarrow \quad LHS = H_0 \Sigma_{s=0} \lambda^s \psi^{(m)}{}_s + H' \Sigma_{s=1} \lambda^s \psi^{(m)}{}_{s-1}$$

$$= H_0 \psi^{(m)}{}_0 + \Sigma_{s=1} \lambda^s [H_0 \psi^{(m)}{}_s + H' \psi^{(m)}{}_{s-1}]$$

$$= H_0 u_m + \Sigma_{s=1} \lambda^s [H_0 \psi^{(m)}{}_s + H' \psi^{(m)}{}_{s-1}]$$

When we now set LHS = RHS, we see that the 0^{th} order terms cancel on each side since they form the zeroth order SE, and we are left with:

$$\Sigma_{s=1} \lambda^s [H_0 \psi^{(m)}{}_s + H' \psi^{(m)}{}_{s-1}] = \Sigma_{s=1,2,} \lambda^s \left[\Sigma_{d=s,s-2\ldots-s} W^{(m)}{}_{(s-d)/2} \psi^{(m)}{}_{(s+d)/2} \right]$$

We then equate powers of λ^s to get

$$[H_0 \psi^{(m)}{}_s + H' \psi^{(m)}{}_{s-1}] = \left[\Sigma_{d=s,s-2\ldots-s} W^{(m)}{}_{(s-d)/2} \psi^{(m)}{}_{(s+d)/2} \right] \qquad s = 1,2,3...$$

Now let's write out explicitly the first two terms in the sum on the RHS

$$RHS' = W^{(m)}_0 \psi^{(m)}_s + W^{(m)}_1 \psi^{(m)}_{s-1} + \Sigma_{d=s-4\ldots-s} W^{(m)}_{(s-d)/2} \psi^{(m)}_{(s+d)/2}$$

where of course any term is really 0 if some index goes negative. Now consider our LHS' = RHS' and move terms across the = sign to get this result:

$$(H_0 - W^{(m)}_0) \psi^{(m)}_s = (W^{(m)}_1 - H') \psi^{(m)}_{s-1} + \Sigma_{d=s-4\ldots-s} W^{(m)}_{(s-d)/2} \psi^{(m)}_{(s+d)/2}$$

Now let's re-index the remaining sum by returning to s+d = 2n s-d = 2k type indices. The sum is over

d = s-4, s-6, ...-s => d-s = -4,-6, -2s => s-d = 4,6,..2s

=> (s-d)/2 = 2,3,..s and we have (s+d)/2 = - (s-d)/2 + s

Define j = (s-d)/2 = 2,3...s and we then have

$$\Sigma_{d=s-4\ldots-s} W^{(m)}_{(s-d)/2} \psi^{(m)}_{(s+d)/2} = \Sigma_{j=2,3..s} W^{(m)}_j \psi^{(m)}_{s-j}$$

which takes us (finally) to Schiff 31.4 which in our notation appears as

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

and now I will write out the first few equations:

$$(H_0 - E_m) \psi^{(m)}_0 = 0 \qquad s = 0$$
$$(H_0 - E_m) \psi^{(m)}_1 = (W^{(m)}_1 - H') \psi^{(m)}_0 \qquad s = 1$$
$$(H_0 - E_m) \psi^{(m)}_2 = (W^{(m)}_1 - H') \psi^{(m)}_1 + W^{(m)}_2 \psi^{(m)}_0 \qquad s = 2$$
$$(H_0 - E_m) \psi^{(m)}_3 = (W^{(m)}_1 - H') \psi^{(m)}_2 + W^{(m)}_2 \psi^{(m)}_1 + W^{(m)}_3 \psi^{(m)}_0 \qquad s = 3$$

The residual summation on the right side includes products such that the two indices add to s. This is of course because in each equation "s", we are talking about a power λ^s that has been cancelled.

Derive 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.

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

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

2. .... which then tells us that (where we have a huge messy extra term A(m,s) that should not be there!)

$$W^{(m)}_s = -A(m,s) + \langle \psi^{(m)}_0 | H' | \psi^{(m)}_{s-1} \rangle \qquad A(m,s) = \text{a certain mess of terms.}$$

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

What does Messiah do?

Let's look elsewhere for assistance. **Saxon** does not quite follow this path, but **Messiah** volume II page 687 does. Here is Messiah's notation compared to Schiff's (really my version of Schiff's)

Messiah	Schiff/PL
$\|0\rangle$	$\psi^{(m)}_0$
$\|1\rangle$	$\psi^{(m)}_1$
V	H'
ε_s	$W^{(m)}_s$
a	m
$\|\psi\rangle$	$\psi^{(m)}$

Right off the bat, Messiah imposes the condition $\langle 0|\psi\rangle = 1$ in his equation XVI.4 . In Schiff notation this says

$$\langle \psi^{(m)}_0 | \psi^{(m)} \rangle = 1 \qquad \Rightarrow \qquad \langle \psi^{(m)}_0 | \Sigma_{n=0} \lambda^n \psi^{(m)}_n \rangle = 1$$

But we know that $\langle \psi^{(m)}_0 | \psi^{(m)}_0 \rangle = 1$, so it must be true that

$$\Sigma_{n=1} \lambda^n \langle \psi^{(m)}_0 | \psi^{(m)}_n \rangle = 0$$

but then this must be true in each order, so we have

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

which is Schiff's 31.6 which he arrived at dishonestly.

Plan B: fails. (Fuzzy Logic)

So what does it mean to "impose" this condition on your assumed form

$$\psi^{(m)} = \Sigma_{n=0} \lambda^n \psi^{(m)}{}_n$$

$$< \psi^{(m)}{}_0 \mid \psi^{(m)} > = 1 \qquad \Rightarrow \qquad < \psi^{(m)}{}_0 \mid \psi^{(m)}{}_s > = 0 \quad s = 1,2,3...$$

I guess one answer is this: just assume you can find functions $\psi^{(m)}{}_s$ that have this property, just as we assumed we could have a λ power series. Then turn all the gears, and if you can solve a problem, then the assumption of this property is then OK. But you have to admit, it is not *obvious* that you can find a correction to the wavefunction in each order of λ that has this property! Just scaling the corrective wave function would not be enough. But again, if we assume the property and in so doing if we do in fact find a correction in each order that works, the assumption is justified. If we find no solution, then the assumption was to strict. [but then we don't ever understand WHY it works, the fuzzy logic approach.]

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

Plan D: succeeds. We learn the correct meaning of ψ' and 31.6 is explained.

Here is the answer, I was overlooking the larger HS picture. We start out with solution $\psi^{(m)}{}_0 = u_m$. But we know that the set of u_k form a complete set which spans our Hilbert Space. So our corrected solution must look like this

$$\psi^{(m)} = u_m + \Sigma_k B_k u_k$$

In other words, there is some exact solution $\psi^{(m)}$ to our perturbed problem, and we must certainly be able to express $\psi^{(m)} - u_m$ as some linear combination of our basis functions since they are *complete*. The question concerns whether or not we should include a contribution to the corrective sum from k = m. Suppose we do and by so doing, we remain completely general. Then we have

$$\psi^{(m)} = u_m + B_m u_m + \Sigma_{k \neq m} B_k u_k = (1 + B_m) u_m + \Sigma_{k \neq m} B_k u_k$$

Now just rescale the solution as follows

$$\psi'^{(m)} = \psi^{(m)} / (1 + B_m) = u_m + \Sigma_{k \neq m} B'_k u_k$$

where of course $B'_k = B_k / (1 + B_m)$. Now having done this, we see that

$$< u_m \mid \psi'^{(m)} > = 1$$

because all the other u_k are orthogonal to u_m. This then sets the scale for $\psi'^{(m)}$ and with the scale so set, we will find that

$$< \psi'^{(m)} \mid \psi'^{(m)} > = \text{some positive number that is most probably } \textit{not} \text{ unity!}$$

Now if we write

$\psi'^{(m)} = u_m$ + other stuff

then we must have

$< u_m |$other stuff$> = 0$ // which is what 31.6 is about

and this is true whether or not we think of "other stuff" as being a power series in λ.

If we choose to normalize (scale) $\psi'^{(m)}$ in this manner, then we give up $< \psi'^{(m)} | \psi'^{(m)} > = 1$, but of course once we have a solution, we can scale *again* to get this last to be true. But scaling in the first manner makes the mechanical perturbation theory simpler.

So from here on, we shall drop the prime on $\psi'^{(m)}$ and replace $B'_k = a_k$ and assume that we are choosing to normalize such that $< u_m | \psi'^{(m)} > = 1$. So we then re-express the above as:

$$\psi^{(m)} = u_m + \Sigma_{k \neq m} [a^{(m)}_k] u_k \qquad (*)$$

$$< u_m | \psi^{(m)} > = 1$$

$$\psi^{(m)} = \Sigma_{n=0} \lambda^n \psi^{(m)}_n$$

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

$$a^{(m)}_k = \Sigma_{n=0} \lambda^n a^{(m)}_{k,n} \qquad k \neq m \qquad (**)$$

We only care about $k \neq m$ because only these appear in our sum (*) above.

- If we turn off the perturbation, that is the same as setting $\lambda = 0$, and in this case there *are* no correction coefficients, so it must be that $a^{(m)}_{k,0} = 0$. Thus, the sum in (**) really begins with n = 1.
- We could define $a^{(m)}_k = 0$ for k = m, and then include it in the (*) sum. This just says we are not allowing any corrective contribution from state k = m, as discussed above.

So our equation (*) now becomes

$$\Sigma_{n=0} \lambda^n \psi^{(m)}_n = u_m + \Sigma_{k \neq m} [\Sigma_{n=1} \lambda^n a^{(m)}_{k,n}] u_k$$

=>

$$\Sigma_{n=1} \lambda^n \psi^{(m)}_n = \Sigma_{k \neq m} [\Sigma_{n=1} \lambda^n a^{(m)}_{k,n}] u_k = \Sigma_{n=1} \lambda^n \{ \Sigma_{k \neq m} a^{(m)}_{k,n} u_k \}$$

and if we equate powers of λ we get

$$\psi^{(m)}_n = \Sigma_{k \neq m} a^{(m)}_{k,n} u_k \qquad n = 1,2,3...$$

Now finally (!) we can see why it is that $< m | \psi^{(m)}_n > = 0$. Due to our chosen normalization of $\psi^{(m)}$, we allow no correction from the |m> basis function, so $\psi^{(m)}_n$ in each order of λ is a linear combination only of the *other* basis functions. Thus, in each order, we get $< m | \psi^{(m)}_n > = 0$.

With this in mind, we can now ***rederive* 31.4** as above (before we tried ψ' and got the messy A(m,s) extra terms in Plan A). When we rederive 31.4, it looks exactly as Schiff has it and our general equation is this:

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

The only difference is that our $\psi^{(m)}_s$ now have the desired normalization property $< m \mid \psi^{(m)}_s > = 0$ for s = 1,2,3.. We finally got to 31.6 but it took a long time and a lot of fiddling to understand why it was possible to do it.

Repeat this last paragraph: We first derived 31.4 by expanding pieces in $H\psi = W\psi$. Then after finding our desired ψ', we expand the pieces of $H\psi' = W\psi'$ where ψ' has a different normalization from ψ. This has zero effect on the expansion and the balancing of powers of λ, the only difference is that we have primes on everything. But then we just drop the primes since this is the ψ was want to use.

Derive 31.7.

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

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

Close our big equation above from the left with $\psi^{(m)}_0 = <m|$. We get 0 on the left because $(H_0 - E_m)$ acting to the left on <m| gives 0, so

$$0 = -<\psi^{(m)}_0 \mid H' \mid \psi^{(m)}_{s-1}> + W^{(m)}_s$$

which then tells us that

$$W^{(m)}_s = <\psi^{(m)}_0 \mid H' \mid \psi^{(m)}_{s-1}> \qquad s = 1,2,3... \qquad \text{// **and this is (31.7)**}$$

This says that, in our approach, if you know $\psi^{(m)}_{s-1}$, you can compute $W^{(m)}_s$ in the next highest order. This is that path we shall follow. The footnote makes the rather startling claim that if you know $\psi^{(m)}_s$, you can compute $W^{(m)}_{2s+1}$ from it, a 1964 references. I just bet this has something to do with Jim Ball style Gaussian quadrature somehow and the properties of our orthonormal basis functions u_k .

First-order Perturbation (246) [non-degenerate case]

Apply 31.7 with s = 1 to get

$$W^{(m)}_1 = <\psi^{(m)}_0 \mid H' \mid \psi^{(m)}_0> = <m|H'|m> \qquad \text{// **which is 31.8**}$$

which is a very famous result for non-degenerate state m's movement in response to perturbation H'. Meanwhile, our 31.4 for s=1 says:

$$(H_0 - E_0)\,\psi^{(m)}_1 = (W^{(m)}_1 - H')\,\psi^{(m)}_0 \qquad s = 1$$

but from above we know that

$$\psi^{(m)}_1 = \Sigma_{k\neq m}\, a^{(m)}_{k,1}\, u_k \qquad \textbf{// which is 31.9}$$

so the above says

$$(H_0 - E_m)\, \Sigma_{k\neq m}\, a^{(m)}_{k,1}\, u_k = (\, W^{(m)}_1 - H'\,)\, u_m$$

Close this from the left with some $u_{k'}$ where $k' \neq m$ and we get

$$\Sigma_{k\neq m}\, a^{(m)}_{k,1} \langle k'|(H_0 - E_m)|k\rangle = \langle k'|\ (\, W^{(m)}_1 - H'\,)|m\rangle = -\ \langle k'|\, H'\, |m\rangle$$

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

$$(E_{k'} - E_m)\ a^{(m)}_{k',1} = -\ \langle k'|\, H'\, |m\rangle$$

$$(E_k - E_m)\ a^{(m)}_{k,1} = -\ \langle k|\, H'\, |m\rangle \qquad k \neq m\backslash$$

$$a^{(m)}_{k,1} = \langle k|\, H'\, |m\rangle\, /(E_m - E_k) \qquad k \neq m \qquad \textbf{// which is 31.10.}$$

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

$$\psi^{(m)}_1 = \Sigma_{k\neq m}\, a^{(m)}_{k,1}\, u_k = \Sigma_{k\neq m}\ \{\ \langle k|\, H'\, |m\rangle\, /(E_m - E_k)\ \}\ u_k$$

$$\psi^{(m)} \approx u_m + \lambda\, \psi^{(m)}_1$$

$$W^{(m)}_1 = \langle m|H'|m\rangle$$

and because m is non-degenerate, we avoid the denominator blow up.

Second-order Perturbation (247) [non-degenerate case]

Let's just blindly do this and see what happens. From 31.7 we have

$$W^{(m)}_s = \langle \psi^{(m)}_0 |\ H'\ |\ \psi^{(m)}_{s-1}\rangle$$
$$W^{(m)}_2 = \langle \psi^{(m)}_0 |\ H'\ |\ \psi^{(m)}_1\rangle$$

$$\psi^{(m)}_1 = \Sigma_{k\neq m}\, a^{(m)}_{k,1}\, u_k = \Sigma_{k\neq m}\ \{\ \langle k|\, H'\, |m\rangle\, /(E_m - E_k)\ \}\ u_k$$

$$W^{(m)}_2 = \langle \psi^{(m)}_0 |\ H'\ |\ \Sigma_{k\neq m}\ \{\ \langle k|\, H'\, |m\rangle\, /(E_m - E_k)\ \}\ u_k\ \rangle$$

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

$= \Sigma_{k \neq m} \; |\langle m| H' |k\rangle|^2 / (E_m - E_k)$ // **which is 31.11**

which agrees with **31.11**.

