Schiff Meta Review Notes PhL started I think 12.5.08

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Chapter 1: The Physical Basis of Quantum Mechanics: (Sections 1-5)

Most comments here are just partially copied from the raw notes, since sections are so short.

1. Experimental Background (2).

How the blackbody problem led Planck to suggest $E = \hbar\omega$ per "mode" to explain the BB spectrum, and this is where $\hbar$ first appeared in the world: photon energy is quantized, we got $E = \hbar\omega$ from Planck in 1900. An example of the "inadequacy" of classical physics. In the end, there were lots of experiments like **photoelectric** (Einstein 1905), and **specific heats** of solids, and **Stern Gerlach**. These all suggested that certain physical parameters took only "quantized" values, hence the name QM was later used. This **discreteness** was one "thread" of early QM discovery. The other thread was the **wave/particle duality**, which involved the second major "equation" of **deBroglie** (1923) that traditional particles also obey the idea that $\lambda = h/p$, not just light particles. Again, that constant h appears. People found that electrons "diffract" just like photons. In 1927, Davisson and Germer found this diffraction and confirmed deBroglie's idea. Table on page 4. So:

$E = \hbar\omega$ energy of photon (1900) $\lambda = h/p$ wavelength of any particle (1923)

2. The Old Quantum Theory (4).

This is basically **Bohr's 1913 "theory of the atom"** which is that an atom has a discrete spectrum and light "photons" of $E=\hbar\omega$ are emitted or absorbed between these discrete levels. It is hard for me to imagine that there was a time before this basic theory existed (less than 100 years ago!). The electron and proton of an H atom could previously have had any energy you wanted, and there was no reason for the thing not to implode, no ground state, etc etc. The big hint of course was that observed atomic emission spectra had discrete lines, and the early **Ritz-Rydberg "combination principle" (1908)** which related spectral lines was consistent with the Born atomic theory.

So Bohr's main idea was to say that the electron in H atoms had a quantized orbital $L_z = m\hbar$ and this led to a simple model with a simple spectrum prediction. This was the second "quantization rule" that appeared in the human mind, the first being $E= \hbar\omega$. This L_z rule follows if you use the deBroglie rule for an electron orbit.

So yes, this is the "**old quantum theory**" and it provided new qualitative explanations of things like the line spectra. Later, the Bohr 1923 "**correspondence principle**" just meant that for large numbers of quanta, your theory had to give classical theory results, so this was a guide for quantum theory models.

Schiff talks first about the fact that the old Q theory was not giving perfect predictions, but now he talks about **"conceptual" problems**, such as the notion of a light "particle" going through one *or* the other whole in a 2-slit experiment. Even if you lower intensity way down so only "one photon at a time" runs through this experiment, covering one slit removes the interference pattern. If a photon goes through one hole, how does the covering or uncovering of the "other hole" affect where that photon goes? The conceptual problem here is our picture of something "going through a hole" in a classical sense. In fact, the entire notion of "**trajectory**" goes out the window, and with it, the idea that "previous position exactly determines future position" also goes away, so there goes "**causality**". It must have been a huge mental shock to people used to the complete in-principle determinism of the mechanical 1800's. We now know

that this experiment is fully explained by the notion of a wavefunction ψ and $\psi^*\psi$ probability, but for the Bohr 1913 atomic theory, there was as yet no SE and no wavefunction.

3. Uncertainty and Complementarity (7).

Various forms of the **uncertainty principle** (UP) were developed from the full "new" QM theory in **1927** by **Heisenberg**, some are listed page 8 top. Associated with this notion that you cannot measure two particle parameters in a complementary set (like p and x) with arbitrary accuracy was the 1928 Bohr **complementarily principle**, a pretty fancy name I think for what the Heisenberg idea really says. But the idea is that there is now an "in principle" claim that no experiment can ever measure both to accuracy better than the UP says.

4. Discussion of Measurement (9).

Here Schiff discusses **three thought experiments**, each of which leads to a form of the uncertainty principle. Each UP is seen really to be just a restatement of results from Fourier Analysis applied to physical situations: the first experiment has a lens focusing light on a screen, the second involves trying to measure an atom's velocity by measuring the emission Doppler shift, and the third is a two slit experiment where you put fluorescing indicators to see which slit your particle went through.

5. Wave packets in space and time (14).

Here we vaguely introduce the **wavefunction** ψ for a "particle" with three properties: it can interfere with itself, it somehow correlates with probability of being somewhere, and it applies to an individual object (not just to an ensemble).

Next, we look at a spatial **wave packet** and we quote from Fourier analysis that $\Delta k \Delta x \geq 1$. When we combine this with deBroglie $p = h/\lambda$, we get the UP, which is encouraging to the idea of thinking of a classical particle perhaps as a wave packet.

Then comes a temporal wave packet spread out over some Δt and Fourier says $\Delta t \Delta \nu \geq 1$. If we combine this with Planck $E = h\nu$, we get the time UP, so more encouragement.

Basically we are going to **treat everything as ψ waves in this book**, so Schiff asks : does this mean we have thrown out the idea of trajectory and the particle half of the wave-particle duality? No, he says, the wave thing will give all particle predictions properly, and later in the book we will do a cloud chamber particle track as an example.

Chapter 2: The Schrodinger Wave Equation (19) (Sections 6-9)

The SE will work for non-relativistic problems describable by a potential V.

6. Development of the SE. (20)

Schiff tries to motivate why the SE (1926) is reasonable, how other similar equations don't work right for plane waves of definite momentum **p**. He then shows that you can interpret the SE as saying $E = p^2/2m + V$ if you *interpret* $E = +i\hbar\partial_t$ and $\mathbf{p} = -i\hbar\nabla$ so these two notions come in early. The word Hamiltonian does not appear.

7. Interpretation of the Wave Function (24)

What does the SE solution $\psi(r,t)$ mean? Main idea is $|\psi|^2$ is **probability** (not $|\psi|$, eg). The bilinear idea appears, and the notion of an expectation value $\langle\psi|Q|\psi\rangle$ is hinted at, without such notation of course. Later we will learn this has to do with scalar product in a Hilbert Space. The choice of $|\psi|^2$ leads to the famous **probability current** he calls **S** in 7.3 p 26 and the **continuity equation** all makes sense. Early use of "distant surfaces" in the math here.

The last subsection talks about **Ehrenfest's Theorem(s)** which say this:

$\partial_t\langle\mathbf{r}\rangle = \langle\mathbf{p}\rangle/m$ like classical $\partial_t\mathbf{r} = \mathbf{p}/m$ = velocity

$\partial_t\langle\mathbf{p}\rangle = -\nabla\langle V\rangle$ like classical $\partial_t\mathbf{p} = -\nabla V$ = force

These two results are derived in full detail using nothing but the SE with a real potential V. Obviously these are two instances of "**the correspondence principle**" mentioned earlier, the connection to the classical world. You might think of these in terms of a wave packet particle, for example.

8. Energy Eigenfunctions (30)

We separate the time t from space r coordinate, find the $e^{-iEt/\hbar}$ idea, where E is the separation variable which we interpret as energy since it then appears in the separated TISE as such. Localized spectrum (bound states) will always be discrete, collision spectrum will be continuous.

Next, Schiff discusses the *shape* of the wavefunction, its "cupping" behavior. It is expo in what I call the wings where $E < V$, and sine-like in the central region where $E > V$. S gives a nice explanation of **why E is quantized**: if you move either direction away from an eigenvalue, the wavefunction which you integrate in from the two sides won't match up with both value and slope, but the right E makes this happen perfectly. Pictures on pages 35-36 show this for lowest two bound states. It follows then that your bound states will have an increasing number of **nodes**, a general fact for any problem you attack. In the collision case, you have both ODE solution "constants" available for matching, so E does not get quantized. In bound states, requirement of only *decaying* expo removes available fitting constants forcing E to be discrete.

9. The 1D Square Well (37) The particle in a box.

S first treats the *infinite* wall box (center at V=0) and we get the trig solutions I marked with A on page 39. We find that the energy eigenvalues are $E_n = E_1 n^2$ with n = 1,2,3... and they alternate sine and cosine with another node for each step in n. Since $\psi=0$ at the walls, this is similar to E field modes in a waveguide.

S then does the *finite* walled box. He obtains the two famous constructions which let you see the eigenvalues for the even and odd cases. Graphic is used since condition is transcendental. He gets these eigenenergies by matching ψ and ψ' at boundaries as usual. He does not go on to solve for the various constants and never writes down the solution wavefunctions. For time-independent ψ, Schiff uses letter u.

He mentions **parity** and if V has it, then non-degenerate solutions are even or odd, and for degenerates you can do GSO.

Chapter 3: Eigenfunctions and Eigenvalues (Sections 10-12)

10. Postulates and Energy Eigenfunctions (46).

Three postulates are mentioned:

(1) every physical parameter has an operator such that $\Omega v_\mu = \omega_\mu v_\mu$

(2) when you measure this parameter, you can only see one of the ω_μ values

(3) when you do a lincom with coefficients A_μ , then $|A_\mu|^2$ is probability of reading ω_μ

S goes on to discuss the **large box** with **periodic BC** idea for handling **collision normalization**. He proves that all nondegenerate eigenfunctions of an operator are **orthogonal**, and he proves that E must be **real**. This is done with the SE and parts integration and those BC's. He gives the **completeness** (closure) statement, and all this is just for the case Ω = E operator. Once you solve the **TISE** for some wavefunctions, it is easy to write a linear combination of them that solves the **TDSE**. No delta functions are used yet. And he proves that <E> is the expectation value of $p^2/2m+V$.

11. Momentum Eigenfunctions (53).

The eigenfunctions of **p** are the **plane waves** which he likes to write using **k**. Since these are not localized, the normalization issue comes up, and this is where he introduces and talks about **delta functions**.

12. Motion of a Free Wave Packet in 1D (60).

Once you say $p = -i\hbar\partial_x$, you find that the Uncertainty Principle is really the same as the usual **Fourier** Integral Transform inequality that looks the same. Using results of this proof, S then constructs the form of a static **minimum packet** that has "minimum uncertainty" so $\Delta x\, \Delta p = \hbar/2$. The result is the Gaussian-like affair in 12.11 which has three parameters you can set: $\Delta x = \sigma$, <p> and <x>, with Δp given by the relation.

He then computes the plane wave coefficients A_k that make up this packet, and then uses the basic phase sum to compute the **packet's shape after time t**. The result is 12.21 page 64. What you learn is that the static packet just **gets wider** at the rate $d\Delta x/dt \sim (\Delta p/m)\, t$, as if it has a width-velocity $v = (\Delta p/m)$. So a packet cannot just sit there in vacuo! We shall learn soon that a packet in a HO potential does not get wider because it is pushed in all the time by the potential, so it has nowhere to go, so to speak.

A **nice application** at section end: if you could make a Bohr electron be a packet, it would spread all the way around orbit before it could even get around once! So the planetary model simply does not apply.

Chapter 4: Bound State Problems (Discrete Eigenvalues) (Sections 13-16)

13. The Famous Harmonic Oscillator (66).

This problem is solved using a **method** that will be reused many times in the chapter.

(1) scale to a **dimensionless variable** ξ ; in so doing, define α as the scaling variable $\xi = \alpha x$ and write α out. Then the grouping of other symbols that includes the energy E is called λ; write it out too.

(2) extract the **large ξ exponential** form for the asymptotic behavior.

(3) assume solution is then a **power ξ^s times a power series** that starts with the power ξ^0. Any function should be so expandable if smooth at the origin.

(4) write the SE for the resulting ξ^s times a power series, insert this series and find the coefficient **recursion relation**. In this case, it steps by 2 and all the a_i for i odd vanish all the time.

(5) show that the solution diverges unless the series **truncates** which means λ = some integer involving the coefficient index. Extract from this integer the "main quantum number" usually called n. Then solve λ = int to find the eigenenergies for E.

(6) then show that the ODE for your **polynomials** is or is close to some historical set of polynomials and then you can use these polynomials to express your solution eigenfunctions. Schiff always gives a selection of properties of the polynomials including the generating function which is crucial in computing integrals involving the polynomials, as they generally cannot be looked up.

For the HO problem, I did all these things in full detail in the raw notes using my patented copy, paste, and edit method. The polynomials in this case are the **Hermites**. Remember that SE appears in 1926, but these polynomials appeared circa 1850.

Schiff then **compares** the HO wavefunctions to what a **classical** HO does, new to me. For the higher order solutions, the probability matches that of the classical oscillator, using the P(x) = k/v(x) idea with a picture taken from Linus Pauling. The lowest states of course look nothing at all like this. Schrodinger (English **Collected Works**) wrote a whole paper comparing QM solutions to classical solutions, and this is one of those items.

Schiff then assumes at t=0 a **gaussian packet in the HO potential** as shown page 75 top. He then computes the time motion, and after much math, gets the very simple result shown bottom of page 75: the packet just bounces back and forth without spreading. The A_k coefficients have a peak value at the energy which is that of the corresponding classical oscillator.

No doubt we shall return to the HO in other formalisms later in the book.

14. 3D Spherically symmetric potentials (76)

In the usual way, we separate the solution for V(r) into $R_\ell(r)Y_{\ell m}(\theta,\varphi)$. The radial equation picks up the centrifugal term $\ell(\ell+1)/r^2$. All $Y_{\ell m}$ have parity $(-1)^\ell$. S writes out the angular momentum L components in angular coordinates and shows that the $Y_{\ell m}$ are eigenfunctions of L^2 and L_z. I think I am familiar with everything in this section. The main idea is to write ∇^2 in sphericals, then do the triple separation of variables. I like Schiff's approach here. He takes time to discuss both the **Legendre** and **associated Legendre** polynomials which provide the θ part of the $Y_{\ell m}(\theta,\varphi)$

15. 3D Square Well (83)

The famous well is defined as a 3D hole (spherical) of depth $V_0>0$, the picture is fine. The radial equation here has constant V in the two regions, and in each it is the **spherical Bessel equation** 15.4 for R and we find $j_\ell(\alpha\rho)$ as the interior solution, and $h_\ell^{(1)}(i\beta r)$ **Hankel** as the exterior one. Joining them up at the boundary r=a gives a different transcendental energy equation for each value of ℓ, and larger ℓ results in more nodes and more energy. Only those for $\ell = 0$ and $\ell = 1$ are written down bottom page 87.

In this problem, we did not follow the usual procedure of extracting the asymptotic behavior then writing a power series, the reason being that at once we have a recognizable ODE at the start, and the Hankel lincom of j and n takes care of the expo fall off outside the well.