Pause to comment: $W^{(m)}_2$ has as numerator the "second order amplitude" connecting state m to itself $\langle m| H' |k\rangle \langle k| H' |m\rangle$ through all *other* states |k>, but those states nearest in energy are going to make the largest contribution due to the denominator. One often hears people like Levitt say you can ignore "far distant" states when doing second order perturbation theory and this would be a good reason why.

Now we do the next equation in 31.4 to get

$$(H_0 - E_m) \psi^{(m)}_2 = (W^{(m)}_1 - H') \psi^{(m)}_1 + W^{(m)}_2 \psi^{(m)}_0 \qquad s = 2$$

$$\psi^{(m)}_1 = \Sigma_{k \neq m} a^{(m)}_{k,1} u_k \qquad a^{(m)}_{k,1} = \langle k| H' |m\rangle / (E_m - E_k) \qquad k \neq m$$

$$\psi^{(m)}_2 = \Sigma_{k \neq m} a^{(m)}_{k,2} u_k$$

So close again from the left with some $\langle k'|$ where $k' \neq m$ to get

$$\text{LHS} = \langle k' | (H_0 - E_m) \Sigma_{k \neq m} a^{(m)}_{k,2} |k\rangle = \Sigma_{k \neq m} a^{(m)}_{k,2} \langle k' | (E_{k'} - E_m) |k\rangle = a^{(m)}_{k',2} (E_{k'} - E_m)$$

Meanwhile, we have

$$\text{RHS} = \langle k' | (W^{(m)}_1 - H') \psi^{(m)}_1 + W^{(m)}_2 \psi^{(m)}_0$$

$$= \langle k' \{ (W^{(m)}_1 - H') \Sigma_{k \neq m} a^{(m)}_{k,1} |k\rangle + W^{(m)}_2 |m\rangle \}$$

$$= \Sigma_{k \neq m} a^{(m)}_{k,1} \langle k'| \{ (W^{(m)}_1 - H') |k\rangle + W^{(m)}_2 |m\rangle \}$$

$$= \Sigma_{k \neq m} a^{(m)}_{k,1} \langle k'| \{ (W^{(m)}_1 - H') |k\rangle \}$$

$$= W^{(m)}_1 a^{(m)}_{k',1} - \Sigma_{k \neq m} a^{(m)}_{k,1} \langle k'| H') |k\rangle$$

$$= W^{(m)}_1 \langle k| H' |m\rangle / (E_m - E_{k'}) - \Sigma_{k \neq m} \langle k| H' |m\rangle / (E_m - E_k) * \langle k'| H') |k\rangle$$

$$= \langle m|H'|m\rangle \langle k| H' |m\rangle / (E_m - E_{k'}) - \Sigma_{k \neq m} \langle k| H' |m\rangle / (E_m - E_k) * \langle k'| H') |k\rangle$$

So set LHS = RHS to get

$$a^{(m)}_{k',2} (E_{k'} - E_m) = \langle m|H'|m\rangle \langle k| H' |m\rangle / (E_m - E_{k'}) - \Sigma_{k \neq m} \langle k'| H') |k\rangle \langle k| H' |m\rangle / (E_m - E_k)$$

$$a^{(m)}_{k',2} = - \langle k| H' |m\rangle \langle m|H'|m\rangle / (E_m - E_{k'})^2 + \Sigma_{k \neq m} \langle k'| H') |k\rangle \langle k| H' |m\rangle / [(E_m - E_k) (E_m - E_{k'})]$$

To get Schiff's notation, take k→n and then k'→k so have

$$a^{(m)}_{k,2} = -\langle k|H'|m\rangle\langle m|H'|m\rangle / (E_m - E_k)^2$$

$$+ \Sigma_{n\neq m} \langle k|H'|n\rangle\langle n|H'|m\rangle / [(E_m - E_n)(E_m - E_k)] \qquad \text{// which is 31.13}$$

Now we can assemble all our results through second order:

$$W^{(m)} \approx \Sigma_{n=0,1,2} \lambda^n W^{(m)}_n = E_m + \lambda W^{(m)}_1 + \lambda^2 W^{(m)}_2$$

$$\psi^{(m)} \approx \Sigma_{n=0,1,2} \lambda^n \psi^{(m)}_n = u_m + \lambda \psi^{(m)}_1 + \lambda^2 \psi^{(m)}_2$$

where we have to now insert these results:

$$W^{(m)}_1 = \langle m|H'|m\rangle$$
$$W^{(m)}_2 = \Sigma_{n\neq m} |\langle m|H'|n\rangle|^2 / (E_m - E_n)$$

$$\psi^{(m)}_1 = \Sigma_{k\neq m} a^{(m)}_{k,1} u_k = \Sigma_{k\neq m} \{ \langle k|H'|m\rangle / (E_m - E_k) \} u_k$$
$$\psi^{(m)}_2 = \Sigma_{k\neq m} a^{(m)}_{k,2} u_k =$$
$$\Sigma_{k\neq m} \{ -\langle k|H'|m\rangle\langle m|H'|m\rangle / (E_m - E_k)^2 + \Sigma_{n\neq m} \langle k|H'|n\rangle\langle n|H'|m\rangle / [(E_m - E_n)(E_m - E_k)] \} u_k$$

So insert away to get

$$W^{(m)} \approx E_m + \lambda\langle m|H'|m\rangle + \lambda^2 \Sigma_{n\neq m} |\langle m|H'|n\rangle|^2 / (E_m - E_n)$$

$$\psi^{(m)} \approx u_m + \lambda \Sigma_{k\neq m} \{ \langle k|H'|m\rangle / (E_m - E_k) \} u_k$$
$$+ \lambda^2 \Sigma_{k\neq m} \{ -\langle k|H'|m\rangle\langle m|H'|m\rangle / (E_m - E_k)^2 + \Sigma_{n\neq m} \langle k|H'|n\rangle\langle n|H'|m\rangle / [(E_m - E_n)(E_m - E_k)] \} u_k$$

We can combine the two $\Sigma_{k\neq m}$ if we like and factor out $\langle k|H'|m\rangle / (E_m - E_k)$ to get

$$\psi^{(m)} \approx u_m + \Sigma_{k\neq m} \{ \langle k|H'|m\rangle / (E_m - E_k) * [\lambda - \lambda^2 \langle m|H'|m\rangle / (E_m - E_k)]$$

$$+ \lambda^2 \Sigma_{n\neq m} \langle k|H'|n\rangle\langle n|H'|m\rangle / [(E_m - E_k)(E_m - E_n)] \} u_k$$

$$W^{(m)} \approx E_m + \lambda\langle m|H'|m\rangle + \lambda^2 \Sigma_{n\neq m} |\langle m|H'|n\rangle|^2 / (E_m - E_n)$$

At this point, we might define $\lambda H' = \mathcal{H}'$ as the actual perturbation, where we suck the smallness parameter "back inside". We exposed if in order to do our perturbation theory. Then we get

$$\psi^{(m)} \approx u_m + \Sigma_{k\neq m} \{ \langle k|\mathcal{H}'|m\rangle / (E_m - E_k) * [1 - \langle m|\mathcal{H}'|m\rangle / (E_m - E_k)]$$

$$+ \Sigma_{n\neq m} \langle k|\mathcal{H}'|n\rangle\langle n|\mathcal{H}'|m\rangle / [(E_m - E_k)(E_m - E_n)] \} u_k$$

$$W^{(m)} \approx E_m + \langle m|\mathcal{H}'|m\rangle + \Sigma_{n\neq m} |\langle m|\mathcal{H}'|n\rangle|^2 / (E_m - E_n) \qquad \text{// which is 31.14}$$

Example of non-degenerate 2nd order perturbation theory: the 1D HO (248)

This will serve as our example for a perturbation through second order

$$H = p^2/2\mu + 1/2\, K\, x^2 + 1/2\, b\, x^2$$
$$= H_0 + \mathcal{H}'$$

where we assume b << K. Recall that the states of a 1D HO are *non-degenerate*, forming a simple ladder of equally spaced runs. We of course know the *exact* answer to this problem to be the following

$$\sqrt{K/\mu} = \omega_{c0} \qquad \sqrt{(K+b)/\mu} = \omega_c$$
$$E_m = (m+1/2)\,\hbar\omega_{c0} \qquad W^{(m)} = (m+1/2)\,\hbar\omega_c$$

So let's compute the energy through second order "doing" perturbation theory. We quote from above

$$W^{(m)} \approx E_m + \langle m|\mathcal{H}'|m\rangle + \Sigma_{n\neq m}\, |\langle m|\mathcal{H}'|n\rangle|^2 /(E_m - E_n)$$

$$= E_m + (b/2)\langle m|x^2|m\rangle + (b/2)^2 \Sigma_{n\neq m}\, |\langle m|x^2|n\rangle|^2 /(E_m - E_n)$$

Most of the notes below deal with the technical issue of how you compute these matrix elements!

Side Problem: what is $\langle m|x^2|n\rangle$ for a HO?

Write

$$x = \sqrt{\hbar/(2\mu\omega_{c0})}\ (a^\dagger + a)$$

$$x^2 = \hbar/(2\mu\omega_{c0})\,(a^\dagger + a)^2 = \hbar/(2\mu\omega_{c0})\,(a^\dagger a^\dagger + a^\dagger a + a\,a^\dagger + a\,a)$$

$|n\rangle = c_n/c_0\,(a^\dagger)^n|0\rangle$ Saxon page 134

$$c_n = (m\omega_{c0}/\hbar\pi)^{1/4} / \sqrt{n!}$$
$$c_0 = (m\omega_{c0}/\hbar\pi)^{1/4} / 1$$

$$c_n/c_0 = 1/\sqrt{n!}$$

$$|n\rangle = (a^\dagger)^n|0\rangle /\sqrt{n!}$$

Then we have

$$\langle m|x^2|n\rangle = \langle 0|a^m (a^\dagger a^\dagger + a^\dagger a + a\,a^\dagger + a^2)(a^\dagger)^n|0\rangle * \hbar/(2\mu\omega_{c0}) * 1/\{\sqrt{n!}\sqrt{m!}\}$$

I thought this would be "the easy way" but it looks very ugly! I see that I went a bit to far. Let's go back here

$$\langle m| x^2|n\rangle = \hbar/(2\mu\omega_{c0}) \langle m| (a^\dagger a^\dagger + a^\dagger a + a\, a^\dagger + a\, a\,) |n\rangle$$

I can see that <u>we really need to look at special cases:</u>

$$\langle m| x^2|m\rangle = \hbar/(2\mu\omega_{c0}) \langle m| (a^\dagger a^\dagger + a^\dagger a + a\, a^\dagger + a\, a\,) |m\rangle$$
$$= \hbar/(2\mu\omega_{c0}) \langle m | a^\dagger a + a\, a^\dagger |m\rangle$$

because we know for example that

$a^\dagger|m\rangle = \sqrt{m+1}\,|m+1\rangle$ Saxon page 135 (51)

$a\,|m\rangle = \sqrt{m}\,|m-1\rangle$ Saxon page 51 (53)

Then we know that

$$a\,a^\dagger\,|m\rangle = a\sqrt{m+1}\,|m+1\rangle = \sqrt{m+1}\,\sqrt{m+1}\,|\,m\,\rangle = (m+1)\,|m\rangle$$

$$a^\dagger\,a\,|m\rangle = a^\dagger\sqrt{m}\,|m-1\rangle = \sqrt{m}\,\sqrt{m}\,|\,m\,\rangle = m\,|m\rangle$$

so we then have

$$\langle m| x^2|m\rangle = \hbar/(2\mu\omega_{c0}) \langle m | a^\dagger a + a\, a^\dagger |m\rangle$$

$$= \hbar/(2\mu\omega_{c0}) \{ (m+1) + m \} = \hbar/(2\mu\omega_{c0})(2m+1)$$

Now Schiff defines

$$\alpha = (\mu K/\hbar^2)^{1/4} \qquad \alpha^2 = (\mu K/\hbar^2)^{1/2} = \sqrt{\mu K}\,/\hbar \qquad \sqrt{K/\mu} = \omega_{c0}$$

$$2\alpha^2 = (2/\hbar)\sqrt{\mu K} \qquad \sqrt{\mu K} = \sqrt{K/\mu} * \mu = \mu\,\omega_{c0}$$

so then

$$2\alpha^2 = (2/\hbar)\sqrt{\mu K} = (2\,\mu\,\omega_{c0}/\hbar) \qquad \text{so} \qquad \hbar/(2\mu\omega_{c0}) = (2\alpha^2)^{-1}$$

so using the α we can say that

$$\langle m| x^2|m\rangle = \hbar/(2\mu\omega_{c0})(2m+1) = (2\alpha^2)^{-1}(2m+1)$$ // **which is page 248 B2**

which agrees with B2 on Schiff page 248.

Now back to our general case

$$\langle m|\, x^2 |n\rangle \;=\; \hbar/(2\mu\omega_{c0})\, \langle m|\, (a^\dagger a^\dagger \;+ a^\dagger a \;+ a\, a^\dagger + a\, a\,)\, |n\rangle$$

We can see that there are really only 3 cases to worry about (and all other cases are 0 **which is page 248 B4**), and we have just done one of them. A second case is this

$$\langle m|\, x^2 |m+2\rangle \;=\; \hbar/(2\mu\omega_{c0})\, \langle m|\, (a^\dagger a^\dagger \;+ a^\dagger a \;+ a\, a^\dagger + a\, a\,)\, |m+2\rangle$$

$$=\; \hbar/(2\mu\omega_{c0})\, \langle m|\, a\, a \;|m+2\rangle$$

But $a\, a \;|m+2\rangle = a\sqrt{m+2}\;|m+1\rangle = \sqrt{m+2}\,\sqrt{m+1}\,|m\rangle$

so we get

$$\langle m|\, x^2 |m+2\rangle = \hbar/(2\mu\omega_{c0})\,\sqrt{m+1}\,\sqrt{m+2}$$ // **which is page 248 B1.**

The third case is then

$$\langle m|\, x^2 |m-2\rangle \;=\; \hbar/(2\mu\omega_{c0})\, \langle m|\, (a^\dagger a^\dagger \;+ a^\dagger a \;+ a\, a^\dagger + a\, a\,)\, |m-2\rangle$$

$$=\; \hbar/(2\mu\omega_{c0})\, \langle m|\, a^\dagger a^\dagger \;|m-2\rangle$$

But $a^\dagger a^\dagger \;|m-2\rangle = a^\dagger\sqrt{m-1}\;|m-1\rangle = \sqrt{m-1}\,\sqrt{m}\,|m\rangle$

$$\Rightarrow \quad \langle m|\, x^2 |m-2\rangle = \hbar/(2\mu\omega_{c0})\,\sqrt{m}\,\sqrt{m-1}$$ // **which is page 248 B3.**

Resume the solution:

Now back to our energy formula:

$$W^{(m)} \approx E_m + (b/2)\,\langle m|\, x^2 |m\rangle + (b/2)^2 \sum_{n\neq m} |\langle m|\, x^2 |n\rangle|^2 /(E_m - E_n)$$

$$= E_m + (b/2)\,\langle m|\, x^2 |m\rangle + (b/2)^2\; |\langle m|\, x^2 |m+2\rangle|^2 /(E_m - E_{m+2})$$
$$+\; (b/2)^2\; |\langle m|\, x^2 |m-2\rangle|^2 /(E_m - E_{m-2})$$