16. The Hydrogen Atom (88)

Schiff opens by showing that for such an atom, we **separate relative from CMS motion** and have the **reduced mass** μ being operative. We then examine the radial R equation, scale the variable to $\rho = \alpha r$ to cause the E term to become ¼ in 16.7 which turns out to be crucial to get a 2-member recursion relation for the coefficients. I transform the equation from R(r) to Q(ρ) to F to L, so there are really four stages! The L turn out to be the **Laguerres**, and these are then discussed in detail. The complete solutions are assembled on page 93, and some of the low order radials are stated; other books like Pauling have many more. S then talks about how each n level ("shell") has **degeneracy n^2**.

I did all of the above calculation in full detail in the raw notes so there are lots of red checks here.

I then went off and learned about the **parabolic coordinates ξ and η** (first time in my life, age 60). There are two conventions so one must be a little careful. I derived x to q curvilinear transformation matrix, then from that got the metric tensor, and from that the Q_i of M&M, and from that I was able to confirm the form of the Laplacian in these coordinates. Then on page 96 I did each step which shows how in fact the SE allows a fully separable solution. The ξ or η solution is then an expo times a power times a **Laguerre** as in 16.34 and in full detail on page 98, without a normalization factor. The same energy formula of course results, and n^2 is still the degeneracy.

The **reason the equation separates** is that $V(r) \sim 1/r = 2/(\xi+\eta)$, and when you multiply things through you get (ξ+η) times other terms and these then allow "separation". The angle φ and its quantum number m is exactly the same as in sphericals and relates to L_z. I have some comments on O(4) but this comes later in Chapter 7.

Chapter 5: Collision Theory: (Sections 17-21)

17. The 1D *Positive* Square Well (a Post)

We set up the distant plane waves on left and right: incident, transmitted, reflected as in 17.1, all outside the potential well. Inside the well we have 17.3 which is combination of $e^{i\alpha x}$ where $\alpha = f(V_o, E)$, very standard in this book. Do all the matching and get lots of results, probability of transmission and reflection as a function of E. The T result is shown in the graph page 104 and has easily understood points of complete transparency at the top of the graph if energy level is above the Post. If E is below the post top, you can still tunnel through a bit, lower left of graph.

The results for both a post and a well are shown as animation frames on the next pages, and I comment on these in the raw notes.

18. Collisions in 3D

Differential and total **cross sections** are defined. Then the **lab and cms frame** angles are compared (θ_o = lab). The formula 18.4 which relates the lab and cms polar angles is true for **elastic or inelastic** collisions, the latter involving some Q in the energy equation. For elastic, $\gamma = m_1/m_2$ but for inelastic it is the more complicated thing in 18.5 which allows for four different masses and some reaction Q. I did all these kinematics in detail in the raw notes. The main result is 18.7 which then relates the cross section in the lab

to that in the cms frame, and that same γ factor appears, so this is elastic or inelastic. This is all non-relativistic.

In the elastic case, you can think about whether the lab **incident particle is lighter or heavier** than the target, and some general rules emerge. If the target is heavier, $\gamma < 1$, there is well defined plot of θ_o versus θ that starts linear for small γ (where lab = cms), and as γ increases, it gets curved such that lab angles above 90 degrees are harder to reach. When $\gamma = 0$ these are fully excluded and $\theta_0 = 1/2\ \theta$. As γ further increases above 1, the lab angle can only reach a maximum angle < 90 degrees which lessens as γ further increases, and two CMS angles correspond to each lab angle. Eventually with a very heavy projectile, it just plows through the target and only $\theta_0 = 0$ occurs.

So much for **kinematics**. On page 115 **the "scattering situation"** is described, and we get the idea that the incoming plane wave is limited by a **collimator** so if you go to a distant point p, (large r), you find that the SE has the solution $f(\theta,\varphi)e^{ikr}/r$ (I show this) where f is some unknown but reasonable function of the angles. The incoming plane wave is the e^{ikz} term in 18.10. When these two terms are relatively weighted in this very simple way, it turns out that $|\mathbf{f(\theta,\varphi)}|^2$ is exactly the differential cross section (in the cms frame), and in this case f is usually called "**the scattering amplitude**". To show this fact, you take each of the two terms in 18.10 and compute its **flux**. You then just use the flux-based definition of cross section and out pops this fact.

19. Scattering by Spherically Symmetric Potentials

This is a very "meaty" section of the book. Although only 13 pages long, it is packed with important stuff for a person interested in partial wave analysis of scattering. As a result, my meta notes are long. It seems that the collision solutions of the SE are just more complicated that the bound state solutions.

Partial Wave Analysis : Derivation of the expansion for f(θ)

The SE can be separated in spherical coordinates just as in the bound state problem. If $f(\theta,\varphi)$ depends only on θ (I think this means spinless or unpolarized experiments), we know we can write the most general SE solution $u(r,\theta)$ as in 19.1, where $R_\ell(r)$ solves the radial SE equation,

$$u(r,\theta) = \Sigma_\ell (2\ell+1) i^\ell R_\ell(r)\, P_\ell(\cos\theta) \qquad 19.1$$

Each *term* in this sum is of course a solution to the SE, and only m=0 contributes so the usual $Y_{\ell m}$ of the H atom have been reduced to $P_\ell(\cos\theta)$ here. The constants $(2\ell+1)i^\ell$ are arbitrarily chosen to simplify later calculations. You can represent a general SE solution as a sum of an amount "in each partial wave". The "partial wave coefficients" are hidden in 19.1 within the **scale** of the radial functions R_ℓ. We don't know the details of R_ℓ in general, but *for large r* we know that R_ℓ has the form shown in 19.7

$$R_\ell(r) \rightarrow A_\ell [\ \cos(\delta_\ell)\, j_\ell(kr) - \sin(\delta_\ell)\, n_\ell(kr)\ ] \qquad 19.7$$

where now we see the **scale** of each summation term given as A_ℓ. The reason for form 19.7 is because at large r there is no potential, so the radial equation is the same as outside the square well which had j and n solutions. Recall the centrifugal term in the radial equation. You can see that the above is just saying α_ℓ

$j_\ell(kr) + \beta_\ell\ n_\ell(kr)$ but written in terms of an amplitude and phase for each ℓ. But since we are at large r, we can use the large r limits of the j and n functions to rewrite the above as

$$R_\ell(r) \ \rightarrow\ (1/kr)\ A_\ell\ \cos\left[kr - \tfrac{1}{2}(\ell+1)\pi + \delta_\ell\right]$$

Therefore, our completely-general SE solution for large r has this form

$$u(r,\theta) = \Sigma_\ell(2\ell+1)i^\ell\ \{\ (1/kr)\ A_\ell\ \cos\left[kr - \tfrac{1}{2}(\ell+1)\pi + \delta_\ell\right]\ \}\ P_\ell(\cos\theta)$$

But we have *another form* for $u(r,\theta)$ which is specific to our scattering experiment boundary conditions:

$$u(r,\theta)\ =\ K\left[\ e^{ikcos\theta}\ + f(\theta)e^{ikr}/r\ \right] \qquad 18.10 \qquad \text{large r} \qquad K = 1 \text{ (see later)}$$

Recall that, with the relative scale between the two terms as shown, $|f|^2$ = cross section. Within this form we can expand the first exponential

$$e^{ikcos\theta}\ = \Sigma_\ell(2\ell+1)i^\ell j_\ell(kr)\ P_\ell(\cos\theta) \quad \rightarrow\ \Sigma_\ell\ (2\ell+1)\ i^\ell\ P_\ell(\cos\theta)\ (1/kr)\ \sin(kr - \tfrac{1}{2}\ell\,\pi) \qquad 19.9$$

The idea next is to *equate* our two forms for $u(r,\theta)$ and match the coefficients of e^{ikr} and e^{-ikr} . One form is just the large r form of the most general solution to the SE, and the other form matches our experimental boundary conditions 18.10. So we have two equating equations. The e^{-ikr} matching equation does not include $f(\theta)$ while the e^{ikr} does. The first equation forces a connection between A_ℓ and δ_ℓ , and then the second gives us an expansion for $f(\theta)$:

$$A_\ell\ = e^{i\delta\ell} \qquad \text{p 119 D}$$

$$f(\theta) = 1/(2ik)\ \Sigma_\ell(2\ell+1)\{\ e^{2i\delta\ell} - 1\ \}\ P_\ell(\cos\theta) \qquad 19.11$$

and this is then the famous **"partial wave expansion for the scattering amplitude"**. In each "partial wave", the scattering is described by a single real number δ_ℓ . Now you can think in some sense that ℓ and θ are conjugate transform variables. In θ space you need the complex number $f(\theta)$, but in the ℓ space you need just the real number δ_ℓ. Notice that the scale of each term comes out $|A_\ell| = 1$, something we did not know when we started. [This is an elastic scattering situation because we assume that nothing "happens to" our scattering particles which make up the μ reduced mass problem.]

Comment on k dependence. In the above, we really should have written $A_\ell(k)$ and $\delta_\ell(k)$ because these are in general functions of k. And of course $R_\ell(r)$ is also a function of k which is of course related to E.

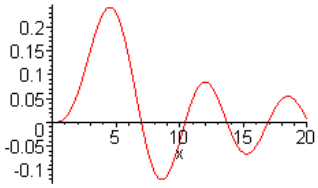
Comment on K: In the above discussion, we write $u(r,\theta)$ in two different ways and then set them equal. In each "way", we choose to parameterize $u(r,\theta)$ in a certain manner, with certain constants, and this includes the choice of overall scaling. We are free to set the overall scale of each "way" as we see fit. If we do it as shown above, with K=1, then our comparison results come out being quite simple. If we set K to an arbitrary value, the first equation above becomes $A'_\ell \equiv A_\ell/K\ = e^{i\delta\ell}$ and the second equation is unchanged (see raw notes red insertions).

Comment on Intrinsic Scattering Complexity and Convergence: In a bound state problem, we think of each ℓ as a separate solution. We think of the H atom as being in some "state" n,ℓ,m . We think about EM transitions between such isolated states.

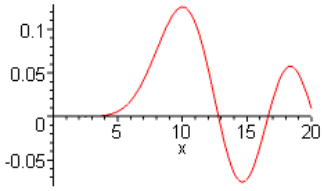
In the scattering problem, our experiment involves a plane wave e^{ikz} moving along the $\hat{z}$ direction. When we "convert this to ℓ space", we find that it contains all ℓ values! We cannot "pick out" a single ℓ value somehow as we can in the H atom, all ℓ are present in the experiment at once. Consider:

$$e^{ikcos\theta} = \Sigma_\ell(2\ell+1)i^\ell j_\ell(kr)\, P_\ell(\cos\theta) \quad \rightarrow \quad \Sigma_\ell(2\ell+1)i^\ell (kr)^\ell\, P_\ell(\cos\theta)/(2\ell+1)!! \quad \text{as } r\rightarrow 0$$

If we look at this incoming plane wave near the scattering center r=0, we get the result shown on the right. If we assume the potential "range" is a, then if (ka)< 1, the driving effect of this plane wave onto elements inside r = a (where scattering occurs) decreases with increasing ℓ according to $(kr)^\ell$ with $r \leq a$. This means that in this case the partial wave expansion is **convergent** and partial wave analysis makes sense. This is why, for a given "a", partial wave scattering analysis is valid for **"low energy scattering"** meaning small ka < 1. More generally, you can plot the $j_\ell(kr)$ for different ℓ's, and larger ℓ j's have their amplitude peaks rather away from the origin, and we reach the same conclusion. Here are some sample Maple plots.



$\ell = 3$



$\ell = 8$

You can see how, if "a" = 2, the ℓ=8 partial wave is not going to do much, but the ℓ=3 is "active".

So, assuming we have a useful partial wave series, on page 120 we arrive at some practical conclusions:

$$d\sigma/d\Omega = |f(\theta)|^2 = 1/k^2 \,|\, \Sigma_\ell(2\ell+1)\; e^{i\delta\ell} \sin(\delta_\ell)\, P_\ell(\cos\theta)\,|^2 \qquad 19.12$$

$$\sigma = 4\pi/k^2 \;\; \Sigma_\ell(2\ell+1)\, \sin^2(\delta_\ell) \qquad 19.13$$

$$\sigma = 4\pi/k \;\; \mathrm{Im}(f(0)) \qquad \text{optical theorem} \qquad 19.14$$

Comment on CMS and Elastic. In all of the above, we assumed we had a two-body system with reduced mass μ and we have been solving the SE in the cms frame of the "relative motion", so all results above are in the cms frame, and θ is the cms angle. When we wrote $u = e^{ikcos\theta} + f(\theta)e^{ikr}/r$ and identified f^2 as $d\sigma/d\Omega$, we used the notion of flux balance: the incoming flux times $d\sigma$ equals the outgoing flux into $d\Omega$. We assumed that no flux was "absorbed" in the process. Our particle 1 is the same before and after scattering as well, we don't have particles 3 and 4 produced. So we have been talking about *elastic* scattering, not inelastic scattering. And V has been real as usual.

Comment on Relativistic. Schiff claims that 18.10, 19.11 and 19.12 (see above) are all still correct. We only derived these results non-relativistically because we used the SE.

General Comment: We could have blindly expanded f(θ) on the Legendres to get

$$f(\theta) = \Sigma_\ell \; f_\ell \; P_\ell(\cos\theta)$$

What we learned from all the above was the *form* of this coefficient

$$f_\ell \;=\; (2\ell+1)\,(e^{+2i\delta\ell} - 1)/(2ik)$$

Not only can we describe the f(θ) with a single real number δ_ℓ (giving f_ℓ) for each partial wave, we know something about the *form* of that number f_ℓ.

How might a theorist compute the δ_ℓ phase shifts? See raw notes for more detail "Calculation of the Phase Shifts". Basically, you assume some V(r) and compute your $R_\ell(r)$ inside some sphere r=a, and you can then compute R'/R at the boundary r = a. Outside this sphere you assume V = 0 and you know from 19.7 above that

$$R_{\ell,\,outside}(r) \;=\; A_\ell\,[\;\cos(\delta_\ell)\,j_\ell(kr) - \sin(\delta_\ell)\,n_\ell(kr)\;]$$

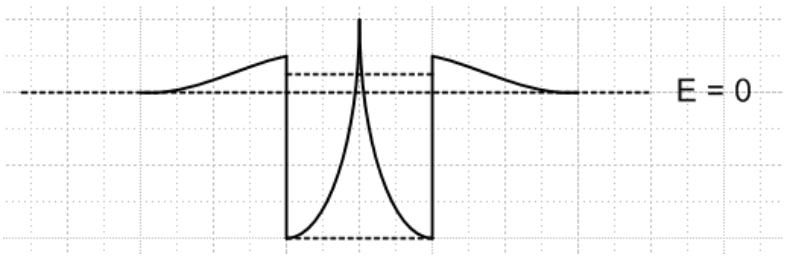
If you then match R'/R at the r=a boundary, you get 19.15 which tells you δ_ℓ in terms of R'/R from your interior calculation, a quantity called γ_ℓ . No examples of this calculation are given yet.