But $(E_m - E_{m+2}) = -2\hbar\omega_{c0}$ and $(E_m - E_{m-2}) = +2\hbar\omega_{c0}$

so we have

$$W^{(m)} \approx E_m + (b/2)\,\langle m|\, x^2 |m\rangle + (b/2)^2/[2\hbar\omega_{c0}]\;\{\;\; |\langle m|\, x^2 |m-2\rangle|^2 - \; |\langle m|\, x^2 |m+2\rangle|^2\;\}$$

We compute that

$$\{..\} = [\;\hbar/(2\mu\omega_{c0})\,\sqrt{m}\,\sqrt{m-1}\;]^2 - [\hbar/(2\mu\omega_{c0})\,\sqrt{m+1}\,\sqrt{m+2}\;]^2$$

$= (\hbar/(2\mu\omega_{c0}))^2 \; [\; m(m-1) - (m+1)(m+2) \;]$

$= (\hbar/(2\mu\omega_{c0}))^2 \; [\; m^2 - m - m^2 - 3m - 2 \;]$

$= (\hbar/(2\mu\omega_{c0}))^2 \; [\; - m \; - 3m - 2 \;] \;\; = (\hbar/(2\mu\omega_{c0}))^2 \; [\; - 4m - 2 \;]$

$= - 2 \; (\hbar/(2\mu\omega_{c0}))^2 \; (1 + 2m)$

So our result is then

$$W^{(m)} \approx E_m + (b/2) \langle m| x^2 |m\rangle + (b/2)^2/[2\hbar\omega_{c0}] \; \{ \;\; |\langle m| x^2 |m-2\rangle|^2 - |\langle m| x^2 |m+2\rangle|^2 \; \}$$

$= E_m + (b/2)^* \; \hbar/(2\mu\omega_{c0})(2m+1) - (b/2)^2/[2\hbar\omega_{c0}] \; 2 \; (\hbar/(2\mu\omega_{c0}))^2 \; (1 + 2m)$

$= (m+1/2) \; \hbar\omega_{c0} \;\; + \;\; (b/2)^* \; \hbar/(2\mu\omega_{c0})^*(2m+1) - (b/2)^2/[2\hbar\omega_{c0}] \; 2 \; (\hbar/(2\mu\omega_{c0}))^2 \;\; ^* \; (1 + 2m)$

$= (m+1/2) \; \hbar\omega_{c0} + \;\; (b/2)^* \; \hbar/(\mu\omega_{c0}) \; ^*(\; m+1/2) - (b/2)^2/[2\hbar\omega_{c0}] \; 4 \; (\hbar/(2\mu\omega_{c0}))^2 \; (m+1/2)$

$= (m+1/2) \;\; [\hbar\omega_{c0} \; + \; (b/2)^* \; \hbar/(\mu\omega_{c0}) \; - \;\; \hbar \; (b/2)^2/[2\omega_{c0}] \; (1/(\mu\omega_{c0}))^2 \;]$

$= (m+1/2) \; \hbar \;\; [\omega_{c0} \; + \; (b/2) \; 1/(\mu\omega_{c0}) \; - \; b^2/[8\mu^2\omega_{c0}^3] \;\;]$

$= (m+1/2) \; \hbar \; \omega_{c0} \; [1 \; + \; (b/2) \; 1/(\mu\omega_{c0}^2) \; - \; b^2/[8\mu^2\omega_{c0}^4] \;\;]$

But $\sqrt{K/\mu} \;\; = \omega_{c0}$ so we then have

$= (m+1/2) \; \hbar \sqrt{K/\mu} \;\; \{ \;\; 1 \; + \; (b/2) \; 1/(K) \; - \; b^2/[8K^4] \;\; \}$

$= (m+1/2) \; \hbar \sqrt{K/\mu} \;\; \{ \;\; 1 \; + \; B/2K \; - \; b^2/(8K^2) \;\; \}$ **// which is page 248 C.**

Now look way back to our "correct answer"

$\sqrt{K/\mu} \;\; = \omega_{c0}$ $\qquad\qquad$ $\sqrt{(K+b)/\mu} \;\; = \omega_c$

$E_m = (m+1/2) \; \hbar\omega_{c0}$ $\qquad\qquad$ $W^{(m)} = (m+1/2) \; \hbar\omega_c$

and we can write

$$\omega_c = \sqrt{(K+b)/\mu} \;\; = \sqrt{K/\mu} \;\; (\; 1 + b/K)^{1/2} = \sqrt{K/\mu} \;\; (\; 1 + 1/2 \; b/K \;\; + (1/2)(-1/2)/2 \; b^2/K^2 + ...)$$

$$= \sqrt{K/\mu} \;\; (\; 1 + b/2K - b^2/8K^2 \;\; + ...)$$

so our exact answer can be expanded as

$W^{(m)} = (m+1/2)\,\hbar\omega_c = (m+1/2)\,\hbar\sqrt{K/\mu}\,(\,1 + b/2K - b^2/8K^2 + ...)$

and this agrees exactly with our energy calculation from second order perturbation theory. In effect, we can think of b as the smallness parameter if we like, or we could replace it with bλ and then set λ = 1 at the end.

So this example took me p12-p16 = 4 pages of scribbling to verify. It was a good exercise using the creation operators which I have sort of skipped on this pass through QM.

Degenerate Case.

Unfortunately, Mr. Schiff does not sparkle in this section and I had to go off and write a huge separate document all on my own. I regarded this as a good exercise, but I am not sure I did it right and have no confirmation yet from other sources. My major Schiff problem is that his notation is not adequate to the task. What I call B'_{ij} for the adjustment of wavefunction u_i in the j direction due to the perturbation, he just calls a_j which seems to be lacking an index. Even in his case of N=2, you need to keep track of this kind of stuff. My attempt was to treat the general case of any N. Admittedly, Schiff devotes only 2 pages to the degenerate case out of his 533 page book, and he decided not to pursue this problem much. He attempted to do what he could without getting involved in a whole new notation.

Now, what other sources to I have on this subject? Now might be a good time to read Saxon on this subject, since I completely skipped the approximation methods chapter on my Saxon read through.

2/26/09. A lot of time has passed since I stopped above this line. Schiff's stuff was so bad that I went off and learned degenerate perturbation theory from Messiah and Kato, lots of notes. I now want to dovetail back into the Schiff flow and continue in his book.

Page 249. My notes "degenerate perturbation theory.doc" Section 12 derive all the equations appearing on this page. Equations **31.15** are the two equations implied by the level 1 diagonalization problem

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

where I use state labels 1 and 2, but Schiff uses m and ℓ . He has always used "m" up to this point. Equation **31.16** is the secular equation $\det(H - W_1 1) = 0$ which we use to find the eigenvalues W_1 for our first order correction. If **31.17** is true, then the two values of W_1 so obtained are the same, and our first order diagonalization fails to remove the degeneracy. This concept is now quite clear to me -- that a degeneracy will be removed in *some* order, unless there is a symmetry which prevents it.

Page 250. Just continuing along. Recall from the above doc that we can write the state correction as

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

and we found it easy to compute the perp space correction amplitudes $B'_{ik,n}$ in first order. This could be written as

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

If we write $|u_{mi}\rangle = a|1\rangle + b|2\rangle$ in ket notation the above becomes

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

and this is what he means by **equation 31.18.** His amplitude $a_k^{(1)} = B'_{ik,1}$. This section was just not very enlightening even after I can derive all the equations.

Removal of Degeneracy in Second Order. (250)

Equation **31.19** comes from 31.4 as he says, I don't bother with it. Equation **31.20** is really the level 2 diagonalization problem which Messiah would write as $H'Q_{om}H' |i,1\rangle = W_{mi,2}|i,1\rangle$. You see the W_2 numbers here, and now his a_m and a_ℓ are new numbers which are going to diagonalize this 2x2 matrix equation.

$$\begin{pmatrix} (H'Q_{om}H')_{11} & (H'Q_{om}H')_{12} \\ (H'Q_{om}H')_{21} & (H'Q_{om}H')_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = W_2 \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

where again I use state labels 1 and 2, but Schiff uses m and ℓ, and here is what Q_{0m} means,

$(H'Q_{om}H')_{ji} = \Sigma_{k\neq m} H'_{jk}H'_{ki}/ (E_m - E_k)$ // he writes sum as S_n' instead of $\Sigma_{k\neq m}$

There is of course a secular equation here for W_2 that he does not write down. The equations 31.21 are those which, if true, imply that the two W_2 values are the same, and we have again failed to remove the degeneracy, even in second order. "unless these equations are true, we do remove degeneracy".

Page 251: Here he just comments on how you can tell by looking at matrix elements of H' whether degeneracy is going to be removed in a given order. I have made similar comments elsewhere. His last paragraph in this section is rather outrageous, saying "it is not difficult to show" . In fact, degenerate perturbation theory is extremely difficult, just ask Kato and those who came after him.

Zeeman Effect without Electron Spin (251)

The main idea here is to say H' = (e/2mc) **B•L** where **L** is the orbital **J** and we ignore spin. He derives this fact from earlier in the book where he adds the EM field to a particle's (non-rel) Hamiltonian using the usual minimal prescription, and then uses the usual constant **B** field expression for **A**. Ratio ($e\hbar$/2mc) = μ_B in Gaussian units, a fact he does not mention. He then uses B_zL_z and assumes our base states are eigenstates of L_z and we then get first order energies as in **31.25**. This is a case where first order breaks a starting 2ℓ+1 fold degeneracy. But we didn't do any math here, we just started off with states that already diagonalized H', we "prediagonalized" if you will. Again, not terribly enlightening, but yes, it is a simple example showing how first order might break degeneracy. And that point is made without getting all balled up in combining **L** and **S**.

First order Stark Effect in Hydrogen n = 2 (252).

Go read the Messiah examples doc for review of the Stark "rotor". There, we first solve the problem to find states $|\ell m\rangle$ with the usual $2\ell+1$ degeneracy. There we see that (1) *first* order energy correction of any state is 0 due to parity; (2) non-zero matrix elements must have m = m'; (3) and must have $\ell = \ell' \pm 1$ from WET. We then compute ε_2 and find proportional to |m| with energy denominator stuff. In this rotor problem, we have $H_0 = L^2/2I$ and $V = -\mathbf{p}\bullet\mathbf{E}$ where $\mathbf{p} = d\,\hat{\mathbf{r}}$ where d is a fixed distance.

Perturbed Energy Levels (253).

The "n=2 state of hydrogen" includes $\ell = 0$ 2S and $\ell=1$ 2P orbitals. Think of these states as $|2,\ell,m\rangle$. Ignore spin, so we have then 4 states of interest, all degenerate in the raw atomic model. Hamiltonian is $H' = -\mathbf{p}\bullet\mathbf{E}$ with $\mathbf{p} = e\mathbf{r}$ analogous to the Zeeman $-\boldsymbol{\mu}\bullet\mathbf{B}$ with $\boldsymbol{\mu} = \mu_B\mathbf{L}$ which we just treated above. In this problem we have $H_0 = P^2/2m$. So in this problem, both H_0 and $H'=V$ are different from the rotor problem treated above. The dipole moment operator p is different. In the hydrogen problem, there is no constant d as there is in the rotor problem. However, in both cases we have V transforms as a (1,0) tensor and behaves basically as "z" which commutes with L_z and thus we get m = m' in both cases. We also get the idea that $\ell' = \ell \pm 1$ in both cases. In the rotor problem, an eigenstate has a definite ℓ so $\varepsilon_1 = 0$ and we computed the ε_2 energy correction. In the hydrogen problem, our n=2 state is a mix of $\ell=0$ and $\ell=1$, four degenerate states, so in this problem there is an ε_1 energy correction! That is the big difference. The level 1 diagonalization problem says $H'\psi = \varepsilon_1\psi$ and is a 4x4 matrix problem. The secular equation is a 4x4 determinant $\det(H'-\varepsilon_1) = 0$. If in our matrix we list off the rows and columns in order $\ell m = 00,10,11,1\bar{1}$, then the result is diagonal except in the upper left 2x2 where we have elements $\langle 00|H'|10\rangle$ etc exactly as he shows it in 31.27, and of course $W_1 = \varepsilon_1$. Schiff then computes these matrix elements directly using the raw H atom wavefunctions from page 93. The z integration gets the z from V, and gets z dependence from Y_{10} which contains another factor of z as shown page 80. So you can do the integral of z^2, then the radial integral is a standard form as shown, and you get a final answer, always nice to get a distinct answer, Schiff gets kudos for that. Quantity a_0 is the Bohr radius so $p = ea_o$ now and result has the right units. So if I did the details, I could show that the constant there is -3 as shown. So now we have a pretty simple determinant to do, I think it says $W_1^2(W_1^2 - q^2) = 0$ where q is our matrix element shown. So yes, roots are 0,0,q and -q. You could of course find the four corresponding eigenfunctions. You can interpret this result as saying this n=2 state of hydrogen behaves as if there are 4 states aligned as he says. So instead of having degeneracy 4, you end up with a splitting where 2 stay put, one goes up and one goes down, by equal distances. So this is a fine example. It is "as if" this H atom state has a "permanent dipole moment" of size ea_o. I agree.

Occurrence of Permanent Electric Dipole Moments (253)

Schiff could have instead computed the ε_2 correction for the H atom ground state. In general, all states will have an ε_2 correction just from the general form of the correction formula. We know this ε_2 problem involves $VQ_{0a}V$ and so in the Stark case this will give a correction proportional to E^2, and this gets interpreted as an "induced dipole moment" where the induced $p \sim E$, and then $p\bullet E$ gives another factor of E. The n=2 case he chose to present instead has an ε_1 correction linear in E, and is in the "fixed dipole moment" class. The practical problem is that it is not very convenient to study H gas in the n=2

level, because it won't stay there. Transitions in and out probably wreck the dipole effect. If you look at Lithium as a perhaps better example, it is a metal and not a gas, and then you get the usual solid state QM effects which I think wreck the idea we are trying to study here. But still, this was a good theoretical example.

Aside: I just looked up what **Steve Chu** did for his prize. Laser beams can be used to "optically trap" small particles by providing an energy minimum at some 3D location. This is now called "optical tweezers" and is used to hold a single bacteria cell in place, for example. Steve used this idea to hold single neutral atoms in place so they could be studied. He has some lecture notes on this subject, his prize was 1997 for work he did I think in the decade prior to that time. His field was "atomic physics" and his atomic trapping required low temperature work. He was in the right place at the right time, and has a family history of overachievers!

Page 254: Here Schiff gives a discussion of electric dipole moments of systems like atoms and simple molecules, with comments on the parity symmetry. As in our n=2 H case, you need some degeneracy to get a "permanent" moment. For nuclei or particles, the only possible direction object is the spin vector S, so you might expect any moments to be aligned with this vector. Nuclei have no E dipoles if P is a symmetry, which it is, recall Levitt. There is something called The Schiff Theorem on the web that is somehow related to this topic.

And so finally ends my long saga with SSPT! A mere 10 pages of Schiff's book, but I ended up spending something like a month on this subject.

---

32. The Variation Method.

Use this method if (1) you are not perturbationally close to some known problem. (2) you have a non-separable problem of some sort.

Expectation value of the energy.

We derive 32.5 which says that the lowest eigenvalue E_o of a bound state problem is $\leq$ an integral of $\psi^* H \psi$ where ψ is an arbitrary SE solution. If you assume a smart form for a trial function for ψ with some free parameters, you can find values of those parameters which will minimize the integral and hopefully get you close to E_0. So this would be how you would apply the variation method to compute a ground state. References are given to Rayleigh (1873) and Ritz (1908), but Schiff does not call this the Rayleigh-Ritz method as I think other books do.

Application to excited states.

Here you make sure your trial function is orthogonal to all known lower states, and you modify the inequality to get something for your excited state energy level.

Ground State of Helium.

A very good example. We write H and take as a trial solution the product of single electron ψ for H atom. However, we are going to have Z be our single variational parameter. Using results from earlier in the book, S computes the KE and PE terms for each electron, which I underlined in red.

Electron Interaction Energy

The $1/r_{12}$ integral is not so easy so Schiff has a whole page 258 showing how you can do this integral.

Variation of the parameter Z.

We combine all our terms as shown top page 259, and vary Z to get Z = 1.69 instead of the nominal Z = 2 for the He nucleus. This result is explained in terms of shielding. The result you get is amazingly only 2% off from the experimental result. The perturbation result is 5% off, so this is better.

Van der Waals Interaction between two H atoms.

The picture of two H atoms far separated is shown page 260 top. Each electron sees three other charges, so there are six 1/r terms, but the four distant ones will be small and are put into H'. First is the proton repulsion, second is the electron repulsion, and third and fourth are the two electron-proton attractions. We then do the usual large R expansions of the various 1/r terms to get 32.12 where x_1 is the x coordinate of $\mathbf{r}_1$. The H_0 solutions have the two H atom form and so are even under parity with respect to a given proton, while the H' term is odd. Thus, the first order perturbation theory ε_1 energy is 0, and this shows that you have to compute ε_2 and it will involve $H'Q_{0a}H'$ as usual, and this means we have $1/R^6$ as the power involved in this energy. That is the point of this entire section, to show why it is $1/R^6$.

Perturbation Calculation -- puts a lower bound on ε_2

Recall comment on pages 193- 194 of Saxon that we normally expect $\varepsilon_2 < 0$ and this is always true for a ground state. The argument there is based on the wavefunction distorting in response to the perturbing force, and this readjustment lowers energy. We are not therefore surprised that the ε_2 for this Van der Waals situation is negative and we therefore have an attractive, albeit weak, force. We use the usual formula for ε_2 as shown in 32.13. By replacing all the E_n with the next higher E_n of the system of two H atoms (which has a non-zero matrix element to the ground state), he replaces 32.13 by an inequality shown in 32.14. Due to symmetry considerations, this * state is when both H atoms are in n=2, and this is used for E* in 32.14. Lots of terms in H'^2 vanish from symmetry, and the inequality result is shown in 32.16. But all we know is that ε_2 is bounded by this negative value and 0. We do know it is some negative value and we have attraction.

Variation Calculation -- puts an upper bound on ε_2

For trial ψ for our ground state, we just scale the H-atom product of u's by (1+AH') by the argument that this will generate a $1/R^6$ term, and A is the varying parameter. We are after all allowed to choose any trial function we want, so I accept 32.17 where we have to normalize as well. The integrand is simplified by throwing out 0 matrix elements, denominator is expanded in usual way, and the integrand is now given by 32.19. Do the variation of A and find $A = 1/E_0$ (a negative value), and now we see why the form 1+AH'

was chosen for ψ. The reason is that our bound is simple as in 32.20. Variation gives an upper bound, while the little perturbation theory gave a lower bound, so we have our answer sandwiched as in 32.21. We are between -8 and -6 scale units, and the right answer is about -6.5, so not bad. Footnote says you have to account for retardation effects when R is larger than λ, and that causes $1/R^7$, but don't really care about such large R separations.

Comment on Van der Waals Forces.

Wiki explains that this term applies to a grab-bag of intermolecular forces. When one or both of the attracted objects have permanent electric dipole moments (or other multipole moments E or M), these VDW forces are relatively strong, such as in water. But the case of our example above involves attraction between neutral two non-polar objects, in our case H atoms. The attractive force in this context is usually called the London force or the London dispersion force. I did a little study of this somewhere with neutral potential wells attracting each other. Schiff gives the London 1930 reference on page 261, an American. An arm-waving explanation of the attraction is that each of the two systems fluctuates and has a *temporary* electric dipole moment, and then you have a temporary version of the dipole-dipole attraction (I suspect this is attractive because as things move together, you reduce the field integral). In our example, the effective potential due to the London force has a minimum, and that is why we have H_2 molecules. Here is some wiki:

"In vacuum, London forces are **weaker** than other intermolecular forces such as ionic interactions, hydrogen bonding, or permanent dipole-dipole interactions. This phenomenon is the **only attractive intermolecular force** at large distances present between **neutral atoms** (e.g., a noble gas), and is the major attractive force between non-polar molecules, (e.g., nitrogen or methane). Without London forces, there would be no attractive force between noble gas atoms, and they **wouldn't exist in liquid form**. London forces become stronger as the atom or molecule in question becomes larger. This is due to the increased polarizability of molecules with larger, more dispersed electron clouds. This trend is exemplified by the halogens (from smallest to largest: F2, Cl2, Br2, I2). Fluorine and chlorine are gases at room temperature, bromine is a liquid, and iodine is a solid. The London forces also become stronger with larger amounts of surface contact. Greater surface area means closer interaction between different molecules."

My potential well example does not involve charges, and this gives an attraction due to "exchange", and this type of force might not be included under the VDW umbrella.

33. Alternative Treatment of the Perturbation Series (263)

We know that any ε_2 calculation requires an infinite summation and so is generally not very pleasant. We have seen how symmetry might limit the sum as in Messiah's rigid rotor. In this section, Schiff talks about some other methods for computing ε_2 which *avoid* doing that infinite sum!

Second order Stark Effect in Hydrogen (how Stark moves the ground state energy)

I don't think I have yet run across this example in another book. We know that it is easy to compute ε_2 if we know ψ_1 ($\varepsilon_2 = W_2 = \langle\psi_0|H'|\psi_1\rangle$) where ψ_1 the first order corrected wavefunction (in the presence of our Stark E field). In this example, Schiff directly *computes* ψ_1 as the solution of a differential equation, which is just the lowest ladder equation in our perturbation set 31.4, and which involves only ψ_0 and ψ_1.

The ODE is 33.2, the solution has the *form* 33.3, and the radial function f(r) is then 33.5, so W_2 is just the integral of 31.7, and the result of that integral is given in 33.7, so $\varepsilon_2 = -(9/4)E^2 a_0^3$. This is an exact answer for ε_2 and as expected, it is negative. Back on page 253, Schiff did a perturbation computation for the ε_1 shift of the hydrogen 2s state (an excited state), and commented that $\varepsilon_1 = 0$ for the ground state. So here he has filled in by doing the ε_2 for that ground state. Credit for this method goes to Kotani 1951. I'll bet there is some simple way to do the infinite sum, by the way!

Polarizability of Hydrogen

In general one writes $\varepsilon_2 = -1/2\ \alpha\ E^2$ where α is the polarizability. So we just computed ε_2 so we know that for H atoms in their ground state, $\alpha = 9/2\ a_0^3$.

Method of Dalgarno and Lewis

OK, this is an oddball entry from 1955. An operator F is discussed, and if you can find one that works, you can compute W_2 for a ground state of some system (and it is noted that all ground states are non-degenerate, so perturbation theory is relatively simple). But you have to solve a differential equation 33.14 for $\psi_1 = |1\rangle$ similar so the Stark section we just did. I have a feeling this is related to the Messiah Kato stuff. I can see that $F = (E_o - H_0)^{-1} H'$ will work always, and maybe you expand the inverse operator somehow. In any event, you define $|1\rangle = F|0\rangle$ and then solve the ODE 33.14 for $|1\rangle$ which is really ψ_1.
(33.16 has a rare notation where ψ_1 is regarded as a ket).

Third Order Perturbed Energy

This section shows that if you continue along with the F operator of Dalgarno, you get a nice result for ε_3 as well, where he uses a perturbation theory result for ψ_2 which I think is a form of

$$|2\rangle = [\ Q_{0a}\, V Q_{0a} \qquad -Q_{0a}^2\, V\, |0\rangle\langle 0|\ ]\ V\, |0\rangle \qquad \text{// } \textbf{Messiah p 194 (27)}$$

from the Messiah non-degenerate notes. Hardly worth a whole section to say that, but he shows the details. We are just reviewing approximation methods and D&L is one such. I imagine lots of methods have appeared in the last 50 years since Schiff's book.

Interaction of Hydrogen with a Point Charge.

This is a Stark-like problem, but we don't have here a *constant* E field except as part of the general field if we do a partial wave expansion of the E field. This problem is solved here using the Dalgarno method. You solve the ODE implied by 33.14 for your $\psi_1(r)$ and use that to compute W_2. We expand in partial waves and the result is shown in 33.22 and the ℓ=1 term gives our Stark second-order result computed earlier. This is an interesting toy problem, what does a point charge do to the ground state of hydrogen. Each partial wave of the E field causes an extra term in $\varepsilon_2 = W_2$. What happens here with ε_1 by the way, he is silent on that. What is $\langle 0|H'|0\rangle$ with H' as in 33.18? Notice that the sum begins with ℓ=1 so the angular part of the integral will vanish for all ℓ. So I think $\varepsilon_1 = 0$ as in regular Stark.

34. The WKB Approximation (268)

Note: In these raw notes, I figured out lots of the fine details such as the Bessel solution, but I was constantly confused about the higher level logic flow of the presentation. I felt I was missing the main idea a lot of the time. I added some long Comments after the fact, and Saxon helped me a lot getting the logic understood. This has now been cleared up and is best presented in the meta notes. So I suggest the reader see those notes and come here only for some particular equation derivation.

The Goldstein Connection

Schiff has reversed Goldstein's notation for S and W, I wonder why? You must do S↔W to convert a Schiff equation to a Goldstein equation! Schiff claims Whittaker Analytical Dynamics as his primary reference from 1927, then Goldstein second. Amazingly I found a site with Whittaker's book on it PDF and I will now take a look to see if Schiff's symbols follow his. This book had at least 3 editions 1904, 1917 and 1927, and my download is the 1917 one. It *does* agree with Schiff on W and does not use an S.

I have reviewed my Goldstein notes. Goldstein uses these symbols:

S = Hamilton's *principle* function = the classical action $\psi(\mathbf{r},t) = \exp[\, i\, S(\mathbf{r},t)/\hbar]$

The Hamilton-Jacobi equation for S is this:

$H(q_i, p_i = \partial S/\partial q_i) + \partial S/\partial t = 0$ $\mathbf{p} = \nabla S$ // Goldstein

Schiff chooses to call this function by the symbol W instead of S. That is of course very unhelpful to the loyal Goldstein reader since Goldstein uses W to stand for Hamilton's *characteristic* function
$S = W(q_i) - Et$. But OK, using Schiff's notation, I agree with page 269 B as stated, and W is then the principle function, not the characteristic function. Equation A is my equation above for ψ where we replace S with symbol W. Equation 34.1 I just derived by simple brute force.

Now on page 270 Schiff completes his confusion by using symbol S for what Goldstein calls W ! Suppose, says Schiff, ψ has the usual time dependence $e^{-iEt/\hbar}$ which means W(r,t) = -Et + S as shown page 270 A. Then as usual in Schiff write $\psi = u(r)\, e^{-iEt/\hbar}$ and of course $u(r) = e^{iS/\hbar}$ as in B. We then go back to 34.1 and replace $\partial W/\partial t = -E$. Also $\nabla W = \nabla S$ so the other two terms are not changed. Write 34.1 then as:

$-E + (\nabla S)^2/2\mu + V - i\hbar/2\mu * \nabla^2 S = 0$ and this is 34.2.

So fine, just think of 34.2 as an *alternate version of the SE*. The reader does not really need to know this has any connection to Hamilton-Jacobi theory. If you want to compare a Schiff equation or statement to a Goldstein equation or statement, you must do S ↔ W.

Approximate Solutions.

Comment #1 : Schiff's logic flow is lacking in this whole section, so I will try to add the missing pieces.

First of all, equations 34.3 and 34.4 are just restatements of the Schrodinger Equation where the

"meat" is encoded into k(x). For a free particle, V(x)=0, k(x) would be a constant and the solution of the first equation would be just the usual $e^{\pm ikx}$. The momentum is p = ħk as usual.

If we are at a position x for which V(x) << E, then the solutions are very close to $e^{\pm ikx}$ where k was the k of the problem with V(x) = 0. If k varies "slowly", then we can talk about $e^{\pm ikx}$ where k would be some average value in the vicinity of x. Of course $k^2(x) \sim E-V(x)$, so we would have to be in a region where E-V(x) "varies slowly" with x. So you can think of a "quasi-static" (wrong word but makes point) solution $e^{\pm ik(x)x}$ where k(x) varies very slowly in some sense.

We would like k(x) not to change much over one "cycle", for example. If k were a constant, over one cycle phase would change by $k\lambda = 2\pi$. If k varies slowly, we might do a linear fit and say k(x) = k + k'x and $k(\lambda)-k(0) = \Delta k = k'\lambda$, so that we pick up extra phase $\Delta k\lambda = k'\lambda^2$ over 1 cycle. So we would like this extra phase to be "small", so we would say $k'\lambda^2 << 2\pi$. This is the same as $(k'/k)\lambda << 1$ which is the same as $k'/k^2 << 2\pi$.

No matter how you say it, we know what we mean by "k changes slowly". Then the idea is that our wavefunction has the general form $e^{\pm ik(x)x}$ and the sine waves become more closely spaced where V(x) drops to low value say in some smooth potential well. As we move toward the turning points, the potential V(x) moves upward and gets closer to E, so the k(x) gets smaller, the oscillations (spatial) slow down. Right at the classical turning point, k = 0 since V = E and we are in the transition from sine to expo behavior, and this simple model $e^{\pm ik(x)x}$ does not work. Writing the condition as $k'/k^2 << 2\pi$ shows that the LHS wants to blow up at a turning point, invalidating our quasi-static model condition. Thus, the turning point needs "special attention" and that is what this Schiff section is mostly about.

Now if we go past the turning point to a region where E << V(x), then we roughly have $\kappa^2(x) \sim V(x)$ and the wavefunction has the form $e^{-\kappa(x)x}$ expo decay. Again, we would like to say that κ(x) does not change much (with change in x) in some sense so we get this quasi-static form of the wavefunction. But now we don't have "cycles" so not clear what not change much means. Suppose κ were a constant, so we have $e^{-\kappa x}$. Then in some distance d away from x=0 we have dropped from 1 to $e^{-\kappa d}$. We might choose d so that this becomes $e^{-2\pi}$ sort of in analogy to λ so that here we have $\kappa d = 2\pi$. Now if $\kappa = \kappa(x)$, then we might say we want the *extra* change this causes to be << $e^{-2\pi}$. We could write $e^{-[\kappa+\kappa' d]d}$ as the change, and we would then like to see $\kappa' d^2 << 2\pi$ up there in the exponent. This then looks like $k'\lambda^2 << 2\pi$ that we got above. So this idea of κ does not change much gets written $\kappa' d^2 << 2\pi$ which is the same as $(\kappa'/\kappa)d << 1$ which is the same as $\kappa'/\kappa^2 << 2\pi$. Seems a good way to do it.

In the sine region, what does the condition $k'/k^2 << 2\pi$ tell us in terms of the potential? We can compute this easily as follows:

$k^2(x) = C\,(E-V(x))$ $\qquad 2kk' = -CV'$ $\qquad k'/k^2 = -CV'/(2k^3) = -CV'/(2C^{3/2}(E-V)^{3/2}$

$$\Rightarrow \qquad k'/k^2 = -(2\sqrt{C})^{-1}\, V' / (E-V)^{3/2} \qquad << 2\pi$$

Again, you see that this might be valid away from the turning point E = V, but at some distance from the turning point, you will lose the condition. Some parallel comment would apply in the expo region.