Sign of V and sign of δ_ℓ . On page 122-3 it is argued that a repulsive potential (classical force directed outward, such as positron-proton scattering) causes a negative δ_ℓ because it pushes the no-interaction Bessel solution j_ℓ radially *outward*, pictures page 123. Conversely, an attractive potential causes positive δ_ℓ and pushes the radial function *inward* relative to the Bessel. If you had a situation where only the ℓ=0 partial wave was active and the attractive potential caused $\delta_o(k) = \pi$ for some k, then 19.11 says f(θ) = 0 and scattering stops, the cross section vanishes (has a zero at that k). A graph showing this appears on page 124 and on the front cover of Schiff's book. This situation has been observed (**Ramsauer-Townsend** Effect) in low energy scattering of electrons off atoms like neon which have a cleanly defined sphere radius a so only ℓ=0 is active it k is low enough (~ 1 eV). At such a k, you get a full transparency to scattering, analogous to what we saw in our 1D scattering off a "post".

Infinite Square Well or Post. Inside nothing happens so γ_ℓ = R'/R = 0 at the boundary and our phase shift solutions are exactly given by 19.20, so here at least is one problem that is easy to solve. S shows that the phase shifts drop off very fast with ℓ, as you expect with a clean boundary. At low energy we find that $d\sigma/d\Omega = a^2$ and $\sigma = 4\pi a^2$, perhaps 4 times larger than you might expect. At high energy, it is $\sigma = 2\pi a^2$. S gives an explanation on page 126 of which this is not πa^2 as you would expect, an overcounting argument.

Finite Square Well or Post. For this problem, we know that the inside solutions are just j's . So this time, instead of getting $\gamma_\ell = 0$, we get $\gamma_\ell = 19.26$ and from this one can in theory compute all those phase shifts δ_ℓ.

Resonance in Scattering. The example used here are the ℓ=0 and ℓ=1 partial waves for the finite square well or post situation just described. From the math 19.27, we see that there can be poles in $\tan(\delta_\ell)$ which should cause resonance peaks in the cross section. An interesting way to interpret such a resonance follows. Suppose we draw the effective potential for some $\ell \geq 0$,



Here we show the shape of the "square well" that the radial equation sees including the centrifugal ℓ term. See 14.17 on page 81 for $\chi_\ell(r)$ for example. Now just this situation arose when we studied the bound states of the square well back on page 83. For $\ell = 1$ we found the transcendental equation 15.17 which one could solve for the energy, and higher ℓ were not treated. This raises an interesting question: could you have a bound state with E>0 as shown by the dotted line above? The answer is no. Mathematically, on page 87 we would not be able to find any j+n Bessel combination that does expo decay since β = imaginary for such an E. Intuitively, if some ψ amplitude existed for such a state (make a packet), the amplitude would leak away toward large r, tunneling through the lip edges, and you would not have a bound state. Probably some book I have explains this well. Still, you can see that you could have a "temporary" bound state at such an energy, and this is what we can identify with the resonance effect. If the scattering E is just above E = 0, and if k is right so there is a real bound state at E = 0 -ε for this ℓ, then you get the resonance effect at that value of E or k, and we see that this will be a low-energy effect since it requires small E = ε' .

General scattering experiment observations:

1. Classical: theorists and experimentalists. In a classical scattering experiment, say Rutherford, you have trajectories which are affected by the scattering potential or force. Classical equations of motion describe the trajectory. For example, in a Coulomb force the trajectory is a half hyperbola. A "theorist" can compute the trajectories from the assumed force and predict a cross section as a function of angle. The "experimentalist" can measure the cross section. There is no "wavefunction", there is no "probability" except to the extent that the incident particle beam is probably spread out over many target atomic diameters so the resulting cross section is statistical in that sense. In principle, classically you could have a precision beam on one charge at a precise impact parameter and then there is nothing probabilistic about the process.

2. Quantum: theorists and experimentalists. In a quantum scattering experiment, there are no trajectories, there is only a wavefunction. This includes an incoming plane wave (not a particle) as shown in 18.10, and an outgoing wave (large r assumed) shown as the second term of 18.10 with scattering

amplitude f(θ). The lateral extent of the incoming plane wave function is a good match to the spread-out experimental beam mentioned in 1 above. The cross section is $|f(\theta)|^2$ so this is what an experimentalist can measure. People want to know what is the potential V(r) that results in this cross section? How can you deduce V(r) from $|f(\theta)|^2$? As in the classical case, we assume some V(r) and try to predict $|f(\theta)|^2$ and then see if experiment agrees.

The connection between V(r) and $|f(\theta)|^2$ is the main point of this Schiff section; it is a quite *indirect* connection. A key idea is to make use of the large-r limits of various functions. The wavefunction for the scattering problem is written in two separate forms. The first form is 18.10 above, which is a large-r form. The second form is 19.1 above, which is a partial wave sum of solutions of the SE for this problem, which SE of course includes V(r). The reason we have this sum is as follows: for V(r), we know the SE solution is separable into radial times angular subfunctions, and in a no-φ situation those subfunctions are just the $P_\ell(\cos\theta)$. So we know that the most general form of the solution is the ℓ sum shown in 19.1 where all we know about $R_\ell(r)$ is that it solves the radial equation including V(r).

For low energy scattering where there are not many active partial waves, the **experimentalist** can measure the cross section at a given k, thereby measuring $|f(\theta)|^2$, and can then hopefully deduce values for the lowest several phase shifts δ_ℓ. The **theorist** meanwhile assumes some V(r) in the core region (small r), computes the exact $R_\ell(r)$ there, and then determines the ratio $\gamma_\ell = R'_\ell(r)/ R_\ell(r)$ at the outer edge of this "internal" region and matches this to the same ratio computed from the mid-region assumed form 19.7, where by the way we also learned the $A_\ell = e^{i\delta}$ so the δ_ℓ determines *everything* in a partial wave. By doing this equating in each partial wave, the theorist can *compute* the phase shifts δ_ℓ.

The δ_ℓ are called "phase shifts" because they measure the shift in the phase of $R_\ell(r)$ relative to that of $R_\ell(r)= j_\ell(r)$, where $j_\ell(r)$ is all there is if you have no scattering, ie, you have just the plane wave and f(θ) = 0. Thus, for low energy scattering, the small set of activated δ_ℓ values provides a **point of contact** between the experimentalist who measures $|f(\theta)|^2$ and deduces the δ_ℓ from 19.12, and the theorist who assumes some V(r) and computes what the δ_ℓ ought to be.

For high energy (but still non-relativistic) scattering, where perhaps hundreds of partial waves are activated, this partial wave method is probably useless. There are too many parameters. But for low energy scattering, perhaps only the S and P wave are activated, and then the entire scattering process can be described by just two real δ parameters and the theory/experiment comparison can be well made.

Comment on Diagonalization. (see raw notes for more detail) The problem of QM is to solve $H\psi = E\psi$ which we can regard as a matrix equation. This is the TISE and it is an eigenvalue equation,

$H\psi = E\psi$ that is $\int d^3r \langle\theta'\varphi'r'| H | \theta\varphi r\rangle\langle\theta\varphi r|\psi\rangle = E \langle\theta'\varphi'r'|\psi\rangle$

or $\Sigma_{\theta\varphi r}\ H_{\theta'\varphi'r',\theta\varphi r}\ \psi_{\theta\varphi r} = E\ \psi_{\theta'\varphi'r}$ // matrix form

The (triply infinite dimension) Hamiltonian matrix shown here is in general completely non-diagonal, it has entries everywhere. This makes the eigenvalue equation very hard to solve. We can transform the matrix equation to another space where θ,φ are replaced by ℓ,m

$H\psi = E\psi$ that is $\int r^2 dr\ \Sigma_{\ell m} \langle\ell' m'r'| H | \ell mr\rangle\langle\ell mr|\psi\rangle = E \langle\ell' m'r'|\psi\rangle$

or $\Sigma_{\ell mr}\ H_{\ell' m' r,\ \ell mr}\ \psi_{\ell mr} = E\ \psi_{\ell' m' r}$ // matrix form

but in general, this does not help much since $\langle \ell' m' r' |\ H\ |\ \ell m r \rangle$ is still a triply infinite general matrix that has all entries. *However*, if $[\ H, \mathbf{L}\ ] = 0$, then we know that $\langle \ell' m' r' |\ H\ |\ \ell m r \rangle = \delta_{\ell,\ell'} \delta_{m,m'} \langle \ell m r' |\ H\ |\ \ell m r \rangle$ and this shows that our H matrix is now hugely, if not completely, diagonal in this ℓ,m representation. It is in block diagonal form with the usual $(2\ell+1)$ size blocks. The matrix equation for H now becomes a set of independent matrix equations which are decoupled from each other:

$\int r^2 dr\ \langle \ell r' |\ H\ |\ \ell r \rangle \langle \ell r | \psi \rangle = E \langle \ell r' | \psi \rangle$ or $\Sigma_r\ H^{(\ell)}{}_{r',r}\ \psi_{\ell r} = E\ \psi_{\ell' r}$

which is now a singly-infinite matrix equation, not a triply-infinite one! In my raw notes, I show for the usual non-relativistic H that the above matrix (integral) equation is the same as the radial Schrodinger differential equation. I also discuss this diagonalization in a notation involving the direct sum of the subspaces that form those diagonal blocks in the full H matrix. In a bound state problem like the H atom, we are used to doing this ℓ-based analysis. In scattering, we do it also and there it is called "partial wave analysis". Instead of being interested in normalized bound state radial functions for a given ℓ, we are interested in the asymptotic form of a scattering wave function for given ℓ and this always involves an ℓ dependent "phase shift".

20. Scattering by Complex Potentials (129)

We are going to discuss an idea called **"the optical model"** whereby we crudely model *inelastic* scattering by a complex potential V. This idea was first proposed late, in 1954. It would apply to scattering where there is some form of "absorption" going on which makes it inelastic. Perhaps the incoming particle is completely grabbed by the target (this would be somehow counted as part of the inelastic cross section), or perhaps the incoming particle scatters, but the target is left in an excited state, which then fits our earlier model with $Q < 0$. The name of this model is quite obvious, since we treat absorption in optics by making a normally real parameter be complex, such as the index, and here we are going to make the phase shift δ_ℓ be complex. This section 20 was added in Schiff's third edition.

If the potential has an imaginary part here called $-V_I$, we show that the integrated continuity equation gains a new term and we have 20.2. We can interpret the new term as the flux that is simply absorbed by the target (ie, in the collision). Since the incoming flux is $j_z = v$, we can interpret this added term divided by the flux as an absorption cross section σ_{abs} and this gives 20.3 showing $\sigma_{abs} = 2\pi/\hbar v \int dV\ |\psi|^2 V_I$.

If we allow $\delta_\ell = \alpha_\ell + i\beta_\ell$, our derivation of the expansion for $f(\theta)$ remains unchanged and is written 20.4, but of course now δ_ℓ is complex so β_ℓ affects $f(\theta)$. The interpretation of $|f(\theta)|^2$ as the *elastic* cross section does not change (!) because the same flux argument as before applies. Thus we get 20.5 for the total elastic cross section, but we see that the β_ℓ part will affect this thing as well as α_ℓ .

Schiff next shows how to derive a partial wave expansion for the total absorption cross section! To do this, he first equates σ_{abs} with the total loss of large-sphere flux according to 20.2 with LHS = 0 and 20.3.

Into this thing he inserts the usual formula 7.3 for the radial flux in terms of function u for which we have our partial wave expansion 19.1 in terms of $\chi_\ell(r)$. By then inserting the large-r form of this function, he finds equation p 132 H and at once we have our result. So here is a summary for total cross sections:

$\sigma_{elastic} = \pi/k^2 \Sigma_\ell (2\ell+1) |1 - S_\ell^2|$ $\quad S_\ell = e^{2i\delta\ell}$ // $= A_\ell^2$ of our former work

$\sigma_{absorption} = \pi/k^2 \Sigma_\ell (2\ell+1) (1 - |S_\ell^2|)$ $\quad \delta_\ell = \alpha_\ell + i\beta_\ell$

and we can add these up to get

$\sigma_{total} = 2\pi/k^2 \Sigma_\ell (2\ell+1) (1 - \mathrm{Re}[S_\ell])$ // a total, total cross section

Reciprocity Theorem. The first business here is to define things carefully. I will not give the details here since they are in the raw notes, but will outline what is happening. We first write define

$\mathbf{k} = k \hat{\mathbf{k}}$ = a potential incoming plane wave vector
$-\mathbf{k'} = -k \hat{\mathbf{k}}'$ = another potential incoming plane wave vector (different experiment, say)
$\mathbf{k_r} = k \hat{\mathbf{r}}$ = radially outgoing vector, same magnitude

Then our old friend 18.10 becomes

$$u_{\mathbf{k}}(r) = \exp(i\mathbf{k}\bullet\mathbf{r}) + f(\mathbf{k_r},\mathbf{k})\, e^{ikr}/r$$

where we can think of $f(\mathbf{k_r},\mathbf{k})$ as being $F(\hat{\mathbf{k}}_\mathbf{r},\hat{\mathbf{k}}, k) = G(\hat{\mathbf{k}}_\mathbf{r}\bullet\hat{\mathbf{k}}, k) = G(\cos\theta, k) = f(\theta)$. If we do a different experiment with the incoming beam momentum being $-\mathbf{k}'$ we could also write

$$u_{-\mathbf{k}'}(r) = \exp(-i\mathbf{k'}\bullet\mathbf{r}) + f(\mathbf{k_r},-\mathbf{k'})\, e^{ikr}/r$$

From this very obscure start, we can show from the SE that, even with complex V,

$$u_{-\mathbf{k}'}\nabla^2 u_{\mathbf{k}} - u_{\mathbf{k}}\nabla^2 u_{-\mathbf{k}'} = 0$$

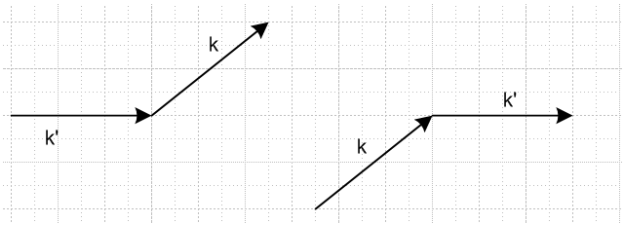
To this equation Schiff applies the Second Green's identity, inserts large-r forms for the u's, and does some further juggling making use of the stationary phase method to evaluate certain integrals. What he ends up with is this very simple result called the **Reciprocity Theorem**, which looks a bit like time reversal symmetry

$$f(\mathbf{k}',\mathbf{k}) = f(-\mathbf{k},-\mathbf{k}') \qquad 20.16$$

If $V(\mathbf{r}) = -V(\mathbf{r})$ we can show that $f(\mathbf{a},\mathbf{b}) = f(-\mathbf{a},-\mathbf{b})$ so the above theorem becomes simpler

$$f(\mathbf{k},\mathbf{k'}) = f(\mathbf{k}',\mathbf{k}) \qquad 20.18$$

where we can just swap the k vectors. Notice that we have not assumed a central potential, so it could have some strong weird angular dependence. Also, V could be complex, so we have absorption going on. So 20.18 says that these scattering amplitudes are the same even in this complex circumstance:



where the incoming beam direction is the second argument of f.