So to conclude, all attention must go to the "transition region" near the turning points if you really want to compute something approximately using this "nearly free particle" model which is called the WKB approximation. The phase we wrote as k(x)x in the above discussion is called S(x)/ħ in the discussion below, so that $u(x) = e^{iS(x)/\hbar}$.

Derivation of 34.6 and 271B and 271D and 271E and 34.7

Now define $k = [\,2\mu(E-V)]^{1/2}/\hbar$ which really says $p = \hbar k = [\,2\mu(E-V)]^{1/2} = \sqrt{2\mu T}$ and $T = p^2/2\mu$. Put this into 34.2 and you get

$(\nabla S)^2 - 2\mu T - i\hbar\nabla^2 S = 0$

$(\nabla S)^2 - \hbar^2 k^2 - i\hbar\nabla^2 S = 0$

or

$i\hbar\nabla^2 S - (\nabla S)^2 + \hbar^2 k^2 = 0$ * // **which is 34.6** if you do 1D with coordinate x.

Now here is the big idea. Imagine S as a power series in $\hbar$

$S = S_0 + \hbar S_1 + \ldots$ // page 271 A

Put this into * above and get

$i\hbar\,[\nabla^2 S_0 + \hbar\nabla^2 S_1 + O(\hbar^2)\,] - (\nabla S_0)^2 - 2\hbar\nabla S_0 \bullet \nabla S_1 + O(\hbar^2) + \hbar^2 k^2 = 0$

The $\hbar^0$ term is this:

$-(\nabla S_0)^2 + \hbar^2 k^2 = 0$ or $-(\nabla S_0)^2 + 2\mu T = 0$ // **page 271 B**

The $\hbar^1$ term is this:

$i\,[\nabla^2 S_0] - 2\nabla S_0 \bullet \nabla S_1 = 0$ // page 271 C

but 1D so that $\nabla S_0 = S_o'$ and so on. The first equation for $\hbar^0$ I recognize as the eikonal equation which name Schiff does not mention. We can solve it in 1D : (let $f = S_0$ and $g = S_1$)

$(df/dx)^2 = p^2$ $(df/dx) = \pm p$ $f = \int dx\, p = \pm\hbar \int dx\, k$ // **which is page 271 D**

The second equation says $i\,(d^2f/dx^2) - 2\,df/dx * dg/dx = 0$. Let $df/dx = s$, so $i\,ds/dx - 2s\,dg/dx = 0$:

$i\,ds/dx / s = 2\,dg/dx$ => $i\,ds / s = 2\,dg$ => $g = i/2 * \ln s$

But $s = df/dx = \pm\hbar k$ so get $g = i/2 * \ln(\hbar k) = i/2 \ln(k) + i/2\ln(\hbar)$. So we have:

$S_o = \pm\hbar \int^x dx'\, k(x')$

$S_1 = i/2 \ln(k) + \text{constant}$ // **which is page 271 E**

Now compute:

$$e^{iS/\hbar} = e^{iS0/\hbar}\ e^{iS1}$$

but

$$e^{iS0/\hbar} = \exp(i \ \pm\hbar \ \int_0^x dx'\ k(x')/\hbar) = \exp[\pm i \ \int_0^x dx'\ k(x')]$$

$$e^{iS1} = \exp(i[\ i/2\ \ln(k) + \text{constant}] = \text{const} * \exp(-1/2\ \ln(k)) = \text{const} * 1/\sqrt{k}$$

So we end up with

$$u(x) = e^{iS/\hbar} = A/\sqrt{k(x)} * \exp[\pm i \ \int_0^x dx'\ k(x')] \qquad \textbf{// which is 34.7}$$

which is 34.7, fine. Of course $k(x) = [\ 2\mu(E-V(x))]^{1/2}/\hbar$ so x-dependence from the potential.

Just replace $\kappa = ik$ to get the other solution 34.8 which we just give a new constant B.

Note that

$$S_1' = ik'/2k$$
$$S_0' = \pm\hbar k$$

$$\Rightarrow \qquad |\hbar S_1'/\ S_0'| \ = \ |k'/2k^2|$$

Comment #2. What exactly has happened above? Suddenly we are mixing in "perturbation theory" where our smallness parameter in some sense is $\hbar$. It is not dimensionless, so we have to keep track of the exact smallness concept later. But we write our "WKB phase" as $S(x) = S_0 + \hbar S_1 + \hbar^2 S_2 + \ldots$. If we keep only the leading S_0 term, we find the following:

$$(\nabla S_0)^2 = \hbar^2 k(x)^2 \qquad \text{or} \qquad (dS_0/dx) = \pm\hbar k(x) \qquad \text{in 1D}$$

which has the solution

$$S_0(x) = \pm\hbar \ \int_0^x dx'\ k(x') \qquad \text{with } u(x) = \exp(iS_0(x)/\hbar) = \exp[\pm i \ \int_0^x dx'\ k(x')]$$

If k(x) were a constant, we would have $u(x) = \exp[\pm ikx]$ which is our expected free-particle solution. This S_0 level is the famous eikonal approximation of optics where S_0 is the wavefront function and the RHS would be the index of refraction $n^2(x)$. The S_0 level is also exactly the "eikonal" model of Goldstein with exactly the RHS shown, namely $\hbar^2 k(x)^2$. Goldstein referred to our $S_o(x)$ as his W(x) which was Hamilton's characteristic function. The "eikonal" equation above is then exactly the Hamilton-Jacobi equation. Here is a clip from my Goldstein notes

W-world	optics world
$S(\mathbf{r},t) = W(\mathbf{r}) - Et$	$P(\mathbf{r},t)$ = the phase = $L(\mathbf{r}) - ct$
$W(\mathbf{r})$	$L(\mathbf{r})$
E	c
$f = 2m(E-V(\mathbf{r})) = 2mT$	$f = n^2(\mathbf{r})$
$(\nabla W(\mathbf{r}))^2 = 2m(E-V(\mathbf{r})) = 2mT$	$(\nabla L(\mathbf{r}))^2 = n^2(\mathbf{r})$

where we should think of $W = S_0$.

Notice that we don't quite get the form $e^{-ik(x)x}$ as conjectured in our previous Comment #1, but we get *something very close* to that:

Suppose $k(x) = k + k'x$ so that the integral gives $kx + 1/2\ k'x^2$. Then we get

$$u(x) = \exp(iS_0(x)/\hbar) = \exp[\pm i \int_0^x dx'\ k(x')] = \exp[\pm i\ (kx + 1/2\ k'x^2)] = \exp[\pm i\ (k + 1/2\ k'x)x]$$

$$= \exp[\pm i\ k_{eff}(x)\ x\ ] \qquad \text{where } k_{eff}(x) = k + k'x/2 \text{ which has half the slope of } k(x).$$

So our eikonal quasi-static solution in 1D has this smooth $k_{eff}(x)$ in the exponent instead of $k(x)$.

If we include the effect of the next S_1 term in our $S(x)$ expansion, the only effect on our solution is to add a multiplicative factor $1/\sqrt{k(x)}$, as shown in detail above. So then we have 34.7 ,

$$u(x) = (1/\sqrt{k(x)}\ ) \exp[\pm i \int_0^x dx'\ k(x')]$$

so presumably this is an *improved* approximate wavefunction form because we have kept two terms in our series instead of one. I guess the next term could be considered, but Schiff does not do that. A key thing to note about the factor $(1/\sqrt{k(x)}\ )$ is that it will be very important near a turning point, since it gets very large since $k \rightarrow 0$, so you would have a huge error in that region if you were to omit it.

He also states the analogous form of the solution in an expo region in 34.8.

Asymptotic Nature of the Solutions (271)

A somewhat wobbly argument is made to show that the second term $\hbar S_1$ is small compared to the first term S_0 provided condition F is true. Assuming you can just "add primes" to things as he has done, he finds that the condition of smallness of the S_1 term relative to the S_0 term is the same as my condition from Comment #1 above which said $k'/k^2 << 2\pi$, modulo a factor of π (see 34.9). As I noted in that same comment, at a classical turning point, we have $p = 0$ (no momentum, no T) so $k = 0$ so $\lambda = \infty$ and you cannot satisfy this WKB approximation condition.

Comment #3: What the hell have we done here to this point? The form u(x) shown in 34.7 is an *approximate solution* to the SE written as 34.2 [or 34.6 in 1D] where we have expanded S in a power series in smallness parameter $\hbar$ and we have kept only the first two terms in the series! This approximation should be good in a situation where you can sort of neglect $\hbar$, which means you are in a sort of classical situation. A condition for validity is that k must vary slowly relative to λ, because only

then is the second term in the just-mentioned series much smaller than the first term (so we think further terms can be fully ignored). Our equation for S in 34.2 becomes, if we drop the $\hbar$ term, the Hamilton-Jacobi classical equation, so this reinforces the idea that we are "somehow" close to a classical situation, but I admit it is not clear in what sense we are "close".

Solution near a Turning Point (272)

This is very obscure [but much later becomes clear]. First, he claims that the Bessel function form 34.10 satisfies 34.3 when $k^2(x) = Cx^n$. I guess the first thing we should guess is that a simple power for k^2 will probably handle some reasonable class of problems. The connection to ξ seems a bit odd, so let's just compute a few things:

Problem 1: Convert the ODE 34.3 from variable x to variable ξ.

$u(x) = A\, \xi^{1/2} k^{-1/2} J_{\pm m}(\xi)$

$\xi = \int_0^x dx\, k(x)$

$d\xi/dx = k(x)$

$k(x)^2 = Cx^n$

$\xi = \int_0^x dx\, k(x) = \sqrt{C} \int_0^x dx\, x^{n/2} = \sqrt{C}\, (1/(n/2+1))\, x^{n/2+1}$ // assume $n/2+1 > 0$

$1 + n/2 = (2+n)/2 = 1/2m$ according to definition of $m = 1/(n+2)$

$2m + mn = 1$ $mn = 1-2m$

$\xi = \sqrt{C}\ 2m\ x^{1/(2m)} = \sqrt{C}\ 2m\ x^{1+n/2}$ // $\xi = \sqrt{C}\, (2/3)\, x^{3/2}$ when $n = 1$, $m = 1/3$

$\xi^{2m} = (2m\sqrt{C})^{2m}\, x$

$x = (2m\sqrt{C})^{-2m}\, \xi^{2m}$

$dx/d\xi = (2m\sqrt{C})^{-2m}\, 2m\, \xi^{2m-1}$

$x^n = (2m\sqrt{C})^{-2mn}\, \xi^{2mn}$

$k = \sqrt{C}\ x^{n/2} = \sqrt{C}\ (2m\sqrt{C})^{-mn}\, \xi^{mn}$

$dk/d\xi = \sqrt{C}\, (2m\sqrt{C})^{-mn}\ mn\, \xi^{mn-1}$

$du/dx = d\xi/dx * du/d\xi = k\, du/d\xi$

$$d^2u/dx^2 = d\xi/dx * d(k\, du/d\xi)/d\xi = k * (dk/d\xi * du/d\xi + k\, d^2u/d\xi^2)$$

$$= k^2\, d^2u/d\xi^2 + k\, dk/d\xi * du/d\xi$$

$$= C\ (2m\sqrt{C})^{-2mn}\, \xi^{2mn}\, d^2u/d\xi^2 + \sqrt{C}\ (2m\sqrt{C})^{-mn}\, \xi^{mn}\, \sqrt{C}\, (2m\sqrt{C})^{-mn}\ mn\, \xi^{mn-1}\, du/d\xi$$

$$= C\ (2m\sqrt{C})^{-2mn}\, \xi^{2mn}\, d^2u/d\xi^2 + C\, (2m\sqrt{C})^{-2mn}\, mn\ \xi^{2mn-1}\ du/d\xi$$

$$= C\, (2m\sqrt{C})^{-2mn}\, \{\, \xi^{2mn}\, d^2u/d\xi^2 + mn\, \xi^{2mn-1}\ du/d\xi \,\}$$

So, we can write (34.3) as follows,

$$C\, (2m\sqrt{C})^{-2mn}\, \{\, \xi^{2mn}\, d^2u/d\xi^2 + mn\, \xi^{2mn-1}\ du/d\xi \,\} + [\sqrt{C}\ (2m\sqrt{C})^{-mn}\, \xi^{mn}]^2 u = 0$$

$$C\, (2m\sqrt{C})^{-2mn}\, \{\, \xi^{2mn}\, d^2u/d\xi^2 + mn\, \xi^{2mn-1}\ du/d\xi \,\} + C\, (2m\sqrt{C})^{-2mn}\, \xi^{2mn} u = 0$$

$$\{\, \xi^{2mn}\, d^2u/d\xi^2 + mn\, \xi^{2mn-1}\ du/d\xi \,\} + \xi^{2mn} u = 0$$

$$\{\, d^2u/d\xi^2 + mn\, \xi^{-1}\ du/d\xi \,\} + u = 0$$

$$\{\, d^2u/d\xi^2 + (1-2m)\, \xi^{-1}\ du/d\xi \,\} + u = 0$$

$$u'' + (1-2m) 1/\xi\, u' + u = 0$$

Problem 2: Show that the following form solves this ODE

$$u(x) = A\, \xi^{1/2} k^{-1/2} J_{\pm m}(\xi)$$

We know that,

$$k^{-1/2} = [\, \sqrt{C}\ (2m\sqrt{C})^{-mn}\, \xi^{mn}]^{-1/2} \sim \xi^{-mn/2} = \xi^{m-1/2}$$

$$mn = 1-2m \qquad -mn = 2m-1 \qquad -mn/2 = m-1/2$$

So we are trying this form, ignore constant,

$$u(\xi) = \xi^m\ g(\xi)$$

$$u' = \xi^m g' + m\, \xi^{m-1} g$$

$$u'' = \xi^m g'' + 2m \xi^{m-1} g' + m(m-1) \xi^{m-2} g$$

Our ODE above now reads

$$u'' + (1-2m)1/\xi\, u' + u = 0$$

$$\xi^m g'' + 2m\xi^{m-1}g' + m(m-1)\xi^{m-2}g + (1-2m)1/\xi\,[\xi^m g' + m\,\xi^{m-1}g\,] + \xi^m\, g = 0$$

$$\xi^m g'' + 2m\xi^{m-1}g' + m(m-1)\xi^{m-2}g + (1-2m)\,[\xi^{m-1}g' + m\,\xi^{m-2}g\,] + \xi^m\, g = 0$$

$$\xi^{m+2} g'' + 2m\xi^{m+1}g' + m(m-1)\xi^m g + (1-2m)\,[\xi^{m+1}g' + m\,\xi^m g\,] + \xi^{m+2}\, g = 0$$

$$\xi^2 g'' + 2m\xi g' + m(m-1)g + (1-2m)\,[\xi g' + m\, g\,] + \xi^2 g = 0$$

$$\xi^2 g'' + 2m\xi g' + m(m-1)g + \xi g' + m\, g - 2m\,\xi g' - 2m^2 g + \xi^2 g = 0$$

$$\xi^2 g'' + m(m-1)g + \xi g' + m\, g - 2m^2 g + \xi^2 g = 0$$

$$\xi^2 g'' + \xi g' + m(m-1)g + m\, g - 2m^2 g + \xi^2 g = 0$$

$$\xi^2 g'' + \xi g' + m^2 g - mg + m\, g - 2m^2 g + \xi^2 g = 0$$

$$\xi^2 g'' + \xi g' - m^2 g + \xi^2 g = 0$$

$$\xi^2 g'' + \xi g' + (\xi^2 - m^2)g = 0$$

and finally we arrive at Bessel's equation A&S page 358 top, and we know that, among other forms, some solutions have the form $g = J_{\pm m}(\xi)$. Thus, we have now verified that

$$u(x) = A\,\xi^{1/2}k^{-1/2}J_{\pm m}(\xi)$$

is in fact a solution of 34.3. I did all these detail just because of the strange definition of ξ.

Problem 3: Find the large x behavior of this u(x),

$$\xi = \sqrt{C}\;\; 2m\;\; x^{1/(2m)} \qquad \text{// from above}$$

We assumed already that $n/2+1 > 0$ which means $1/2m > 0$ which means $m > 0$. So $x^{1/2m}$ is x to some positive power, so as x gets large, ξ also gets large.

Use A&S page 364 to claim that

$$J_{\pm m}(\xi) \rightarrow \sqrt{2/\pi}\;\; \xi^{-1/2}\cos(\,\xi - m\pi/2 - \pi/4)$$

Then we have

$$u(x) \rightarrow A\,\xi^{1/2}k^{-1/2}J_m(\xi) = A\,\xi^{1/2}k^{-1/2}\sqrt{2/\pi}\;\; \xi^{-1/2}\cos(\,\xi - m\pi/2 - \pi/4)$$

$= A\sqrt{2/\pi}\ k^{-1/2} \cos(\xi - m\pi/2 - \pi/4)$

so this matches 34.7 where A is a different constant A.

Comment #4. We know that $k^2(x) = C\,[E - V(x)]$ so "it is what it is" for a given problem. However, we are going to focus on the region surrounding a classical turning point and we make this be at x = 0. We then imagine that we approximate $k^2(x)$ as a simple power of x in this region.

$f(x) \equiv k^2(x) = C\,[E - V(x)]$
$f'(x) = -CV'(x)$
$f''(x) = -C\,V''(x)$
$f^{(n)}(x) = -C\,V^{(n)}(x)$

$f(x) = f(0) + x\,f'(0) + x^2 f''(0)/2 + \ldots$

$= 0 - CV'(0)\,x - C\,V''(0)\,x^2 + \ldots$

In general, we don't expect V'(0) = 0 at a turning point (unless we go out of our way to select an energy E and a V(x) that allows this to happen). Thus, the common situation near a turning point will be this:

$f(x) = k^2(x) \approx [-CV'(0)]\ x$

which is what is drawn on page 273, and is called a "linear" turning point. For any V(x) and E, there will always be some leading term in this Taylor series expansion, call it Cx^n . So that is WHY Schiff has assumed this form for $k^2(x)$. The light finally shines.

Now back to the main logic flow. We showed above that 34.10 solves 34.3 when $k^2 = Cx^n$, a special case. The claim made here is that if you add the term θ(x) shown in 34.12 to get equation 34.11, then 34.10 solves 34.11 for any $k^2(x)$. It must be that when k^2 has the special form, θ = 0. Let's verify that:

$k^2 = Cx^n \qquad 2kdk = Cnx^{n-1}dx \qquad k' = Cnx^{n-1}/2k = Cx^n nx^{-1}/2k = knx^{-1}/2$

$k'' = -knx^{-2}/2 + k'nx^{-1}/2$

$\theta(x) = 3\,(knx^{-1}/2)^2/4k^2 - (-knx^{-2}/2 + k'nx^{-1}/2)/2k + (m^2-1/4)\,k^2/\xi^2$

$= 3\,(nx^{-1}/2)^2/4 - (-knx^{-2}/2 + k'nx^{-1}/2)/2k + (m^2-1/4)\,k^2/\xi^2$

We have to eliminate ξ using $\xi = \sqrt{C}\ 2m\ x^{1/(2m)}$ so

$1/\xi^2 = (1/2m\sqrt{C}\,)^2\,x^{-1/2m} = (1/2m\sqrt{C}\,)^2\,x^{-1-n/2}$

$k(x)^2 = Cx^n$

$k^2/\xi^2 = Cx^n \ (1/2m\sqrt{C})^2 \ x^{-1-n/2} = (1/2m)^2 \ x^{-1+n/2}$

OK, I am sure it works, ditch this detail.

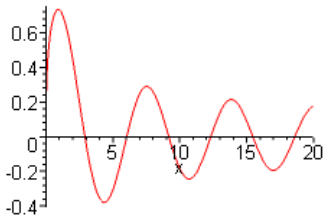
Comment #5. I am now happy to say that $k^2(x) = Cx^n$ in the region of a turning point. Schiff's entire discussion from 34.11 through the middle of page 273 is meant to convince us that if we keep *several* terms of the Taylor series I mention in my last Comment #4, those extra terms don't matter much. It is a strange way he uses to argue this. I am happy to just use the leading term and be done with it. He argues that his $\theta(x)$ modifier is very small at x=0 so our Bessel solution is still good for "any $k^2(x)$".

Linear Turning Point (273)

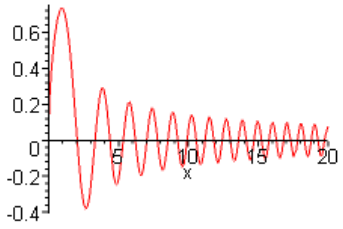
We assume the leading term of $k^2(x)$ near a turning point at x=0 is of the form Cx^n, and we know that n=1 will be the most common situation, the linear turning point, corresponding to m = 1/3, see Comment #4 above. In this case we know that the variable ξ is given by $\xi = \sqrt{C}\ (2/3)\ x^{3/2}$ and our sine behavior as we move away from x=0 is given by the form 34.10, since this is the solution of our Schrodinger Equation 34.3 given $k^2(x) = Cx$. This is of course only a solution near the turning point x = 0 since that is where we are modeling our $k^2(x)$ by the leading power in its Taylor expansion about that point.

Here is a plot of $J_{1/3}(\xi)$ for the variable going 0 to 20

```
plot(BesselJ(1/3, x),x=0..20);
```




```
plot(BesselJ(1/3, x^(3/2)),x=0..20);
```



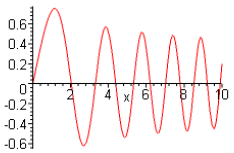
and you see it comes in quite steeply. If we throw in the $x^{3/2}$, things don't change much, just faster acceleration as shown on the right above. But we have extra factors in 34.10 that we need to add. From above,

$k^{-1/2} = [\sqrt{C}\ (2m\sqrt{C})^{-mn}\ \xi^{mn}]^{-1/2} \sim \xi^{-mn/2} = \xi^{m-1/2}$ // $= \xi^{1/3-1/2} = \xi^{-1/6}$

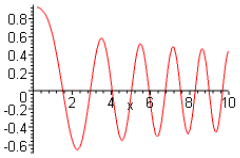
$\xi^{1/2}\ k^{-1/2} = \xi^{1/2}\ \xi^{-1/6} = \xi^{1/3} \sim x^{1/2}$

So we can throw in an extra factor $x^{1/2}$ to get a better look at what our m = +1/3 solutions 34.10 do

```
plot(x^(+1/2)*BesselJ(+1/3, x^(3/2)),x=0...10);
```




```
plot(x^(+1/2)*BesselJ(-1/3, x^(3/2)),x=0...10);
```

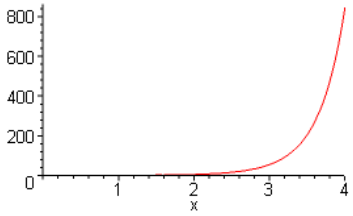


In general, the solution near the turning point on the sine side will be some kind of linear combination of these two solutions.

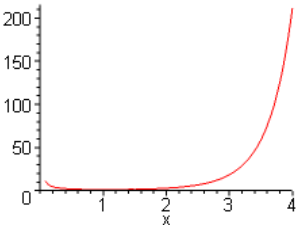
So this is showing what happens in the sine area near a turning point at x = 0 (this would be a "left side" turning point, matching figure page 273). You see that the wavelength gradually increases as you approach the turning point. Of course the fact that it is ∞ at the turning point is not very clear just looking at these plots.

If we go to κ = ik and ignore overall phase, we can just replace our two plots J with I as in 34.14, and we get these plots on the "expo side" of a linear turning point. Both blow up for large x Maple shows and the limits show.

```
plot(x^(+1/2)*BesselI(+1/3, x^(3/2)),x=0..4);
```

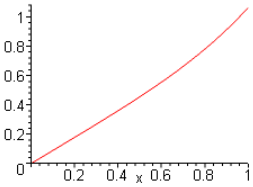



```
plot(x^(-1/2)*BesselI(-1/3, x^(3/2)),x=0..4);
```

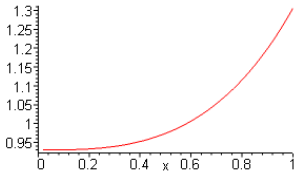


But we are really interested in small x where our model is viable, and then the plots look like this:

```
plot(x^(+1/2)*BesselI(+1/3, x^(3/2)),x=0...1);
```




```
plot(x^(+1/2)*BesselI(-1/3, x^(3/2)),x=0..1);
```



So in the expo region, you also can have a linear combination of these two solutions. The game will be to make things "match up" at x=0 which is the boundary between the sine and expo regions. Notice that the left solution goes to 0, but the other goes to a constant (offset axis).

Connection at the Turning Point (274)

As noted above, we have two candidate solutions on each side. The sine side is the region 1 side. The four solutions are given names in 34.14, and the small x limits are shown in page 274 A, making use of the facts shown in 34.15. Two solutions are constants, and two are linear in x at x = 0, in agreement with my plots above.

Here if we set $B_+ = -A_+$, the u_1^+ solution "matches" the u_2^+ solution, and if $B_- = +A_1$, the u_1^- solution "matches" the u_2^- solution. So we have two separate solutions called + and - which seem to pass

through our turning point being continuous and reasonable (not clear whether the slope is continuous, I bet it is).

Assuming we make these constant assignments, we have two good solutions called just u^+ and u^- that we can regard as "valid" (usable?) for all x (even though we know they are invalid for large |x| because our k(x) no longer has the assumed form -- but see meta notes!). The limits of the two solutions for large |x| are then shown in 34.16 which you obtain from the J and I limits and the assumed constant matching.

The big question: what do we do next?

Asymptotic Connection Formulas (275): Derive 34.17.

Now suppose you consider the solution $\psi = u^+ + u^-$. Looking at 35.16, you can compute the limit of such a solution for with $+\infty$ and $-\infty$ on x. Here is what I got on scratch paper:

$x \to +\infty$ $\quad (\pi k/2)^{-1/2} [\cos(\xi_1 - 5\pi/12) + \cos(\xi_1 - \pi/12)]$

$= (\pi k/2)^{-1/2} 2 \cos(\pi/6) \cos(\xi_1 - \pi/4)$

$= (\pi/2)^{-1/2} 2 \cos(\pi/6) * k^{-1/2} \cos(\xi_1 - \pi/4)$

$x \to -\infty$ $\quad (2\pi\kappa)^{-1/2} \{ \exp(-\xi_2) 2i \sin(\pi/3) \exp(-i\pi/2) \}$

$= (2\pi)^{-1/2} 2 \sin(\pi/3) * \kappa^{-1/2} \exp(-\xi_2)$

Let's multiply both results by $(\pi/2)^{1/2}$ and we get

$2 \cos(\pi/6) * k^{-1/2} \cos(\xi_1 - \pi/4)$ $\quad +\infty$

$1/2 * 2 \sin(\pi/3) * \kappa^{-1/2} \exp(-\xi_2)$ $\quad -\infty$

Then divide both sides by 2 and get

$\cos(\pi/6) * k^{-1/2} \cos(\xi_1 - \pi/4)$ $\quad +\infty$

$\sin(\pi/3) * 1/2 \kappa^{-1/2} \exp(-\xi_2)$ $\quad -\infty$

Now it happens that the two trig functions are equal because the two angles add to 90 degrees, both are .866, so scale this out and we get (and add arbitrary C)

$C * k^{-1/2} \cos(\xi_1 - \pi/4)$ $\quad +\infty$ $\quad$ **// which is 34.17**

$C * 1/2 \kappa^{-1/2} \exp(-\xi_2)$ $\quad -\infty$

Here is what this means. If you use the $\psi = u^+ + u^-$ function, if it has the expo side asymptotic limit shown on the second line, then its sine side asymptotic limit must be as shown on the first line (with the same relative constant). I am not sure how I would use this fact [see later], but I at least understand where it is

coming from. This is a realistic solution because it has expo decay on the expo side. No other linear combination achieves this goal.

So this is the first "connection formula". The second one must involve η somehow in the linear combination, but we are not told the combination! I guess I will have to wait to see an example.

Energy Levels of a Potential Well (276).

Here is our big application. We have some generic smooth potential well as shown page 276. There are of course two turning points. We start with the turning point on the left at x_1. We want expo decay to its left, and sine to its right, so we "use" our connection formula 34.17. What this means is that we assume to the right of the turning point that $\psi = k^{-1/2} \cos(\xi_1 - \pi/4)$ where $\xi_1 = \int_{x_1}^{x} dx\, k(x)$. The lower end is just because we have the turning point at $x = x_1$ instead of $x = 0$. We are not assuming any particular form for k(x), it is just whatever the potential V(x) makes it be, for a given E.

Now we want to do a mirror image "deal" for the right turning point. For this point we want

$$\xi'_1 = \int_{x_1}^{x_2} dx\, k(x)$$

for reverse penetration into the sine region. make x smaller, ξ_1 gets larger. Then we have $\psi = k^{-1/2} \cos(\xi'_1 - \pi/4)$ if we work to the left from the right turning point. Of course k = k(x). Then we do this little math:

$$\cos(\xi'_1 - \pi/4) = \cos\left[\int_{x_1}^{x_2} dx\, k(x) - \pi/4 \right] = \cos\left[\int_{x_1}^{x_2} dx\, k(x) - \int_{x_1}^{x} dx\, k(x) - \pi/4 \right]$$

where we add the integral from x_1 to x and then subtract it out again. We then pick some fixed point x out in the middle somewhere (perhaps around x = 0, but anywhere in the middle is fine), and we require that our two WKB forms for ψ have at least the same magnitude, if not the same sign. So we require that

$$k^{-1/2} \cos(\xi_1 - \pi/4) = \pm\, k^{-1/2} \cos\left[\int_{x_1}^{x_2} dx\, k(x) - \int_{x_1}^{x} dx\, k(x) - \pi/4 \right]$$

Since we are at some specific x, the k factors cancel, and we can define η as the x1→x2 integral and we also change signs on

$$\cos\left(\int_{x_1}^{x} dx\, k(x) - \pi/4 \right) = \pm \cos\left[\int_{x_1}^{x_2} dx\, k(x) - \int_{x_1}^{x} dx\, k(x) - \pi/4 \right]$$

$$\cos\left(\int_{x_1}^{x} dx\, k(x) - \pi/4 \right) = \pm \cos\left[-\int_{x_1}^{x_2} dx\, k(x) + \int_{x_1}^{x} dx\, k(x) + \pi/4 \right]$$

$$\cos\left(\int_{x_1}^{x} dx\, k(x) - \pi/4 \right) = \pm \cos\left[\int_{x_1}^{x} dx\, k(x) - \int_{x_1}^{x_2} dx\, k(x) + \pi/4 \right]$$

$$\cos\left(\int_{x_1}^{x} dx\, k(x) - \pi/4\right) = \pm \cos\left[\int_{x_1}^{x} dx\, k(x) - \pi/4 - \int_{x_1}^{x_2} dx\, k(x) + \pi/2\right]$$

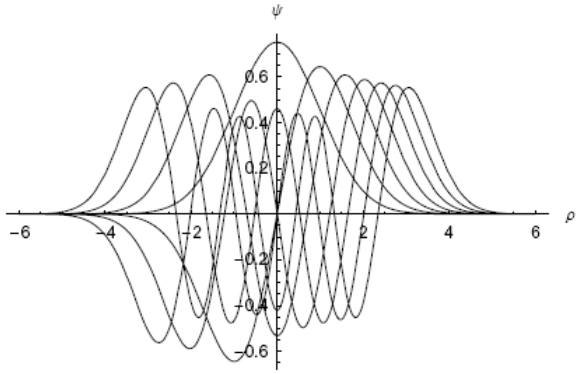
$$\cos(\varphi) = \pm \cos\left[\varphi - \left\{\int_{x_1}^{x_2} dx\, k(x) - \pi/2\right\}\right] = \pm \cos[\varphi - \eta]$$

Of $\eta = 0$ we have a match with a + sign. If $\eta = \pi$, match is with a minus sign. We know that k(x) is positive inside the well, so the integral of it is positive, so not going to get $\eta = -\pi$. So we achieve our matching condition at our selected interior point x as long as

$$\int_{x_1}^{x_2} dx\, k(x) - \pi/2 = 0,\pi,2\pi,.... = n\pi \qquad n=0,1,2..$$

$$\int_{x_1}^{x_2} dx\, k(x) = (n+1/2)\pi \qquad n=0,1,2.$$

Now, here is the reason for ± in the cosine equation above (which Schiff does not mention). We could have a positive sign expo decay going off to the right, and a negative expo decay going off to the left, and then our two "connection rules" would introduce a factor of -1, and that is the - of the ± . If both decay expos have the same sign, then you get the + of the ±. Here for example are the HO lowest 7 wavefunctions,



where the decay expos are all made positive on the right. Then half the solutions have a negative expo on the left, and half have positive, so both signs occur. As you gradually increase E, you increase k(x), and you increase our little integral $\int_{x_1}^{x_2} dx\, k(x)$. Each time the integral hits a value $(n+1/2)\pi$, we have another

WKB solution to our problem, and we know the "next" solution has "one more node". In fact, n is exactly the number of nodes and n=0 would give you E of the ground state, although our approximation is not really supposed to work in that regime. It is more intended for when there are lots of nodes in the well.