Generalized Optical Theorem. Schiff now repeats all of the above manipulations with a different starting point:

$$[u_{\mathbf{k}'}{}^{*}\nabla^2 u_{\mathbf{k}} - u_{\mathbf{k}}\nabla^2 u_{\mathbf{k}'}{}^{*}] = -\,4mi/\hbar^2\, V_I\, u_{\mathbf{k}'}{}^{*}\, u_{\mathbf{k}}$$

After turning all the same cranks, he then says we should consider $V_I = 0$ (V real) and he then shows that we get this result:

$$\int d\Omega_{\mathbf{r}}\, f^{*}(\mathbf{k}_{\mathbf{r}},\mathbf{k}')\, f(\mathbf{k}_{\mathbf{r}},\mathbf{k}) = 2\pi i/k\ [f^{*}(\mathbf{k},\mathbf{k}') - f(\mathbf{k}',\mathbf{k})] \qquad \text{// gen opt theorem V real}$$

If $V(\mathbf{r}) = -V(\mathbf{r})$ then we can do the swap and rewrite this as

$$\int d\Omega_{\mathbf{r}}\, f^{*}(\mathbf{k}_{\mathbf{r}},\mathbf{k}')\, f(\mathbf{k}_{\mathbf{r}},\mathbf{k}) = 4\pi/k\ \mathrm{Im}[f(\mathbf{k}',\mathbf{k})] \qquad \text{// gen opt theorem V real, } V(\mathbf{r}) = -V(\mathbf{r})$$

If you do perturbation theory (Born approx) in parameter α for f, then you see that although f is order α, Im(f) will be order α^2 as from the LHS. This is all unitarity stuff.

Now we let V be complex again, and he shows that from 20.20 with $\mathbf{k}' = \mathbf{k}$ you can get this result

$$\int d\Omega_{\mathbf{r}}\ |f(\mathbf{k}_{\mathbf{r}},\mathbf{k})|^2 + \sigma_{\mathbf{abs}} = 4\pi/k\ \mathrm{Im}[f(\mathbf{k},\mathbf{k})]$$

But the integral is just the total elastic cross section, so we have

$$\sigma_{\mathbf{tot}} = \sigma_{\mathbf{elas}} + \sigma_{\mathbf{abs}} = 4\pi/k\ \mathrm{Im}[f(\mathbf{k},\mathbf{k})] \qquad \text{// optical theorem} \qquad \text{V complex}$$

where of course $f(\mathbf{k},\mathbf{k})$ is the forward direction scattering amplitude. We have thus generalized our previous optical theorem to (1) non-central $V(\mathbf{r})$; (2) complex V. Schiff notes that this optical theorem is true very generally, and follows from unitarity arguments, so applies to relativistic case or case with no potential at all. He gives some comments on this from a paper he once wrote.

21. Coulomb Scattering (138)

This problem does not fit into the standard mold of $\psi = e^{ikz} + f(\theta)\, e^{ikr}/r$. The reason is that you can't get "far enough away" from a 1/r potential to get this form. You cannot specify a nice radius r = a and say that V = 0 outside that radius. The mathematical reason for this is given on page 57 of my raw notes and in the text after equation 19.3 on page 117. For a potential that drops off faster than 1/r, you *can* get far enough away. It is related to the fact that $\int dr/r^{1.00} = \ln r$ which diverges, while $\int dr/r^{1.01} \sim 1/r^{.01}$ is finite. So the correct form for solving the Coulomb problem turns out to be

$$\psi = e^{ikz}\ (e^{inln[k(r-z)]}) + f_c(\theta)\, e^{ikr}/r * (e^{-in\ ln[2kr]})$$

where we have the extra () factors shown. I refer to the entire first term as the Coulomb Plane Wave in my notes. We still have $d\sigma/d\Omega = |f_c(\theta)|^2$ because the extra log phase factors don't affect the distant out/in flux ratio. Arriving at this form is somewhat non-obvious and there are two methods of finding it.

Parabolic Method. The first method is pursued by Schiff. It turns out that the Coulomb problem is *exactly* solvable with no expansion required if you do it in parabolic coordinates, and this has some mysterious connection to a certain O(4) group symmetry of the Hamiltonian for this problem -- I have not tracked that down. Slyly, Schiff solved the H atom in these coordinates in the previous chapter, to get us used to the parabolics. The exact solution is quite simple: $\psi(r,\theta) = F(-in,1,ik(r-z)) = F(-in,1, 2ikr\sin^2\theta/2)$, where $n = (\mu ZZ' e^2/\hbar^2)/k$ is a dimensionless "energy" variable, $E = \hbar^2k^2/2\mu$, where F is the Φ confluent hypergeometric function. If you look up the asymptotic expansion of this function and keep only the leading terms, you get a form exactly like that shown above with those extra factors. You can then identify what $f_c(\theta)$ is, and amazingly you then find that $d\sigma/d\Omega = |f_c(\theta)|^2$ = the classical Rutherford formula. There is n-dependence in the phase of $f_c(\theta)$ which can cause quantum effects for identical particles, where you would have to perhaps use $|f_c(\theta) \pm f_c(\pi-\theta)|^2$.

Note: Before I read about Φ and Ψ functions in Bateman, I was horribly confused about the W_1 and W_2 functions used by Schiff, and I saw them also in the Messiah Coulomb section and an appendix, so I got heavily side-tracked trying to connect these W_i to something in the normal "special functions literature". That caused the generation of some of my supporting ODE math documents. In the end, it all got completely cleared up.

Spherical Method. The second method pursued by me and only indirectly by Schiff is to solve this problem directly in spherical coordinates, once you know the general asymptotic ψ form shown above. In this method, you use the usual partial wave expansion over ℓ, and the radial Schrodinger equation is found to again be a confluent hypergeometric function equation, but the parameters a,b,z are all different from what they were in the parabolic solution. *This* HG equation's solutions are the functions F_ℓ and G_ℓ which are studied in A&S chapter 14 and are officially known as "the Coulomb Wave Functions" (that is, the ones in spherical coordinates where z = kr is the main argument of the HG functions). Like all functions of any radial SE, these functions approach sine and cosine forms for large r, since the χ radial equation ignoring V(r) and the centrifugal term is just the 1D wave equation in kr. Moreover, only the F_ℓ functions make a finite $R_\ell(r)$ at r=0, so we know the solution has the general form as a partial wave sum of the F_ℓ with some unknown amplitudes I call B_ℓ.

It turns out that, unlike with e^{ikz}, the Coulomb Plane Wave e^{ikz} ($e^{inln[k(r-z)]}$) contains only an incoming piece. As with the non-Coulomb case, the $f_c(\theta)$ term has only an outgoing piece. If we make a partial wave expansion for $f_c(\theta)$ with some unknown weights f_ℓ , and if we do a partial wave expansion of the Coulomb plane wave, and if we set the sum of these two things to the large-r limit of the sum over F_ℓ solution with its unknown B_ℓ weights (F_ℓ →sine has in *and* out pieces), we are able to determine the values of B_ℓ and f_ℓ . This method is quite similar to what was done in the general V(r) non-Coulomb case where we found that $f_\ell = (e^{2i\delta_\ell} - 1)$. In that case, the -1 is due to the outgoing piece of e^{ikz} which in effect we have to subtract off. In the Coulomb case, the Plane Wave has no outgoing piece, and we get just $f_\ell = e^{2i\sigma_\ell}$ where this phase $\sigma_\ell = \arg \Gamma(\ell+1+in)$ is called "the Coulomb phase shift". I do this calculation in document "radial equation.doc" and also in the "seat of pants" section of the raw notes.

Schiff does not do this Coulomb derivation in spherical coordinates, but does touch upon it and does a partial wave analysis of the parabolic result to obtain 21.21 which is basically the F_ℓ solution mentioned above. The tough problem was getting the normalization to match the parabolic normalization of unit flux.

Modified Coulomb. The next topic is what happens when you have some nuclear force interaction deep inside the Coulomb interaction, as happens in an atom. In this case it is easy to show that instead of just F_ℓ, you have some unknown mix of F_ℓ and G_ℓ in the Coulomb region, and this just causes some extra phase shift which is called δ_ℓ , but is not the same as that obtained in the general case without Coulomb. Thus, you get $f_\ell = e^{2i(\sigma_\ell+\delta_\ell)}$ and this is presented in an exactly equivalent form in 21.27, where the change caused by the nuclear interaction is broken off as the second term.

Messiah (or maybe GW) treats a fancier case that includes shielding outside the Coulomb atom so there are three regions of interest, but I have not read that analysis yet, I don't think it is too complicated.

The final section talks about large n being the true classical limit where quantum phase effects even for identical particles doing Coulomb scattering go away.

All in all, this was a very tough section because almost every single equation requires about 2-10 pages of detailed algebra and calculus and special function lookups to verify. I left no stone unturned, hence all equations have red checks. The reason was that I have always felt "weak" when it comes to any kind of partial wave analysis and those "phase shifts" that are constantly spoken of in the particle physics world. Also, I have always wondered what was meant by "Coulomb wave functions".

I later read the corresponding sections in Saxon and Messiah, and found nothing terrifically new there.

Chapter 6: The Matrix Formulation of QM : (Sections 22-25)

22. Matrix Algebra (149). This section summarizes "the basic facts" about finite square matrices. We see rules for doing det(AB) and tr(AB) and $(AB)^{-1}$ and such. Hermitian and Unitary matrices are defined.

Next, the notion is presented that a similarity transformation $SAS^{-1} = A'$ preserves the form of any matrix equation. Then comes a discussion of possibly diagonalizing matrices. First, the λ_i are just regarded as the elements of the diagonalized (by some similarity) matrix, assuming it can be done. This leads at once to the secular equation $\det(A-\lambda I)$ for the N values λ_i. The "roots" λ_i are so called because

this secular thing is a polynomial of degree N. Similarity A to B does not change the roots. Oddly, it is not stressed in this section that the λ_i are eigenvalues of the eigenvalue problem Au = λu, perhaps because we are just talking here about matrices and not vectors. Away from a root λ_i, the equation (A-λI)u = 0 has the only solution u = 0, so Au = λu has no non-trivial solution. Only at the roots λ_i is it possible to have a non-trivial solution of Au = λu.

Schiff mentions functions of matrices such as $e^{\mathbf{A}}$.

He then says you can imagine either or both indices going infinite but the ideas remain.

He mentions various theorems: (1) a Hermitian matrix can always be diagonalized; (2) the diagonal elements will be real. (3) If two Hermitian matrices commute, they can be simultaneously diagonalized.

23. Transformation Theory: representations (155)

Schiff examines unitary transformation matrices W,U and V. Each of these "links" two of the three representations which I will call energy, coordinate, and arbitrary. The diagonal operators in the three cases are H, R and Ω. The linkage matrix is always unitary if in each space you have a clean identity representation for "1", that is, normalizations are preserved. In each representation, we can choose to look at matrix elements of the Hamiltonian H operator if we want to. In the case of U which links energy and coordinate space representations, the columns of $U^{\dagger}$ are eigenfunctions. This seems now like a lot of aimless shuffling around, maybe Schiff is just trying to get the reader familiar with the infinite matrix idea. Well, I think he wants to develop a reservoir of complex looking equations which then all simplify when he does the bra ket notation on page 165.

My own summary would be this: [these are of course just specific examples]

change of representation on a *state*:

$$\langle \mathbf{p} \mid \psi \rangle = \langle \mathbf{p} \mid \mathbf{r} \rangle\langle \mathbf{r} \mid \psi \rangle$$

$$\psi'_{\mathbf{p}} = U_{\mathbf{p},\mathbf{r}}\, \psi_{\mathbf{r}}$$

$$x'_i = R_{ij}\, x_j$$

$$\psi'(\mathbf{p}) = \int d^3r\, U(\mathbf{p},\mathbf{r})\, \psi(\mathbf{r}) = \int d^3r\, e^{i\mathbf{p}\bullet\mathbf{r}/\hbar}\, \psi(\mathbf{r})$$

When we actively rotate a vector x, we give it a new name x' so that we can tell it from the original x. Similarly, when we "rotate" a wavefunction (ie, change representation using some unitary transformation), we should give it a new name. It *must* have a new name because it does NOT have the same functional form. This is just like giving the Fourier Transform of a function a new name because there is a new functional form. Next, we work with an operator, and again use a prime for the name change.

change of representation on an *operator*:

$$H'_{\mathbf{p},\mathbf{p}'} = U_{\mathbf{p},\mathbf{r}}\, H_{\mathbf{r},\mathbf{r}'} U^{-1}{}_{\mathbf{r}',\mathbf{p}'}$$

$$H' = UHU^{-1}$$

$$\langle p \mid H \mid p' \rangle = \langle p \mid r \rangle\langle r \mid H \mid r' \rangle\langle r' \mid p' \rangle$$

You can transform only one side or the other if you want. Suppose $H'_{\mathbf{p},\mathbf{p}'}$ is diagonal, as it would be for a free particle if H were the Hamiltonian. Then we get

$$U^{-1}H' = HU^{-1}$$

$$U^{-1}_{r,p''}\ H'_{p'',p} = H_{r,r'}U^{-1}_{r'p} = f(p')\ U^{-1}_{r,p}$$
$$H_{r,r'}[U^{-1(p)}]_{r'} = f(p')\ [U^{-1(p)}]_{r'}$$

This last line shows then the idea that, in this case, the columns of U^{-1} are the eigenfunctions of H. So a general idea is that if you look at a matrix transformation where one end is diagonal, then the transforming matrix will consist somehow of the eigenfunctions of the matrix in the non-diagonal representation. In the above case, that non-diagonal representation is $H_{r,r'}$.

Also in this section, we sort of *drift* into this idea:

$$< r \mid \Omega \mid \psi> \ = \ \Omega^{op} < r \mid \psi>$$

where Ω^{op} is a possibly differential operator. Well, really Ω will just be some Ω(R,P), a function of the hamiltonian type coordinates and momenta (both operators), and the idea is simply that $p^{op} = -i\hbar\nabla$. It is all based on this simple fact:

$$<x \mid P \mid \psi > \ = <x \mid P \mid p > < p \mid \psi > \ = <x \mid p \mid p > < p \mid \psi > \ = p <x \mid p > < p \mid \psi >$$

$$= p\ e^{ip.x} < p \mid \psi > \ = -i\nabla\ e^{ip.x} < p \mid \psi > = -i\nabla <x \mid p > < p \mid \psi > = -i\nabla <x \mid \psi >$$

$$= p^{op} <x \mid \psi >$$

Here I have three different objects floating around: P = HS operator, p = a number, p^{op} = differential operator. Notice in particular that

$$<x \mid P \mid x' > = p^{op} <x \mid x' > \ = p^{op}\ \delta^3(x-x')$$

Since p^{op} involves differential operators, this matrix is not regarded as diagonal.