A quantization Rule (277)

From classical action-angle variables we know that $J = \int pdq$ is an action variable and has dimensions of angular momentum. Our rule above was that

$$\int_{x_1}^{x_2} dx\, k(x) = (n+1/2)\pi = \int_{x_1}^{x_2} dx\, p(x)/\hbar$$

=>

$$\int_{x_1}^{x_2} dx\, p(x) = (n+1/2)\pi\hbar = (n+1/2)h/2$$

=>

$$2 \int_{x_1}^{x_2} dx\, p(x) = (n+1/2)h = J$$

where the 2 provides the "full cycle" integration of the pdq integral. So this duplicates the Bohr-Sommerfeld quantization rule of the "old Bohr model" of the atom, except we have an extra h/2 tacked on. But again, we don't expect accuracy for low n values.

Special Boundary Conditions (277)

Three situations are considered. The first is the solid infinite wall as a turning point at x=0. In this case, we don't care about the expo side of the turning point because $\psi = 0$ there for sure. We would then take the linear combination of the u^+ and u^- solutions shown in 34.16 which gives $\sin(\xi_1)$ because this for sure goes to 0 at the wall. So I accept page 277 A on this basis. We ignoring the J functions and just using the large argument limits even though we are talking about "close to the wall" at x = 0. We pretend the large argument solutions are valid even right up to the wall.

If you have a square step, he comments on what you might do there.

The radial equation of a problem for $\ell = 0$ is like the infinite wall since $\psi(r=0) = 0$, so again you use the sine form, where now of course ξ_1 is a radial integral of k. For larger ℓ, things are not so simple says Schiff.

Tunneling Through a Barrier (278).

This is sort of the inverse of our potential well problem. This particular barrier is assumed to be in some problem's radial equation so horizontal axis is r, and the usual centrifugal term is included as shown in the picture page 278. We really should think explicitly of the example he discusses, I will call it reverse alpha decay. Suppose we shoot in an α particle with Z'=2 toward a nucleus Z. Our particle has a wavefunction something like I have drawn in pencil on page 278 (on the right side). In the expo region, our amplitude for tunneling would be something like $\exp(-\xi_2)$ at the radius $r_1 = R$ due to the turning point at radius r_2. We saw such a tunneling expo tail on page 104 for shooting particles at a post. The probability will be $\exp(-2\xi_2)$ since we have to square, and ξ_2 = integral away to the left from the turning point at r_2 so $\xi_2 = \int_{r_1}^{r_2} dr\, \kappa(r)$ = a positive number. Thus, the thing he calls P in 34.32 is our probability of penetration in terms of the ratio squared of the two amplitudes. That is to say, $P = [\psi(r_1)/\psi(r_2)]^2 << 1$ in general for our picture at least. This squared ratio is just $\exp(-2\xi_2)$ so *we have a way to compute this ratio* since we know $\kappa(r)$! We crudely set $r_1 = R$, the nuclear radius inside of which we have some strong hadronic attraction which accounts for the fact that the effective potential shown in Fig 30 dives negative inside this radius. The centrifugal term is what is pushing it up outside together with the Coulomb repulsion, and that is

what causes the peak shown. So we compute $\int_{r_1}^{r_2} dr\, \kappa(r)$ from our assumed simple Coulomb potential in this region and we get a result shown in 34.24 which is a function of the incoming alpha particle speed v and a dimensionless energy parameter called γ (both depend on E). There are two terms, one with 1/v and the other with v, so a bit complicated. Multiply this by 2 and you have your exponent and you then have P = $\exp(-2\xi_2)$. The idea is that this would be proportional to what I would call an "acceptance" rate, or absorption rate since I am thinking of the inverse problem. For the decay problem, the expo tail goes the other way as I have now shown in pencil on the left side. Then the rate is decay rate, proportional to P for this problem, which involves exactly the same integral $\int_{r_1}^{r_2} dr\, \kappa(r)$. This then gives a little model for decay rates as functions of E and Z. I forgot to say this model is for $\ell = 0$ and in this case, the rise in the barrier from the right side is due to the Coulomb repulsion between the alpha particle and the nucleus, and there is no centrifugal factor contribution. You have to imagine the α particle as having some kind of ψ inside the barrier, maybe in an ℓ=0 S state. I don't follow where he gets his timescale τ from, maybe $\hbar/\Delta E$ where ΔE is some nuclear value, some bound state level you have to pry the α from. Obviously there is much more one could say about this little model. If ΔE = 10 MeV say, maybe you would get his number. I forget typical nuclear binding forces. He says that the fit to E and Z is very good in many situations, so the little model here must be a good one.

He then comments on my "acceptance" inverse problem which would a nuclear rate calculation. We saw on page 141 how this has a certain Gamow factor which we computed using Coulomb scattering from a point charge (R=0). P must be this same Gamow factor, he claims. This is sort of example 2.

Example 3 is to consider a particle with E=0. If ℓ>0, the little κ integral is ∞ so P = 0 and you really can have a bound state at E= 0. He discussed this topic earlier as he said. You cannot have one for E > 0, though you can have a temporary resonance state. For $\ell = 0$ you get finite integral, finite P, cannot have a bound state for E = 0.

Comment: In this last tunneling section, we were able to compute useful stuff using "WKB methods" without ever solving any QM problems! We just used the WKB expected expo decay form at any turning point. We know without WKB that things are expo, but WKB is telling us the *exponent* of that decay! That exponent can be computed as $\int k(r)\, dr$ in each problem, where k is just a function of E and V(r). Notice that we don't do any "matching up" in the barrier problem as we did in the well problem. This is really a scattering problem, not a bound state problem, though we are in the bound state approx chapter. We don't match things up, but we compute a decay rate formula from a ratio P = $[\, \psi(r_1)/\psi(r_2)]^2$ as described above. The expo forces this ratio.

I wonder how Saxon handles all this stuff. I will meta review the above, then read Saxon and see what he might have to add to the soup. I don't think he will bother with those Bessel functions, he will just use the trig limits somehow I suspect.

35. Methods for Time-dependent Problems (279)

Three methods will be reviewed: TDPT, adiabatic, and sudden.

Time Dependent Perturbation Theory(280).

This TDPT is used in the later Chapter 11 to explain radiation from atoms which is probably the most important single phenomenon in the physical world from a human perspective. There, the atomic states are eigenstates of some H_o and radiation causes a small H' which causes transitions between the atomic states. First order perturbation theory is usually enough to handle the situation. In this section the basics are set out in general form.

We take the usual TDSE and blindly refunctionalize $\psi(x,t)$ into $a_k(t)$ where $a_k(t)$ are the usual coefficients of a full energy basis function expansion for ψ so that the refunctionalized SE is **35.5.** Fine.

Interaction Picture (281)

In my pencil notes top of that page, I show that 35.5 is just the interaction-*picture* SE projected into the energy *representation*, just as Schiff carefully states in the text. All the pieces needed to show this fact appear on the page. Dirac first did this so the interaction picture is often called the **Dirac picture**. Schiff confuses things a little bit by omitting the S suffix on H on the first page. I think the idea is that "default" implicit subscript is S and we will in fact work with H'_S.

First Order Perturbation (282)

If we then power series $a_k(t)$ into a smallness λ series and stuff it into 35.5, the appearance of $\lambda H'$ (now showing λ) offsets the series by one power on the right side and we end up with 38.5. The notation is now $a_k^{(s)}$ where this coefficient goes with λ^s. The time derivative is still present on the LHS of 35.8 if your eyes can see a dot that is 1/100th of mm in diameter. The basic idea is going to be to start a system off probably at $t=-\infty$ in some specific energy eigenstate "m", and then apply these equations in an iterative fashion. We can then watch to see how all the amplitudes change in time. We expect probability to flow out of our starting state and into some other states. The solution to the bottom equation of the ladder is shown in 35.9

Harmonic Perturbation (282).

Assume now $\sin(\omega t)$ as the time dependence of H'(t), and let it run only from t=0 to $t=t_0$. The integrand in 35.9 is then two expos and we can trivially integrate to get **35.11**. I always am thinking of ω_{km} as an energy separation where E_k is the upper level if this thing is positive, as in 35.4, so we see at once a resonance situation with the second term in 35.11. I think the first term would be a resonance for a down-transition and will later by seen as "stimulated emission". For now we are going to knock an electron from bound state k out into the continuum band with energy E_k, so this is what k on a_k means. The square of $a_k^{(1)}(t)$ is computed and has the usual sinc function shape as in **35.12** and the page 284 picture.

Transition Probability and the Golden Rule (283)

Now a slightly sloppy argument is made as follows: the x axis in that figure is $\omega_{km} - \omega$. Suppose you have a band of continuum states that can be the final state such that these states are all about the same throughout the width of the central sinc peak. You can think of ω as fixed, and ω_{km} as varying as you move across this set of continuum states varying E_k . In this case, since the area of the central peak is $\propto t_0$, we can argue that $|a|^2/t_0$ = a transition *rate*. In the usual fashion, we install an energy-density of states $\rho(k)$ as in **35.13** and express our rate, now called "w", as in that equation. I suppose we could put in a

delta function for a bound state situation, though that seems to violate the argument just made. As t_0 is made larger, the sinc peak moves toward a delta function, and we can assume that $\rho(k)$ and the matrix element are constant over the range of E_k where we have our peak. We are left with an integral 0 to t_0 but since only the central peak contributes, we can set these integration limits to $-\infty$ and $+\infty$ and do the integral in closed form and we end up with the **Golden Rule #2** shown as **35.14.** Another approach would be just to say that in the limit t_0 gets large, we really have a delta function inside and it kills the dE_k integral. { I know this is done with a delta function in other sources I have.}

Example: Ionization of Hydrogen (285)

This certainly seems like the right prototype example to examine at this point. We use the H atom ground state as the obvious starting state. The final state should be a fancy Coulomb wave function since the ejected electron is then sitting in a Coulomb field, but we will fudge that and put the final electron in a standard issue plane wave. One can use shielding perhaps of a surrounding media to justify this as a practical assumption.

Density of Final States (186)

The mysterious density of states is computed in the usual way with result **35.18,** where we use L^3 cubic box normalization for this 3D problem. The correspondingly normalized plane wave states are in **35.17**. I will worry about the normalization details at some later time, I don't think it is a big issue, this all comes up in the exact same way when you do scattering cross sections.

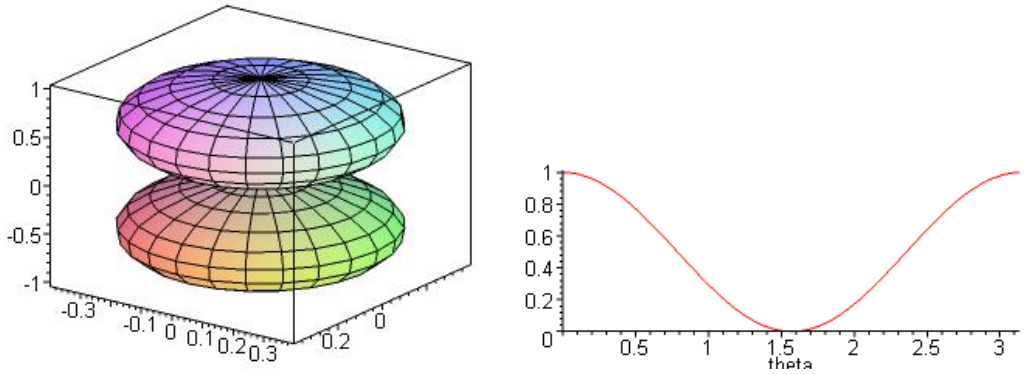
Ionization Probability (287)

So we need the matrix element $|H'_{km}|^2$ where the m state is our H ground state 35.16, and where the k state is the plane wave 36.17 in direction $\hat{\mathbf{k}}$. The picture on page 287 shows angles for the matrix element internal spatial integration. Align integration $\hat{\mathbf{z}}$ with $\hat{\mathbf{k}}$, the angle to integration point **r** is called θ' which you see as $e^{-ikr\cos\theta'}$ (minus sign since in the ψ* side). The angle of **E•r** is called θ" so see z" = rcosθ" in the integral. The d^3r thing is aligned with k so θ" must be replaced by the usual formula page 287 A. The second term vanishes under the dφ' integration and we let the dust settle and view the result of this integration which is page **288A**. Square this and insert into the Golden Rule using the phase space 35.18 and we get a result for w as in **35.20**. This is reminiscent of a differential cross section but we have a semiclassical EM field here. If we let the E field define direction, this rate is 0 in both the forward, backward and sideways directions!

The matrix element is $\propto \cos\theta$, why is this? In the classical field approach, the E field produces a force **F** = **E**q which kicks out the electron, so we would expect the kicked-out electrons to be most in the direction the field points, so that is where the cosθ comes in the amplitude (which gets squared). In QED, this E field would be from a photon coming in from the side, save that problem for another day. So our result has this form:

$$dw/d\Omega = \text{stuff} * \cos^2\theta$$

```
plot3d(cos(phi)^2, theta = 0..2*Pi, phi = 0..Pi, coords=spherical);
plot(cos(theta)^2, theta = 0..Pi);
```



No experimental data is presented for this example, nor do we even get a comment. The experiment would have to be done as a photon-hydrogen scattering experiment really. For us, it was just a toy practice problem.