Schiff carries on in this section, and I am comfortable with everything he says. He mentions the QM Hilbert space. The Hermitian adjoint operator can be understood from matrix language like so:

$$<x \mid A \mid x'> \ = <x \mid A\ x'> \ = < B\ x \mid x'> \qquad \text{// conjecture that some such B exists}$$

$$< B\ x \mid x'>^* = <x' \mid B\ x> \ = <x' \mid B \mid x >$$

Thus we have $B_{x',x} = A_{x,x'}^* \ = \ A^\dagger_{x',x}$. Therefore $B = A^\dagger$.

24. Equations of Motion in various Pictures (167)

THE PICTURES

The first part of this Section concerns the three "pictures". This subject is very clear and sharp.

Schrodinger Picture. We start with the TDSE acting on a vector in HS:

$$i\hbar\partial_t| \beta_S(t) > = \ H \mid \beta_S(t) > \qquad => \qquad | \beta_S(t) > \ = e^{-iHt/\hbar} \mid \beta_S(0) >$$

This IS the SE, you can "close" with any representation you want, usually one uses <r|. That is to say, you can project the above "state vectors" onto any set of "axes" you want. It is trivial then to show that:

$$d/dt\ [\ <\alpha_S(t)\ |\ \Omega_S(t)\ |\ \beta_S(t)>\ ]\ \ =\ \ <\alpha_S(t)\ |\ \{\partial_t\Omega_S(t)\}\ |\ \beta_S(t)> + <\alpha_S(t)\ |\ [\Omega_S\ ,\ H]\ |\ \beta_S(t)>/(i\hbar)$$

and this is what we always want to know, how does some matrix element (often an expectation value of an operator of interest to us) move in time. The RHS first term with the $\partial_t\Omega_S(t)$ refers to the possible "explicit" time dependence of an operator, such as a time-varying B field being applied, say. The commutator arises by just using the above SE twice. This is the Schrodinger Picture, the "normal" picture, and we have S subscripts on the state labels to remind us. *Apart from* possible "explicit" operator dependence on time, in the Schrodinger picture it is the states that move and the operators that don't move (in time). A state vector describes a trajectory, so to speak, in Hilbert space, while the marble pillar like operators stay fixed to the firmament.

Heisenberg Picture. The Heisenberg picture wants to see the reverse. It wants to see state vectors stay fixed while the *operators* move around in time. We can rewrite the above equation like this:

$$d/dt\ [\ <\alpha_S(0)\ |\ e^{iHt/\hbar}\ \Omega_S(t)\ e^{-iHt/\hbar}\ |\ \beta_S(0)>\ ]$$

$$=\ \ <\alpha_S(0)\ |\ e^{iHt/\hbar}\{\partial_t\Omega_S(t)\}\ e^{-iHt/\hbar}\ |\ \beta_S(0)> + <\alpha_S(0)\ e^{iHt/\hbar}|\ [\Omega_S\ ,\ H]\ e^{-iHt/\hbar}\ |\ \beta_S(0)>/(i\hbar)$$

where we have done nothing other than insert pairs like $1 = e^{-iHt/\hbar}\ e^{+iHt/\hbar}$ in various places. According to Schiff, we now have to treat $\Omega_S(t)$ and $\partial_t\Omega_S(t)$ as two *distinct* Schrodinger picture operators, and we transform each according to the same rule to move them to the "Heisenberg picture"

$$\Omega_H(t) \equiv e^{iHt/\hbar}\ \ \Omega_S(t)\ \ e^{-iHt/\hbar}$$
$$(\partial_t\Omega)_H(t)\ \equiv e^{iHt/\hbar}\ (\partial_t\Omega_S(t))\ e^{-iHt/\hbar}$$
$$H \qquad = e^{iHt/\hbar} \qquad H \qquad e^{-iHt/\hbar}$$

and the last line shows that H does not change at all, so we don't bother with a subscript yet on it. We could say $H = H_S = H_H$. Now if we insert these two definitions and the third fact into the above, we get

$$d/dt\ [\ <\alpha_S(0)\ |\ \Omega_H(t)\ |\ \beta_S(0)>\ ]\ \ =\ \ <\alpha_S(0)\ |\ (\partial_t\Omega)_H(t)\ \ |\ \beta_S(0)> + <\alpha_S(0)|\ [\Omega_H\ ,\ H]\ |\ \beta_S(0)>/(i\hbar)$$

But now comes the key point: on the LHS we can move the d/dt operator *inside* since the states don't depend on t. Once we do this, the claim is that the equality is true for all possible states on either side at time 0, so it must be true in an operator sense. Then we have

$$d/dt\ \Omega_H(t)\ \ =\ (\partial_t\Omega)_H(t)\ +\ \ [\Omega_H\ ,\ H]\ /(i\hbar) \qquad\qquad |\ \beta_H> \equiv |\ \beta_S(0)>$$

and this then says how the operators move in the Heisenberg Picture. The states are fixed in time, and we write them as shown on the right above. It is this Picture that will allow us to connect to Poisson Brackets of classical mechanics.

Interaction Picture. The famous Interaction Picture used in perturbation theory lies halfway between the above two pictures. We can "develop" this picture starting from the Schrodinger picture and moving forward, or from the Heisenberg picture and moving backward. I choose the forward direction here. First, we just define things as follows, then we will see where these definitions lead. We assume for this picture that H has the following special form

$$H_S = H_o + H'_S(t)$$

where H_o does not have explicit time dependence, and where it will turn out that H_o will be the same in either the S or I picture, so we don't bother with an S subscript on H_0. We then define our states and our operators using "movement" by just H_0 instead of the full H (as we did going from the S to the H picture):

$$| \beta_S(t) > = e^{-iH0t/\hbar} | \beta_I(t) >$$

$$\Omega_I(t) \equiv e^{iH0t/\hbar} \Omega_S(t) e^{-iH0t/\hbar}$$
$$(\partial_t\Omega)_I(t) \equiv e^{iH0t/\hbar} (\partial_t\Omega_S(t)) e^{-iH0t/\hbar}$$
$$H_I = e^{iH0t/\hbar} H_S e^{-iH0t/\hbar} = H_0 + e^{iH0t/\hbar} H'_S(t) e^{-iH0t/\hbar} = H_0 + H'_I(t)$$

This picture is more complicated that the H picture because the states still have residual time movement. So our first job is to see what the SE looks like for these new states. Start with the normal S picture SE:

$$i\hbar\partial_t| \beta_S(t) > = H_S | \beta_S(t) > \quad => \quad i\hbar\partial_t \{ e^{-iH0t/\hbar} | \beta_I(t) >\} = H_S\{ e^{-iH0t/\hbar} | \beta_I(t) >\}$$

$$=> H_0\{ e^{-iH0t/\hbar} | \beta_I(t) >\} + e^{-iH0t/\hbar} i\hbar\partial_t | \beta_I(t) > = H_0 e^{-iH0t/\hbar} | \beta_I(t) > + H_S' e^{-iH0t/\hbar} | \beta_I(t) >$$

Notice now that two terms exactly cancel and we are left with

$$e^{-iH0t/\hbar} i\hbar\partial_t | \beta_I(t) > = H_S' e^{-iH0t/\hbar} | \beta_I(t) >$$

$$=> \quad i\hbar\partial_t | \beta_I(t) > = e^{+iH0t/\hbar} H_S' e^{-iH0t/\hbar} | \beta_I(t) > = H'_I | \beta_I(t) >$$

Thus, we conclude that in the I picture, the I states are "driven" only by H'_I, as if H_o did not exist:

$$i\hbar\partial_t | \beta_I(t) > = H'_I | \beta_I(t) > \qquad \text{// SE in the I picture}$$

$$- <\alpha_I(t) | i\hbar \overleftarrow{\partial_t} = <\alpha_I(t) | H'_I \qquad \text{// } H'_I \text{ assumed Hermitian}$$

Now let's go back to our S picture matrix element equation above which we repeat here

$$d/dt [<\alpha_S(t) | \Omega_S(t) | \beta_S(t) >] = <\alpha_S(t) | \{\partial_t\Omega_S(t)\} | \beta_S(t) > + <\alpha_S(t) | [\Omega_S , H] | \beta_S(t) >/(i\hbar)$$

We now process this equation as earlier, but this time we insert $1 = e^{-iH0t/\hbar} e^{+iH0t/\hbar}$ in those "various places" to get

$$d/dt\ [\ <\alpha_I(t)\ |\ e^{iH0t/\hbar}\ \Omega_S(t)\ e^{-iH0t/\hbar}\ |\ \beta_I(t)>\ ]$$

$$= \quad <\alpha_I(t)\ |\ e^{iH0t/\hbar}\{\partial_t\Omega_S(t)\}\ e^{-iH0t/\hbar}\ |\ \beta_I(t)> + <\alpha_I(t)e^{iH0t/\hbar}|\ [\Omega_S\ ,\ H]\ e^{-iH0t/\hbar}\ |\ \beta_I(t)>/(i\hbar)$$

or

$$d/dt\ [\ <\alpha_I(t)\ |\Omega_I(t)|\ \beta_I(t)>\ ] \quad = \quad <\alpha_I(t)\ |\ (\partial_t\Omega)_I(t)\ |\ \beta_I(t)> + <\alpha_I(t)|\ [\Omega_I\ ,\ H_I]\ |\ \beta_I(t)>/(i\hbar)$$

This time we cannot just move the d/dt inside on the left, we have to deal with the states varying in time, so there is more work to do. This is very similar to the work we had to do to get the S picture version on this equation in the first place. There will be three terms when we expand the LHS:

$$LHS = \{d/dt\ \ <\alpha_I(t)\}\ |\Omega_I(t)|\ \beta_I(t)>\ +\ <\alpha_I(t)\ |\ \{d/dt\ \Omega_I(t)\}|\ \beta_I(t)>\ +\ <\alpha_I(t)\ |\Omega_I(t)\ \{d/dt\ |\ \beta_I(t)>\}$$

For the first and last term, we can use our I picture SE derived above to get

$$LHS = -<\alpha_I(t)\}\ |\ H'_I\ \Omega_I(t)|\ \beta_I(t)>/(i\hbar)\ +\ <\alpha_I(t)\ |\ \{d/dt\ \Omega_I(t)\}|\ \beta_I(t)>\ +\ <\alpha_I(t)\ |\Omega_I(t)\ H'_I\ |\ \beta_I(t)>/(i\hbar)$$

$$= <\alpha_I(t)\ |\ \{d/dt\ \Omega_I(t)\}|\ \beta_I(t)> + \ <\alpha_I(t)\ |[\Omega_I(t),\ H'_I\ ]|\ \beta_I(t)>/(i\hbar)$$

So our equation LHS = RHS now reads:

$$<\alpha_I(t)\ |\ \{d/dt\ \Omega_I(t)\}|\ \beta_I(t)> + \ <\alpha_I(t)\ |[\Omega_I(t),\ H'_I\ ]|\ \beta_I(t)>/(i\hbar)$$

$$= \ <\alpha_I(t)\ |\ (\partial_t\Omega)_I(t)\ |\ \beta_I(t)> + <\alpha_I(t)|\ [\Omega_I\ ,\ H_I]\ |\ \beta_I(t)>/(i\hbar)$$

If we move the H'_I commutator term to the RHS, we get $H_I - H'_I = H_0$ so we then have

$$<\alpha_I(t)\ |\ \{d/dt\ \Omega_I(t)\}|\ \beta_I(t)> = <\alpha_I(t)\ |\ (\partial/\partial t\ \Omega)_I(t)\ |\ \beta_I(t)>\ +\ <\alpha_I(t)|\ [\Omega_I\ ,\ H_o]\ |\ \beta_I(t)>/(i\hbar)$$

Again we argue that, since this just be true at time t for any states on either side, we find that

$$d/dt\ \Omega_I(t)\ = (\partial/\partial t\ \Omega)_I(t)\ +\ [\Omega_I\ ,\ H_o]\ /(i\hbar)$$

and this tells how the operators move in the I picture. Just a reminder: an operator might have explicit time dependence indicated by $\partial/\partial t\ (\Omega)$, but usually this is not the case. Apart from this possible dependence, the main source of the movement of the I picture operators comes from $[\Omega_I\ ,\ H_o]\ /(i\hbar)$.

So this picture seems hardly very useful because both states and operators move (even operators which have no explicit time dependence). This picture finds its use in perturbation theory as we shall see in Chapter 8, in the case that $H' << H_o$ so that the I picture SE results in "slow" motion in time of the I picture states. A full appreciation of why this is useful must wait, but here we have laid the groundwork.

I think Messiah calls these pictures "representations" and I think Schiff was good to call them "pictures" to avoid confusion with the notion of different representations in the time independent SE situation, such as <r| and <p|.

In retrospect, I'll bet developing the I picture from the H picture would require less algebra that the way I just did it from the S picture to the I picture.

As this point, Schiff just draws our attention to what time-dependent matrix elements of an operator look like in the S picture if the states happen to be energy eigenstates:

$$\langle k_S(t) |\Omega_S| k'_S(t)\rangle = \exp[i(E_k - E_{k'})t/\hbar\,] \langle k|\Omega_S|k'\rangle$$

where we see the famous "phasor energy difference" appearing. Perturbation theory soon to come!

Connection to Classical Mechanics and Goldstein.

In his Chapter on Canonical Transformations (within the context of Hamiltonian Mechanics), Goldstein defines "Poisson Brackets" [a,b] which should not be confused with "Lagrange brackets {a,b}" which are in a certain sense the inverse of the PB's. That PB definition is this:

$$[u,v]_{\mathbf{q},\mathbf{p}} \equiv \Sigma_{\mathbf{i}} \left(\partial u/\partial q_{\mathbf{i}}\ \partial v/\partial p_{\mathbf{i}} - \partial u/\partial p_{\mathbf{i}}\ \partial v/\partial q_{\mathbf{i}}\right)$$

where the $q_{\mathbf{i}}$ and $p_{\mathbf{i}}$ are the coordinates and canonical momenta of Hamiltonian mechanics. Goldstein shows many interesting properties of these brackets, one being that they are invariant under an arbitrary canonical transformation, so $[u,v]_{\mathbf{q},\mathbf{p}} = [u,v]_{\mathbf{Q},\mathbf{P}}$. A simple calculation shows these fundamental facts to be true

$$[q_{\mathbf{i}},q_{\mathbf{j}}] = 0 \qquad [p_{\mathbf{i}},p_{\mathbf{j}}] = 0 \qquad [q_{\mathbf{i}},p_{\mathbf{j}}] = \delta_{\mathbf{ij}}$$

which are certainly suggestive of our QM commutators, apart from i$\hbar$ factors. He goes on to show that

$$-\partial F/\partial p_{\mathbf{k}} = [F,q_{\mathbf{k}}] \quad \text{and} \quad +\partial F/\partial q_{\mathbf{k}} = [F,p_{\mathbf{k}}] \qquad F = F(\mathbf{p},\mathbf{q})$$

If we set F = H, the Hamiltonian, then we can combine the above with the usual Hamilton's equations of motion to get:

$$[q_{\mathbf{k}},H] = \partial H/\partial p_{\mathbf{k}} = \dot{q}_{\mathbf{k}} \qquad [p_{\mathbf{k}},H] = -\partial H/\partial q_{\mathbf{k}} = \dot{p}_{\mathbf{k}}$$

But then when we think about some arbitrary object F = F(**p**,**q**), the above imply

$$[F,H] = \dot{F}$$

If we have an F with some explicit time dependence F = F(**p**,**q**, t), then you can show that you have to subtract off the explicit time dependence since the PB drives only the non-explicit time motion, so

$$[F,H] = \dot{F} - \partial F/\partial t$$

We then arrive at the very important **Poison Bracket Equation of Motion**

$$dF/dt = \partial F/\partial t + [F,H]_{PB}$$

where again, F is some classical variable and general function like F = F(**p**,**q**, t), and $[F,H]_{PB}$ is the Poisson Bracket thing defined above.

We may compare this last result with our Heisenberg Picture result

$$d/dt\ \Omega_H(t) = (\partial_t \Omega)_H(t) + [\Omega_H , H] /(i\hbar)$$

So the rule is this: to convert from a classical variable to a QM operator, you alter the classical PB equation of motion by making this replacement

$[F,H]_{PB} \rightarrow [F , H] /(i\hbar)$ // where the QM commutator appears on the RHS

As an example, consider this simple application of the above:

$[q_i,p_j]_{PB} = \delta_{ij} \rightarrow [q_i,p_j] /(i\hbar)$ => $[q_i,p_j] = i\hbar\delta_{ij}$

Where, when and how did this commutator first appear in Schiff, you might ask. It is defined in Chap 6 page 170, and then discussed on page 175 right in context with our PB stuff. Warning: Schiff uses {..} for his PB, to distinguish them from Goldstein, but thereby causes confusion with Goldstein's Lagrange brackets which are {...}, but OK. So the entire first 5 chapters of Schiff made no use of commutators. They are really part of the "matrix formulation" of QM, since matrices can have non-zero commutators.

The notion of "processing" a classical variable F into a QM HS operator by doing $[F,H]_{PB} \rightarrow [F,H]/(i\hbar)$ is known I think as the "first quantization" of a classical system. Field theory then involves a certain "second quantization". There is the technical issue of taking a symmetric average before quantizing, and an example of this appears on page 236 with the Runge-Lenz vector (→ QM operator), see 30.5. You do this to get something that is Hermitian and can therefore be an operator for an observable. I think there are other examples in Schiff where this is done.

Long Example: First Quantization of classical E&M.

We know all about EM with potentials **A** and φ and fields **E** and **B** (Schiff calls them H, but H always makes me think of Hamiltonians) . In this section, Schiff applies the ideas of the previous section to get all these things converted to QM operators! There is a lot going on here, so I will try to "organize" things a bit. We will end up with an equation of motion for the Heisenberg operator **r** .

1. What facts do we know from classical E&M. Here are some of them:

$L(r,v) = 1/2\ mv^2 + q/c\ \mathbf{v}\bullet\mathbf{A}(\mathbf{r},t) - q\varphi(\mathbf{r},t)$ // classical Lagrangian

$m\dot{\mathbf{v}} = -q\ \nabla\varphi + (q/c)\ \mathbf{v} \times \mathbf{B}$ // Lagrange's equations from the Lagrangian above

So yes, we have here the Lorentz Force on the RHS of this equation. Then for H this gives

$H = (\mathbf{p} - e\mathbf{A}/c)^2/2m + e\varphi$ // classical

$H = \mathbf{p}^2/2m - e/2m\,(\mathbf{p}\bullet\mathbf{A} + \mathbf{A}\bullet\mathbf{p}) + (e/2m)^2\,\mathbf{A}^2 + e\varphi$

So this is the operator QM Hamiltonian now. Let's now try the operator $\Omega = \mathbf{r}$ and our Heisenberg rule:

$d/dt\ \Omega_H(t) = (\partial_t\Omega)_H(t) + [\Omega_H , H]\ /(i\hbar)$

$\dot{\mathbf{r}} = 0 + [\mathbf{r} , H]\ /(i\hbar) = (1/m)\,(\mathbf{p} - e\mathbf{A}/c)$ // claimed if you do that commutator

$\ddot{\mathbf{r}} = (\partial_t\dot{\mathbf{r}}) + [\dot{\mathbf{r}} , H]\ /(i\hbar) = (-e/mc)\,(\partial_t\mathbf{A}) + [(\mathbf{p} - e\mathbf{A}/c) , H]\ /(i\hbar m)$

When you do these last commutators, you get the mess shown in 24.37. But then this simplifies as shown in 24.38 and we get our QM version of the Lorentz force law:

$m\ddot{\mathbf{r}} = eE + (e/2c)\,[\dot{\mathbf{r}}\ \mathbf{x}\ \mathbf{B} - \mathbf{B}\ \mathbf{x}\ \dot{\mathbf{r}}\ ]$

where we see that for our QM operator result, the "symmetrized form" of **v** x **B** shows up. All these operators are in the Heisenberg Picture so are of type Ω_H .

I omit comments on the virial theorem, see raw notes.

25. Matrix Version of the HO (167)

I am not happy with Schiff's presentation here, but I could probably rewrite it and be happy. Saxon I think did a better job. It is linear combinations of p and x that, when normalized, become the $a^\dagger$ and a raising and lowering operators and yes $H = (a^\dagger a + 1/2)\,\hbar\omega_c$. And yes, we can actually write out the matrices for a and $a^\dagger$ as shown on page 183 where we start at the lowest state and imagine these as infinite matrices where you never reach the lower right corner. And yes, by fiddling around you can come up with a Rodriguez form for the Hermite wavefunctions.

Now why exactly is this the "matrix theory" of the HO? We know there are energy eigenstates, and we know we can enumerate them by some numbers from the ground state up. Yes, $\langle n|H|m\rangle$ is a matrix. And yes, we can write out matrices explicitly for a, $a^\dagger$, p and x and they only have elements just off the main diagonal. There is just something wrong (at least for me) with the logic flow in this section.

Chapter 7: Symmetry in QM : (Sections 26-30)

26. Space and Time Displacements (188). We are told that if you exponentiate **p** or H, you get an operator that does space or time translation of a state. This operator U is unitary and is "the usual exponential". He talks in general here about groups and their generators and the fact that [U,H]=0 means that a translated SE equation is also a SE solution. This is sort of an odd section.

27. Rotation and Unitary Groups (194). He mentions isomorphism of SO(3) to a sphere of points. He shows that **L** = **r** x **p** do generate physical rotations. **J** x **J** = i$\hbar$**J** is the Schiff way, he does not like ε_{ijk}.

He talks about Lie Algebras just a bit, then he solves this one for its states |j,m> and the eigenvalue spectrum for J^2 and J_z, He shows the matrices for small j values, including j = 3/2 which I normally don't mess with, see page 203. You do all this work by defining and then using the the $J_\pm$ operators. The generator matrices for any value of j have values only on or next to the diagonal. He then shows that the spherical harmonics are the angular momentum eigenfunctions in the angular coordinate representation, whereas |j,m> are eigenkets in the general HS j-manifold. A double size isomorphism sphere is the covering group and is simply connected.

He then talks about U(n) and SU(n) and how many real parameters there are for each (n^2 and n^2-1). The "rank" of a group is how may Casimir type generators there are, and SU(2) has rank 1.

He then talks specifically about SU(3) which has 3^2 - 1 = 8 parameters, hence 8 generators. The lowest order matrix representation of the generators λ_i are 3x3 matrices, ie, this is the basic representation the way Pauli's are for SU(2). He writes down all 8 of these babies and finally uses ε_{ijk} type notation. Then he claims that you can represent all 8 of these SU(3) generators as functions of the r,p coordinates of a particle! These are listed on page 211, where the first three are our usual L_i for j=1, and the other 5 are part of what he calls a quad tensor, though it seems a little mixed up to me. It turns out that the L = r x p generators given here don't correspond to the $\lambda_{1,2,3}$ spin matrices and he talks about that a little, I don't think this is a major problem. Remember that these 8 generators have names λ_i just as J_i have names. His purpose in giving this SU(3) detail is this: he computes one of the two Casimirs on page 212 where α and β are free parameters in that quad tensor definition. If you choose α,β properly, then this Casimir will commute with the 3D HO Hamiltonian, and that means you can analyze the HO states in terms of the SU(3) eigenfunctions and spectrum. More on this later in the "dynamical symmetry" section end of chap.

28. Combination of Angular Momentum States; Tensor Operators (212) One of my pet subjects. He has a whack at it, but does not get down to talking direct sum and product stuff. He mentions the triangle rule and I try to explain this term in the raw notes. He plays around and finds the effect of $J_\pm$ on the combination states and computes the C-G coefficients for some lower cases.

Next, he is off defining (spherical) tensor operators in analogy with [$L_\pm(\theta,\varphi)$, $Y_{\ell m}(\theta,\varphi)$] and we have that world of pain. Then he claims that combining two such operators, an operator and a state, or two states, are all controlled by the C-G coefficients in the same manner. His grand finale is a proof of the Wigner Eckhart theorem. We never get any rotation matrices or D matrices or anything like Tinkham does.

This stuff is something every QM book has to deal with, and Schiff has done a solid workman's job, but I just don't like it very much. Some day I will write my own version of this (something every physicist says to himself or herself all the time). There are whole books just on this narrow subject, but I doubt they would do it "my way".

29. Space and Time Inversion (224) One comment I forgot to note in the above comments: symmetry almost always implies degeneracy. That is, [H,U] = 0 means that if ψ is a solution, so is Uψ (with the same energy eigenvalue) and often Uψ won't just be a multiple of ψ, so there is your degeneracy. As an example, if $[H,L^2] = 0$ you will find degeneracy $2\ell+1$ in each ℓ subspace, such as in $Y_{\ell m}(\theta,\varphi)R_{\ell E}(r)$ for the H atom.

The parity discussion here is strange (I keep thinking that about Schiff's sections), and suddenly we are talking about the intrinsic parity of an elementary particle. Our more mundane use of this is to say that if [P,H] = 0, then you can make your problem solutions have definite parity, as with particle in a box or HO. The deeper idea is that an elementary particle is itself a "solution" of a problem and as such has

certain eigenstate quantum numbers including spatial parity and spin etc. This is Poincare Group stuff. Even the mass is a quantum number of that group.

We are reminded that certain operators have certain space inversion properties. The QM result always follows the classical result. Vectors negate, axial vectors like L do not.

Next comes **time reversal** which is unusual because you have to represent it with an anti-Hermitian operator of the form T = UK where U is unitary and K means complex conjugation. There is a nice general result for the T operator for a particle of spin S: it is $T = \exp(-i\pi S_y)K$ which is a matrix appropriate for the spin of the particle. For S = 1/2, this simplifies to $T = -i\sigma_2 K$ and I think this is how it appears in BD vol 1. It turns out that $T^2 = -1$ for a half-integral spin particle. If you have a system like an atom containing an odd number of electrons, then $T^2 = -1$, and this means that $T\psi$ is not a multiple of ψ, so $T\psi$ and ψ are degenerate (assuming [H,T] = 0), and in crystals this double degeneracy is seen and goes by the name **Kramer's Degeneracy** (1930).

Schiff claims that all non-degenerate energy eigenfunctions are real in a system that has time-reversal invariance and shows this. Most of our systems have this property. Of course the $Y_{\ell m}$ are degenerate in the H atom so this does not apply to them. In scattering we had real phase shifts for example, but when we make the potential go complex (implying some kind of irreversible thermal process like absorption), then we got complex phase shifts.

30. Dynamical Symmetry (234) We are reminded again that symmetry often implies degeneracy.

The comment about problems being solvable in multiple coordinate systems implies extra degeneracy, but reason is not made clear, I could not write down my version of the reason very well, but I see the idea that having a large pool of degenerate states allows the possibility at least of having them fit into more than one symmetry-set of eigenfunctions, and each symmetry set might be associated with a type of coordinate system, the way spherical harmonics are associated with spherical coordinates and associated Laguerres with parabolic coordinates.

Here we deal with symmetries that Schiff claims have no 3D geometric basis. The two examples considered here do have *classical* dynamical symmetries. This may not be the case for other QM problems with dynamic symmetry.

Example 1: Degeneracy in the H atom: SO(4)

We have already solved this in parabolics and sphericals, and we know there is the n^2 degeneracy that seems accidental at least in the spherical case. Here we are going to see that the Hamiltonian in fact has a certain SO(4) symmetry that is geometrical but only if you go into a 4D hyperspace. People have figured out the geometric model there, but we don't need to do that here.

We start with Kepler orbits and we know that **L** is conserved and in QM becomes 3 Lie generators. It turns out there is a second little-known conserved vector called the RLR vector and Schiff calls it **M**, but most people call it $\mathbf{A} = \mathbf{p} \times \mathbf{L} - mk\hat{\mathbf{r}}$ where k/r is the potential. So both **L** and **M** commute with H for a perfect 1/r potential. For other powers, only **L** is conserved, and **M** is not conserved and this causes orbits to precess!

It turns out that **L** and **M** are 6 generators which generate the SO(4) Lie Algebra (when M is properly scaled, and when we stay within a given H = E manifold). You can separate this into two decoupled SO(3) Lie algebras with generators **I** and **K**, and these of course have the usual representation. We find however that we must have i = k, so degeneracy is $(2i+1)(2k+1) = (2k+1)^2 = n^2$ since this last thing turns out to be the energy principle quantum number. The energies and degeneracies just fall out in our

lap, given that we have done a lot of algebraic homework, eg, if we have derived things like 30.6 which Schiff warns is not simple. We do not get the eigenfunctions by this method, however.