Second Order Perturbation -- two-photon processes (288)

Schiff dues not do this but describes the results. If you take our level 1 amplitude 35.11 and jam that into the level 2 ladder equation 35.8 with s = 1, you get the $a_k^{(2)}(t)$ amplitude. But now you are integrating an expo like $e^{i(\omega km-\omega)t}$ in the level 1 amplitude against $e^{i\omega km\ t}$ so now you get resonances at $2\omega_{km}$ and at $-2\omega_{km}$ and at 0. These are identified with **two-photon processes**. Somehow, this semi-classical model knows that there is some small probability that two "quanta" of EM energy can conspire together to do an ejection of the electron. Schiff comments that when doing this level 2 theory, you have to be careful to have your E field turn on slowly relative to ω or you get artifacts of a fast turn on confusing the picture. I don't know without looking whether any book I have discusses this second order theory, though I will of course be looking at Saxon soon. Maybe my laser books talk about this stuff.

Adiabatic Approximation (289). Choice of Phases.

The idea here is this: suppose your Hamiltonian H(t) varies only very slowly. Then at any instant of time, you have a SE which says $H(t)u_n(t) = E_n(t)u_n(t)$ so that the whole problem changes slowly. The eigenenergies change, the eigenstates change since H changes. At any instant of time the SE is happy and "in equilibrium", hence the name adiabatic from thermodynamics (reversible). One's gut feeling is that if you start a system in $u_m(t)$ at t=0 and then evolve very slowly, then you should stay in the state $u_m(t)$ although the nature of this state changes very slowly in time. You could pause and hold the evolution at any time and you would stay in $u_m(t)$ for that time.

Most of this section is a rather elaborate set of manipulations to get to **35.26**. The manipulations start by defining $a_n(t)$ as coefficients in **35.23**. If we compare this equation to 35.3, we see that our $a_n(t)$ here are slightly different from those used in the TDPT due to the exponent. In TDPT we have $-i E_n t/\hbar$ in the exponent, but here we have the *integral* of $E_n(t)$. If $E_n(t)$ were constant, the a_n would be the same. Basically, this is nothing more than what I like to call a "refunctionalization" of the SE, and Schiff says as much top of page 291. We are again in the energy representation (not coordinate), but nothing is said about our "picture" here. Along the way, we do a tricky phase adjustment of our base states $|n(t)\rangle$ which allows us to say that $\langle n(t)|\ \partial/\partial t\ |n(t)\rangle = 0$. This reminds me of the Schiff/Messiah condition $\langle n|0\rangle = 0$

normalization in SSPT. The idea is that the change in a state n(t) is only in the direction of the *other* base states. I have no problem with how this was done.

Now once we have 35.26, we apply our adiabatic assumption set. We assume that the states move so slowly in term period 0 to t (our period of interest), that we can treat the $E_n(t)$ as constants, which means that the difference $\omega_{kn}(t)$ is treated as a constant. The exponent in 35.26 is then just $e^{i\omega knt}$ which is what you then see in page 291A. [he has two typos here because he changed from n to m] We also assume that $\omega_{km}(t)$ = constant where it appears in the denominator of 35.26, we assume also that $a_n(t)$ is nearly constant there, and so is $\partial H/\partial t$. Everything is assumed to move slowly in time relative to our time frame 0 to t. We then set $a_n = a_m\delta_{m,n}$ to say we are going to start off 100% in some state "m" ($m \neq k$) , and that then kills off the sum in 35.26 setting n = m. This then gives us result **291 A** where the only non-super-slow time dependence is in the expo factor. We then integrate equation A to get **35.27** which is our main result. Assuming the factors multiplying the phase factor are small (we said H can only change slowly), this says that the amplitude in any other state "k" is small *and stays small*, just cycling around forever as a small complex number. Thus, we have mathematically justified our gut feeling at the start that we basically stay in the state "m" if we started there. The reason: the amplitude to be in any other state as time goes by remains very small, that is what 35.27 says.

Connection with TDPT.

Now if H changes at a frequency that can be on the order of ω_{kn} , we expect to have a resonance effect and we expect our adiabatic assumption to break down. After all, if $H = H_1e^{i\omega t}$ then dH/dt = iωH and then p 291 A tells us that $\dot{a}_k \sim 1$ which is no longer small. So this would not be a "slowly varying H". Schiff considers this slightly differently. He imagines that $H = H_o + \lambda H'$ and that H' has the ω dependence, so we are back in the TDPT framework. Our result for $\dot{a}_k(t)$ then takes the form **p 291 B** which integrates to result **35.28** which is very similar to our perturbation theory result 35.11 (remember that the a_k are defined slightly differently). If we are close to resonance, in fact these results duplicate each other. In the resonance limit $\omega \rightarrow \omega_{kn}$, the limit of the second term in 35.28's parentheses is in fact just i t, and we replicate the TDPT result that we are moving from state m into state k at a linear rate in time. So this is completely different from the normal adiabatic result that says you stay in the initial state "m".

No examples are given here of the adiabatic approximation (but see below). It is just a concept, and to see if you are in the adiabatic regime you evaluate the size of the factors in 35.27. Schiff provides an interesting adiabatic condition in words where I put the red bracket. The condition is roughly this, where the dimensions match, and where we are saying the factors in 35.27 are << 1:

$$\langle k| \partial H/\partial t |m\rangle / \hbar\omega_{km} \ll \omega_{km}$$

where both sides have dimensions 1/time. Suppose roughly $H = H_1\sin(\omega t)$. Then this condition becomes

$$\omega \cos(\omega t) \langle k| H_1 |m\rangle / \hbar\omega_{km} \ll \omega_{km}$$

$$\langle k| H_1 |m\rangle \ll \hbar\, \omega_{km}^2/\omega$$

Then if ω is in the range of ω_{km} , this says

$\langle k| H_1 |m\rangle << \hbar\omega_{km}$

which I think we could still arrange. But this is in fact wrong because you have to go back to 35.26 and put in the time dependence of H, and then you get the resonance result 35.28 which says you will have linear growth of other eigenstates no matter how small <H> is.

The Sudden Approximation. (292)

The first section has result 35.30. This says that an initial pure eigenstate "m" can end up in any state of the post-change Hamiltonian which is not orthogonal to the initial state. That is

$b_\mu = a_m \langle \mu|m\rangle$

The initial state had E_m but the final states have $E_\mu \neq E_m$ in general. So our "sudden" change in the Hamiltonian changes the energy of the system ? (later in our example where we suddenly shift our wooden board, we are surely adding energy to the system).

We want now to consider the time interval $(0,t_0)$, the region before it, and the region after it. So here is the situation in each region (H_i is some kind of "intermediate" Hamiltonian which provides a segue between H_0 and H_1)

	$t = 0$		$t = t_0$	
H_0		H_i		H_1
$\|n\rangle$ and E_n		$\|\kappa\rangle$ and E_κ		$\|\mu\rangle$ and E_μ
u_n		w_κ		v_μ
a_n		c_κ		b_μ
$\psi = \Sigma_n a_n \|n\rangle e^{-iEnt/\hbar}$		$\psi = \Sigma_\kappa c_\kappa \|\kappa\rangle e^{-iE\kappa t/\hbar}$		$\psi = \Sigma_\mu b_\mu \|\mu\rangle e^{-iE\mu t/\hbar}$

I don't need the letters u,w and ν for now since the subscript nature tells the kind of state. And we assume each set of states is orthonormal in each region.

If we match ψ at t=0 from two sides we get

$\Sigma_n a_n |n\rangle = \Sigma_\kappa c_\kappa |\kappa\rangle$

which tells us two things, depending on how we close from the left:

$a_n = \Sigma_\kappa c_\kappa \langle n|\kappa\rangle$ $\qquad$ $c_\kappa = \Sigma_n a_n \langle \kappa|n\rangle$ (*)

If we similarly to a match at $t = t_0$ we get

$\Sigma_\kappa c_\kappa |\kappa\rangle e^{-iE\kappa t0/\hbar} = \Sigma_\mu b_\mu |\mu\rangle e^{-iE\mu t/\hbar}$

and again this tells us two things depending on which state we close with from the left:

$$c_\kappa = \Sigma_\mu b_\mu \langle\kappa|\mu\rangle e^{-i(E\mu - Ek)t/\hbar} \qquad\qquad b_\mu = \Sigma_\kappa c_\kappa \langle\mu|\kappa\rangle e^{-i(E\kappa - E\mu)t0/\hbar} \quad (**)$$

The right result above (**) appears on the first line of 35.31. We can then insert result (*) for c_κ and we then get the second line of 35.31 as a double sum.

$$b_\mu = \Sigma_\kappa c_\kappa \langle\mu|\kappa\rangle e^{-i(E\kappa - E\mu)t0/\hbar}$$

$$= \Sigma_\kappa \Sigma_n a_n \langle\kappa|n\rangle\langle\mu|\kappa\rangle e^{-i(E\kappa - E\mu)t0/\hbar}$$

$$= \Sigma_n a_n \Sigma_\kappa \langle\mu|\kappa\rangle e^{-i(E\kappa - E\mu)t0/\hbar}\langle\kappa|n\rangle$$

Now we could do the operator replacement right at this stage before saying t_0 is small, let's do it that way. We can first write

$$\Sigma_\kappa |\kappa\rangle e^{-i(E\kappa - E\mu)t0/\hbar}\langle\kappa| = \Sigma_\kappa e^{-i(E\kappa - E\mu)t0/\hbar} |\kappa\rangle\langle\kappa| = \Sigma_\kappa e^{-i(Hi - E\mu)t0/\hbar} |\kappa\rangle\langle\kappa|$$

$$= e^{-i(Hi - E\mu)t0/\hbar} \Sigma_\kappa |\kappa\rangle\langle\kappa| = e^{-i(Hi - E\mu)t0/\hbar}$$

Now insert this result into our b_μ expression above to get

$$b_\mu = \Sigma_n a_n \Sigma_\kappa \langle\mu|\kappa\rangle e^{-i(E\kappa - E\mu)t0/\hbar}\langle\kappa|n\rangle = \Sigma_n a_n \langle\mu| e^{-i(Hi - E\mu)t0/\hbar} |n\rangle$$

$$= \Sigma_n a_n \langle\mu| e^{-i(Hi - H1)t0/\hbar} |n\rangle$$

which is our final result. then we can expand it for small t_0 as an operator and say

$$b_\mu \approx \Sigma_n a_n \langle\mu| 1 - i(H_i - H_1)t_0/\hbar |n\rangle \qquad \textbf{// which is 35.32}$$

If we compare this to page 291 A, we see that the intermediate region has no effect if t_0 is small enough. Otherwise, for small t_0 , this result gives us an estimate of the error in p 292 A.

Comment: In practice, we are not going to instantaneously change a Hamiltonian from H_0 to H_1. It will take some small amount of time (t_0) to effect the change, and during the change we assume some unknown intermediate Hamiltonian H_i is acting. Equation 35.32 above gives us a condition on things to determine whether or not we are allowed to use the instantaneous formula for the change. That formula would just be this:

$$b_\mu = \Sigma_n a_n \langle\mu|n\rangle \qquad \text{// as given in 35.30}$$

This is what you get if you allow an instant change from H_0 to H_1 at t = 0.

Now suppose our initial system in t<0 is in a single state m, so that $a_n = \delta_{n,m}$. Then 35.32 says

$b_\mu \approx \langle\mu| 1 - i(H_i - H_1)t_0/\hbar |m\rangle$

But suppose $H_1 = H_0$ so we in effect applied a short pulse of some sort to a system, then let it run again. Then the final state μ will be another state of H_0 and we can just call that k if we like. So

$b_k \approx \langle k| 1 - i(H_i - H_0)t_0/\hbar |m\rangle = \delta_{k,m} - i\, t_0/\hbar \langle k|H_i - H_0|m\rangle$ **// which is p 293 B**

So this is the amplitude that our system starting in state "m" got into state "k". If k = m, our amplitude to still be in m drops a bit from 1, and if $k \neq m$, the amplitude rises a bit from 0.

HO Example of Adiabatic Approximation (294 top)

System is a wooden board lying flat on a table. The board is has a short vertical post which attaches to a spring which horizontally connects to a mass. The mass can move without friction on the horizontal board. For the adiabatic experiment, we imagine putting the oscillator in some state, then we move the board *slowly* horizontally relative to a coordinate system attached to our table. Thus, we slowly change the rest position of the oscillator when we do this. This position is called a(t). In the sudden case, we jerk the board horizontally a distance a and watch what happens.

Our H is shown in p 294 A. How slowly must be move the system so we can use the adiabatic approximation? We want the factors in 35.27 to be small. If the HO starts in the ground state |n> = |0>, we need to compute

$\langle k|\partial H/\partial t|0\rangle = \langle k| -K\dot{a}\,(x-a)|0\rangle = -K\dot{a}\ \langle k|\,(x-a)|0\rangle$

Page 72 (13.18) shows that the only matrix elements to another state will be to state <k| = <1| and we can then say

$\langle 1|\partial H/\partial t|0\rangle = \langle 1| -K\dot{a}\,(x-a)|0\rangle = -K\dot{a}\ \langle 1|\,(x-a)|0\rangle = -K\dot{a}\,\langle 1|x|0\rangle$

where we look up this matrix element. The result is that the "factors in 25.27" are as given in 35.33 and this is what we want to be small to justify the adiabatic approximation. In words, this says that the velocity you move the system $\dot{a}$ must be small compared to the effective KE velocity of the HO in its ground state, since $1/2\ mv^2 \sim 1/2\ \hbar\omega_c$. I did all the math here, this last claim omits factors of 2. But here finally is a reasonable example of the adiabatic approximation. If it starts in a ground state and we move our board slowly, it stays in the ground state, and the amplitude into the first excited state is very slight and is 0 to any other state.

HO Example of Sudden Approximation (294 bottom)

We suddenly translate the board a distance a to the right, so the next EQ position as at x = a. Let's assume the change really does happen instantaneously at t = 0. We apply our t=0 continuity rule from above

$c_\kappa = \Sigma_n a_n \langle\kappa|n\rangle$

where |n> will be the ground state of the oscillator having a(t)= 0, while <κ| will be an eigenstate of a new oscillator centered at a(t) = a. We start out in a state $a_0 = 1$, so rewrite the above as

$c_n = \langle n'|0\rangle$

We need to know the eigenstates of both these systems. I think we can say this:

$|0\rangle$ = ground state of starting system = $u_0(x) = \sqrt{\alpha}\, \pi^{-1/4} \exp(-\alpha^2 x^2/2)$

$\langle n'| = u_n'(x) = N_n H_n(\alpha[x-a])\exp(-\alpha^2[x-a]^2/2) = u_n(x-a)$

$c_n = \sqrt{\alpha}\, \pi^{-1/4} \int dx\ u_n^*(x-a) \exp(-\alpha^2 x^2/2)$ // **which is 35.34**

Schiff points out that we have already done this integral in its shifted second form on page 75 but we need to change the sign of a. The result must be this:

$c_n = A_n(-a) = (-\alpha a)^n \exp(-(\alpha a)^2/4) / (2^n n!)^{1/2}$

$= (-1)^n(\alpha a)^n \exp(-(\alpha a)^2/4) / (2^n n!)^{1/2}$

So this gives us a distribution of the activation of all the modes "n". But this means that right after our sudden change, we have a wavefunction that is ψ(x,0) = the Gaussian shown in 13.21 with peak at x = -a (instead of peak at x=a). We know what the HO will do after this time because we computed it on page 75 H. The quantum wave packet sloshes back and forth like a classical oscillator forever, never spreading. What is the classical operation here? This is just what would happen to a classical system if you jerk the board to the right.

end of chapter 8 !!! This was a very long voyage. 3/5/09 7 PM