The commutator of M with M has a + sign as shown in 30.11, and this is correct if $E < 0$. For $E > 0$, it turns out that this commutator has a sign change due to two i factors, and they you have 6 generators which make SO(3,1) which is the Lorentz Group. It happens that I have written a lot about these 6 generators in my "meandering " doc, and the decoupled generators there are the Weyl left and right **L** and **R** generators, and we get the full possible spectrum of representations there ($\boldsymbol{\ell}$,r), such as the spinor $1/2 \oplus 0$ and the vector $1/2 \oplus 1/2$, and all that good stuff. For a scattering problem, you should have this same SO(3,1) symmetry since $E > 0$, and this might tell you something about scattering, but Schiff does not pursue this subject.

Example 2: Degeneracy in the 3D Harmonic Oscillator: SU(3)

In this problem the Cartesian solution shows energy to be $(n+3/2)\hbar\omega_c$ and degeneracy is $(n+2)(n+1)/2$. We select our SU(3) α and β numbers to make the Casimir C be something that commutes with the HO H. We use here those physical generators made from the p and r values of our particle and in fact they all commute with H, all 8 of them! Schiff stops short of carrying through the details in this case. The reader does not know much about SU(3) representations, so Schiff would have to do lots more groundwork to take this through. Presumably you would end up with the right energy formula and with the right degeneracy, just using the SU(3) symmetry and no SE. The reader is no doubt sufficiently impressed to just learn that the HO Hamiltonian has some kind of exotic SU(3) symmetry in the first place.

Chapter 8: Approximation Methods for Bound States : (Sections 31-35)

31. Stationary Perturbation Theory (245)

NONDEGENERATE CASE

This chapter was just fine except when it treated degeneracy, which is when I had to look to Messiah, so let's focus here on the non-degenerate case results. The idea is to expand both a state ψ and its energy W in a power series in smallness parameter λ, insert into the SE, and get a set of "ladder equations" which I usually just call "the perturbation equations". So here are the opening moves for non-degenerate state "m":

$$W^{(m)} = \Sigma_{n=0}\, \lambda^n W^{(m)}{}_n \qquad \psi^{(m)} = \Sigma_{n=0}\, \lambda^n \psi^{(m)}{}_n \qquad H = H_0 + \lambda H' \qquad H_o u_k = E_k u_k$$

$$W^{(m)}{}_0 = E_m \qquad \psi^{(m)}{}_0 = u_m$$

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

The above ladder equations are **31.4**, and can be written uniformly as follows,

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

You have to do a standard grid reordering of summation to get this result, and I do that in great detail in the raw notes.

Schiff normalizes states such that $< \psi^{(m)}_0 \mid \psi^{(m)}_s > = 0$, s>0, which says all the state correction is orthogonal to the starting state. Schiff failed to explain how this normalization could be arranged and I wasted a lot of time figuring this out. I did Plan A,B,C and only succeeded in my Plan D showing how it works. It was then easy to derive the main energy correction formula

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

which says you only need the state correction to one level lower than the energy you seek. This at once gives the very famous first order energy correction

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

At this point, Schiff starts using his "a" coefficient notation which proved a total disaster when he got to degeneracy, but for our non-degenerate case, it is just fine. The a's are the change coefficients at level s,

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

which compare to my general case allowing degeneracy,

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

so we can identify $a^{(m)}_{k,s} = B'_{ik,s}$ from my notation. We then use the lowest ladder equation to obtain this result for the level 1 coefficients

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

So we then quickly obtain the bottom layer of perturbation results as follows,

$$W^{(m)}_1 = H'_{mm}$$

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

$$W^{(m)}_2 = <\psi^{(m)}_0 \mid H' \mid \psi^{(m)}_1> = \Sigma_{k\neq m}\ |H'_{km}|^2 /(E_m - E_k) \qquad \text{// \textbf{which is 31.11}}$$

We regard energy $W^{(m)}_2$ sort of at level 1 because it can be obtained directly from $\psi^{(m)}_1$. We can then use the next ladder equation to get

$$a^{(m)}_{k,2} = -H'_{km}H'_{mm} / (E_m - E_k)^2 + \Sigma_{n\neq m} H'_{kn}H'_{nm} / [(E_m - E_n)(E_m - E_k)] \qquad \text{// \textbf{which is 31.13}}$$

Schiff likes to say <k|H'|m> instead of the space-saving, clarity improving H'_{km}. This is about as far as Schiff goes with these perturbation equations, and he then starts into examples.

It is worth pausing here to record how Messiah delivers the above results in the non-degenerate case. First, here is the general ladder equation (V = H', ε = W a = m)

$$|s> = Q_{0a}\,[(V-\varepsilon_1)|s-1> - \varepsilon_2|s-2> - .... - \varepsilon_{s-1}|1>] \qquad \text{// } \mathbf{16.11\ Messiah}$$

and here are expressions for the first and second level state corrections

$$|1> = Q_{0a}\,V\,|0> \qquad \varepsilon_1 = <0|\,V\,|0> = <m|\,H'\,|m> = H'_{mm}$$

$$|2> = Q_{0a}\,(V-\varepsilon_1)|1> = Q_{0a}\,(V-\varepsilon_1)\,Q_{0a}\,V\,|0> \qquad \text{// } \mathbf{Messiah\ p\ 194\ (27)}$$

$$= Q_{0m}\,H'Q_{0m}\,H'\,|m> - H'_{mm}\,Q_{0m}^2\,H'\,|m>$$

where Messiah uses the compact operator (for state a = m)

$$Q_{0m} \equiv Q_0\,(E_m - H_0)^{-1}Q_0 \qquad Q_0 \equiv 1 - P_0 = \Sigma_{k\neq m}|k><k| \qquad P_0 = |0><0| = |m><m|$$

It is easy to show based on the above that $Q_{0m}^n = Q_0\,(E_m - H_0)^{-n}Q_0$ which we use below for n=2. Here for example is how you would obtain Schiff's $a^{(m)}_{k,2}$ expression from Messiah:

$$a^{(m)}_{k,2} = <k|2> = <k|\,Q_{0m}\,H'Q_{0m}\,H'\,|m> - H'_{mm}\,<k|\,Q_{0m}^2\,H'\,|m>$$

Note that in Messiah notation, |2> refers to the level 2 correction of unperturbed state |0> which I am here identifying with the unperturbed state "m" , but Messiah thinks of as "a".

For the first term we get, using $<k|\,Q_0 = <k|$, since k is in the perp space of <m| ,

$$<k|\,Q_{0m}\,H'Q_{0m}\,H'\,|m> = <k|\,Q_0\,(E_m - H_0)^{-1}Q_0\,H'\,Q_0\,(E_m - H_0)^{-1}Q_0\,H'\,|m>$$

$$= (E_m - E_k)^{-1}\,<k|\,H'\,Q_0\,(E_m - H_0)^{-1}Q_0\,H'\,|m>$$

$$= (E_m - E_k)^{-1}\,<k|\,H'\,\Sigma_{k'\neq m}|k'><k'|\,(E_m - H_0)^{-1}\,\Sigma_{k''\neq m}|k''><k''|\,H'\,|m>$$

$$= (E_m - E_k)^{-1}\,\Sigma_{k'\neq m}\,\Sigma_{k''\neq m}\,(E_m - E_{k'})^{-1}\,<k|\,H'\,|k'><k'|k''><k''|\,H'\,|m>$$

$$= (E_m - E_k)^{-1}\,\Sigma_{k'\neq m}\,(E_m - E_{k'})^{-1}\,<k|\,H'\,|k'><k'|\,H'\,|m>$$

$$= (E_m - E_k)^{-1}\,\Sigma_{k'\neq m}\,(E_m - E_{k'})^{-1}\,H'_{kk'}H'_{k'm}$$

$$= \Sigma_{k'\neq m}\,H'_{kk'}H'_{k'm}/\,[(E_m - E_{k'})\,(E_m - E_k)]$$

$= \Sigma_{n \neq m} H'_{kn} H'_{nm} / [(E_m - E_n)(E_m - E_k)]$

which is the second and more complicated term in Schiff's $a^{(m)}_{k,2}$ as quoted above. The other term is much easier to compute

$$- H'_{mm} \langle k| Q_0 m^2 H' |m\rangle = - H'_{mm} \langle k| Q_0 (E_m - H_0)^{-2} Q_0 H' |m\rangle$$

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

The advantage of the operators in Messiah is that you can write compact equations and see better what you are actually doing, and you only need to go into the messy sum forms when it is time to compute something. It is like using $R_y(\theta)$ instead of writing out a 3x3 rotation matrix.

Harmonic Oscillator as Example of non-degenerate perturbation theory.

Schiff now undertakes his first and only non-degenerate **example**. He takes a harmonic oscillator and writes H as

$$H = p^2/2\mu + 1/2\ K x^2 + 1/2\ b x^2$$
$$= \quad H_0 \quad + \quad H'$$

where b is small. Obviously we know the exact answer to this problem by combining the last two terms, so this example provides a nice test of our method. The energy corrected through second order is this:

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

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

where we directly apply our formulas from above. The big problem now is computing these matrix elements for the harmonic oscillator states. This is most easily done (I feel) using the $a^\dagger$ and a creation type operators and I show all the gory details in the raw notes. The painful infinite sum associated with the second order correction becomes finite because all matrix elements $\langle m| x^2 |n\rangle$ are zero except some near the diagonal. The matrix element results are stated as equations B1-B4 on Schiff page 248 and we properly find that we have generated the first three terms of a smallness power series expansion of the known exact result. So the test is a success!

DEGENERATE CASE

Note: I now have much documentation on the general degeneracy problem in SSPT. Probably a good starting point is "degenerate perturbation theory.doc" located in the Schiff directory where I tried to "roll my own" solution. Other notes are in the Messiah Chapter 16 folder (meta, round 1 and round 2 notes), and the Kato folder within that. I have not written a separate document that cleanly describes how this all works, but some of my documents have "summaries" which I think are pretty good. This is a large subject and I think there is recent work that does it well that I have not studied (ie, more recent than the Kato

era). Saxon did things differently and was not much help to me. Probably some of the classic QM texts I do not have treat this subject cleanly.

At this point, Schiff starts into his degenerate case presentation. He limits his interest to two states he calls m and ℓ, where m was the state we worked with up to this point which was non-degenerate, but which now has a degenerate partner ℓ. In my notation, I call these two states 1 and 2. The level 1 problem as we clearly understand later from Messiah and Kato is then is to diagonalize this equation

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

The first step is to solve the secular equation for the two solutions W_1 which Schiff shows in **31.16.** If the two numbers are different, then the diagonalized equation has different diagonal elements and we can proceed with the method as I describe elsewhere to find the state correction as Schiff shows in 31.18. This equation may be found in my Messiah Round Two R2 notes where I find that

$$| 1; n, \varepsilon_1> = \Sigma_{n'=1,N} C_{n'} |0; n',\varepsilon_1> + \Sigma_{k \in \mathcal{E}oa\perp} c_k |k>$$

where

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

Here, $B'_{ij,1} = C_j$ and $B'_{ik,1} = c_k$ from my B coefficient notation . This is a general result not just for 2 degenerate states. My answer for $B'_{ij,1}$ is in terms of basic quantities like V_{kn} while Schiff's in 31.18 is in terms of the a,b numbers which form the eigenvectors of the above diagonalization problem, so his result is a sort of intermediate result that is not too useful for computation (but was easy to derive).

If after diagonalization the two diagonal elements of H' are the same, you have to proceed to the level 2 diagonalization problem in an attempt to "break the degeneracy". In Messiah notation, this problem may be written as

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

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

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

So all four elements of the above 2x2 matrix have these Q_{0m} sums. The first step as usual is to write the secular equation to find the W_2 values (and see if they are different now!). The secular equation appears as 31.20 in Schiff.

And so ends Schiff's degenerate case effort, and the section is now going to end with a few degeneracy examples. I feel Schiff did this whole degeneracy thing half-baked whereas Messiah gives us a whole loaf. I now have pretty good notes in many documents on the degeneracy situation, including very detailed notes on the Kato method that Messiah outlines.

So here are the examples which conclude the section:

Zeeman Effect without Electron Spin (251) // verbatim from raw notes

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 $B_z L_z$ 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 $2\ell+1$ 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 for the H atom n = 2 excited state (252).

The ground state has $\varepsilon_1 = 0$ because it has definite ℓ and parity symmetry kills off ε_1. The n=2 state has three p and one s orbital and is thus a mixture of ℓ=0 and ℓ=1 and in this case there *is* a non-zero ε_1 which is what this example computes. This is a 4x4 level diagonalization problem where we start with those four n=2 levels being degenerate. The result is that two states stay put, one goes up and one goes down by the same amount, so ε_1 values are 0,0,q,-q. Because of the way this splitting works, this system behaves as if two states have a permanent dipole moment!

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 ~ E, and then p•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. But presumably there are some systems that can hold a permanent dipole moment and Schiff comments on this in his closing section. I think he had a special interest in this subject.

32. The Variation Method (255)

Let ψ be some general linear combination of SE eigenstates as in 32.1. You can then derive the exact inequality shown in 32.4 which says $E_o \leq \langle\psi|H|\psi\rangle$ if ψ is normalized. But a general linear combination of eigenstates ψ of some H is really more or less an arbitrary function since the eigenstates form a complete basis. So the idea is to pick some reasonable "trial function" for ψ that has one or more parameters, put it into the RHS of the above inequality and look for parameter values which minimize the energy integral. If your trial function form is smart, having the right symmetries of the problem for example, you will find that your integral is very close to the actual E_0. So this method lets you compute an upper bound for a ground state energy. Schiff says that you can come up with similar inequalities for excited state energies if you pick a trial ψ that is orthogonal to all lower bound state wavefunctions, but he

does not pursue this much (p 256). He gives the Rayleigh (1873) and Ritz (1908) references on page 256.

Schiff then gives us two examples. The first is for the **ground state of He**, an H-like atom with 2 electrons. The trial form of the solution is the product of the two H atom 1S states, see 32.7, where the parameter we are going to vary is Z, which is nominally 2 for a He atom. For this problem, H is shown in 32.6. He then computes $\psi^* H \psi$. The e^2/r_{12} term in H is the hard integral and he expends page 258 showing how this is done. The result for $\psi^* H \psi$ from all terms is given on the top of page 259 as a function of Z. When you vary Z to minimize the matrix element, the result is Z = 1.69 and the energy obtained is only high by 2% compared to the experimentally measured number. Shielding is the interp.

The second example is the **Van der Waals attraction** between two neutral H atoms. On page 260 we have the basic setup and statement of H. This is interpreted as H_0 + H' and Schiff first does a *perturbation* calculation for ε_1 and ε_2. He finds $\varepsilon_1 = 0$ due to parity, and gets a lower bound for ε_2 shown in 32.16. We expect ε_2 to be negative for any ε_2 calculation for a system ground state. Only then does he start the *variation* calculation using the trial function form for ψ shown mid page 262. Doing the matrix element, he ends up with an upper bound (which is what variation always gives) for ε_2. So these two methods *sandwich* the resulting VDW energy as shown in 32.21, and the correct answer does fall in this fairly narrow range. In my raw notes, I have some good general wiki info on Van der Waals.

33. Alternative Treatment of the Perturbation Series (263)

This is a somewhat odd section of Schiff. He talks here about other ways people have computed second order energy corrections ε_2 . Normally you are faced with an unpleasant infinite sum as we know. In the several examples of this section, the method used instead is to compute the first-order wavefunction correction Messiah would call |1> and Schiff calls ψ_1, then we know $\varepsilon_2 = W_2 = \langle\psi_0|H'|\psi_1\rangle$. So the game here is to compute ψ_1 directly from the lower ladder equation 31.4 that involves ψ_0 and ψ_1. This is of course an ODE that you want to solve for ψ_1 and it involves H'.

His first example to illustrate this method is to compute the ground state ε_2 correction for an H atom doing Stark Effect. I quote my raw notes directly:

> **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 wavefunction correction (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 $\varepsilon_2 = -(9/4)E^2a_0^3$. 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 $\varepsilon_2 = -\frac{1}{2}\,\alpha\,E^2$ where α is the polarizability. So we just computed ε_2 so we know that for H atoms in their ground state, $\alpha = 9/2\ a_0^3$.

Schiff goes on to sort of recast this type of solution using a method of "Delgarno and Lewis" (1955) which involves a Messiah-like operator F, and he says $|1\rangle = F|0\rangle$ which looks a lot like Messiah's $|1\rangle = Q_{0a}V\,|0\rangle$. You still have to solve an ODE 33.14 for $|1\rangle$, then $W_2 = \langle 0|H'|1\rangle$. He goes one more step and computes $|2\rangle$ and gets $W_3 = \langle 0|H'|2\rangle$. I don't think anything "new" is really happening with this DL method, compared to what I just reviewed in the Stark section above.

He then gives one more Delgarno and Lewis method example where he solves the ε_2 correction for an H atom in the presence of a point charge, I would call this a "Stark like" problem. He gets involved with a partial wave series for the 1/r' term of H' where r' is the distance between the external charge at R, and the electron at r. It is then a Jackson-like solution and we end up with a partial wave sum for ε_2 of which the $\boldsymbol{\ell}$=1 term agrees with our Stark Effect calculation.

As I say, this seems an oddball section. It was of course not present in his first 1949 edition. I wonder if it was sort of breaking news and he jammed it into the second 1955 edition and kept it into the 1968 which I have. I cannot find a viewable 1955 edition on the web, so not sure about this.

34. The WKB Approximation (268)

Background: Relation between WKB and Classical Mechanics.

Goldstein and Schiff reverse the usage of symbols S and W which is too bad. In the first paragraphs below, I will use S' and W' for what Schiff calls S and W when I am talking about *QM* functions, and I will use S and W for classical quantities.

Goldstein uses symbol $S = \int L\,dt$ = the classical action = Hamilton's *Principle* Function. Schiff and Whittaker instead use W for this same object, so it is this W that must satisfy the classical Hamilton-Jacobi equation (HJE): $\partial W/\partial t + H(r,\mathbf{p}=\nabla W) = 0$. Now, in QM if we re-functionalize a SE solution as $\psi = \exp(iW'/\hbar)$, we can write the SE in terms of W' as shown in 34.1 where the last term is proportional to $\hbar$. If we set $\hbar$=0, this re-functionalized SE for W' is exactly the HJE! So in some sense, W'→ W as $\hbar\to 0$. In this limit, the QM function W' becomes the classical action of classical mechanics, an interesting correspondence principle statement way out in the HJ boonies.

As in classical HJ theory, it is more useful for constant energy situations to use Hamilton's *characteristic* function which Goldstein calls W = S + Et, but which Schiff calls S' = W'+Et. So our WKB development will use this characteristic function Schiff calls S', which we know will have as its classical limit the classical "abbreviated action" which is $\int p\dot{q}\,dt = \int p\,dq$. The re-functionalized SE written in terms of S' is stated in 34.2. If we let $\hbar\to 0$, we get S'→S.

All the above is just "background material" for the work ahead in this section. We now remove the prime from the QM quantity S' and just call it S. We can regard 34.2 merely as a refunctionalized SE and be done with it, but it is interesting to see how this becomes a well-known classical equation when $\hbar\to 0$. We are going to make a power series expansion in $\hbar$, $S = S_0 + \hbar S_1 + \hbar^2 S_2 + \ldots$, so in a sense, the WKB method is "perturbing around the classical theory".

The Main WKB Solution Form.

Our refunctionalized SE is 34.2 written in terms of S as discussed above. This of course contains the usual E - V(x). It is convenient to refunctionalize this expression as k(x) or κ(x) depending on the sign of the expression, as shown in 34.5. When we do this, our SE in terms of the original ψ wavefunction (Schiff calls TI wavefunctions u) is given in 34.3 and 34.4. If we then refunctionalize u as $u = \exp(iS/\hbar)$ [where S is now the QM analog of Hamilton's *characteristic* function which is the *abbreviated* action] , we duplicate equation 34.2 as shown in 34.6 in 1D with variable x. This chapter deals ONLY with 1D applications of WKB. We next expand $S = S_0 + \hbar S_1 + \hbar^2 S_2 + ...$ and, in a manner similar to what we did in perturbation theory, we have a "ladder" of equations where we match powers of $\hbar$. The lowest equation in the ladder is for S_0 and this is the eikonal equation p271 B which we could write more conventionally as $(\nabla S_0)^2 = \hbar^2 k(x)^2$. The solution is $S_o = \pm\hbar \int^x k(x')dx' = \pm \hbar\xi(x)$ where we anticipate changing variable soon from x to ξ which is the integral of k as shown. This integral of k is the key player in WKB theory! Notice that S_0 is the classical abbreviated action which we usually write as $\int pdq$. Going to the next ladder equation, the solution for S_1 is as shown page 271 E, and we then find that

$$u = \exp(iS/\hbar) \approx \exp(i[S_0 + \hbar S_1]/\hbar) = k(x)^{-1/2} \exp(\pm i \int^x k(x')dx') = k^{-1/2} \exp(\pm i\, \xi(x))$$

so the S_1 stage of things just adds the leading factor $k^{-1/2}$. This form for u is not an exact solution of the SE because we have neglected higher terms in our expansion like $\hbar^2 S_2$. This is an approximate solution of the SE which is valid in certain situations which we will explain, and this approximate solution is called The WKB Approximation. This solution is shown in 34.7 and the corresponding one in terms of κ is shown in 34.8. You can just think of κ = ik if you like.

The condition of validity is that $k'/k^2 << 1$ which means k fractionally varies slowly as x varies over a DeBroglie wavelength λ. For a bound state or barrier scattering problem, this condition is generally OK as long as you stay "a few wavelengths away" from classical turning points which are the places where E = V so k = 0. When k ~ 0, you violate the WKB condition, but somehow it seems we can use WKB anyway "right through" a turning point, as we shall see. It seems to provide the right "connection" through the turning point, though the wavefunction itself near the turning point might be quite inaccurate. These comments are made clearer below.

The Bessel Function Connection.

We are always going to be worrying about WKB near turning points which is the main area of focus. Near turning points, we will assume that $k^2(x) = Cx^n$ where this would be the leading term in a Taylor series expansion of your k(x) at the turning point and $n \geq 1$. Almost always the turning point occurs where V(x) has some non-zero slope (the pictures you always draw) and in this case n = 1 and this is called a "linear turning point". But we can remain general and assume n with m = 1/(n+2) as a convenient second descriptor (a fraction). For such a k(x), you can *exactly* solve the SE 34.3 and the two solutions are $u^{\pm}(x) = \xi^{1/2} k^{-1/2} J_{\pm m}(\xi)$ as shown in 34.10 with ξ as shown above. Notice that we are assuming here a power for k(x), not for V(x) which is more typical. Of course no practical problem is going to have k(x) being a simple power. We are claiming that this is a viable SE solution *near a turning point* in which region we

approximate k(x) as a power. For a turning point at x=0, we can write $\xi = \sqrt{C}\ 2m\ x^{1+n/2}$ and with n=1 this says $\xi = \sqrt{C}\ (2/3)\ x^{3/2}$, so no big mystery with ξ. For the expo side of a turning point, replace k with κ and replace J with I, and so we arrive at 34.13.

What does this do for us? Suppose we *start* with these Bessel solutions at a turning point at x=0. The solutions are valid there because the power assumption for k(x) is good there. We can look at the small x limits of the Bessel functions as in 34.15 and this is certainly reasonable. What about large x? This took me a while to understand, and the next several paragraphs are explanation.

Theorem: If things are reasonable (smooth, lots of waves, etc) and you are not close to a turning point, then the WKB form of the SE solution is $u = k^{-1/2} \exp(\pm i\, \xi)$, where $\xi = \int^x k(x)dx$. Notice that these solutions depend on k(x) both directly through $k^{-1/2}$ and through the integral which gives ξ. If you were to change k(x), you change the solution through both these dependencies, but the *form* stays the same.

My theorem reinforces a fact that might not be obvious: in such a region, the solutions of the SE ***must*** be these WKB solutions, the only flexibility allowed is linear combinations of them! The WKB solutions are not specific to k(x) being a power or anything like that, just that k(x) is non-pathological and we are away from turning points.

Now, suppose near x = 0 we assume k(x) has the power form, and we have our Bessel form of the solutions. We can identify the notion of "moving away from the turning point" with the notion of "taking large x in the Bessel solutions". As we thus "continue" the Bessel solutions away from the turning point, we move into the realm of WKB validity, and the solutions in this limit ***must*** be the two WKB form solutions. Now, suppose we allow k(x) to sort of smoothly morph from the power form to some arbitrary but smooth form away from the turning point. Then those continued-away Bessel solutions themselves change, but only through the two k(x) dependences just noted. They still have the required WKB form!

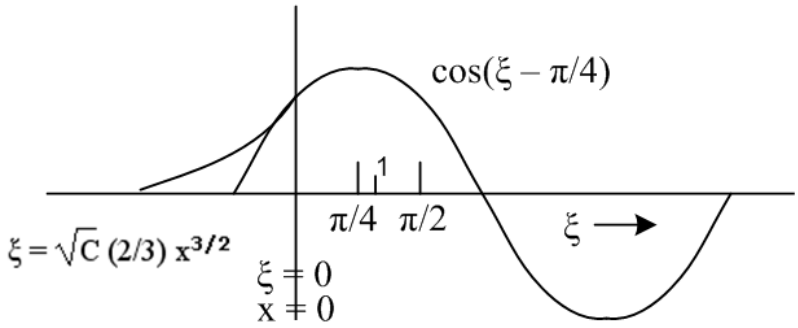
So, first of all, when we take the large-x limits of our Bessel solutions (maintaining at first the power form of k(x)), we should not be surprised to see that these solutions have the WKB form! These Bessel solutions solve the SE and a solution of the SE must have the WBK form away from turning points. In the second "thought experiment" step, as we then gradually "bend" k(x) into some other shape away from the turning point, the limits of our Bessel solutions maintain that WBK form, but in detail they of course change because k(x) is changing.

Thus we arrive at the nice conclusion that the Bessel solutions for large x blend perfectly into our required WKB *form* away from the turning points, even as we lose the power form of k(x) which was true only at the turning points. The key to this is writing the solutions (Bessel or WKB) in terms of k and ξ. This fact is implicit in what Schiff does, he never made it clear to me how this was working, but I think I now understand it. Schiff's equation 34.16 then shows exactly this fact I am now explaining.

And of course you can continue in either the sine or the expo side and everything said above is still true. The Bessel solution is valid in a region on both sides of the turning point. So, very clearly we can think of the solutions he calls u^+ and u^- as solutions not just near the turning point, but far away from the turning point as well, even though k(x) is different away from the turning point. Again, this change in k(x) is accounted for within the $1/\sqrt{k}$ and ξ factors in the solution forms. Of course he had to do the little matching at x=0 shown page 274 A. On page 274 bottom I have written in the "matched" solutions on the two sides (1 and 2), and on bottom page 275 I show exactly what the sum solution looks like, and this is the one that "kills the expo" on the expo side and is thus the right solution for a normal turning point.

Linear Turning Point.

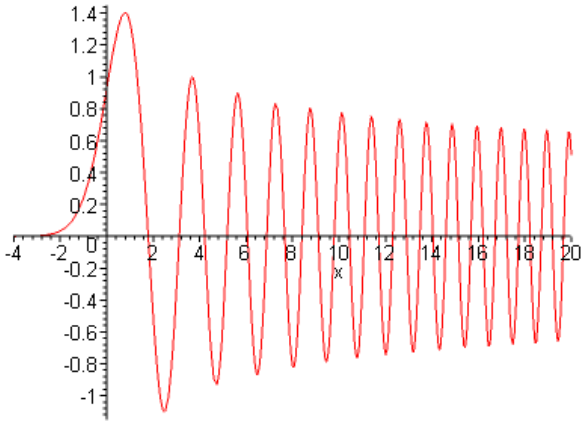
So, now consider a normal **linear turning point**. In order to have expo decay on the expo side, we must use the sum solution whose limits on the two sides are given by 34.17. This says that on the sine side, the wave in terms of ξ as a coordinate *look as if* it would penetrate 1/8th of a wavelength (π/4) through the turning point! Here is a picture:



The vertical line is the turning point at ξ = 0. The potential V(x) and k(x) are not shown in this picture. The horizontal axis is ξ, not x ! We show the wavefunction on the right *as if* the asymptotic form of the Bessel solution were valid right up to the point x=0 on the right. Since the peak of cos(ξ-π/4) is at ξ = π/4 as drawn, it follows that if we kept drawing this sine wave, it would have the shape shown on the left -- it would continue 1/8th of λ before it reaches the value 0. This is just a little construction to help us see roughly how much the wavefunction penetrates the barrier into the expo side. In reality, on the left side the wavefunction has expo decay with 1/e drop in 1 unit on the ξ scale, as I have roughly drawn it (I have shown where 1 is on the right). Also in reality, the wavefunction on the right sides near x = 0 really has the Bessel form which I have not tried to draw. If is a smooth sine-like function that eventually turns into the cos(ξ-π/4) sine wave as you go off to the right. In ξ space, the spatial frequency of the sine wave in the large ξ limit is always "1", but if you were to plot things in terms of x, you would see that the frequency varies with x, and the frequency would increase as you move away from the turning point and k ~ E-V gets larger.

Here for a linear turning point with C = 1 are the actual plots in terms now of x, not ξ :

```
> f := x -> x^(-1/4)*x^(3/4)*(BesselJ(1/3,x^(3/2)) + BesselJ(-1/3,x^(3/2))):
> plot(f(x),x=0..10,numpoints=100):
> g := x -> x^(-1/4)*x^(3/4)*(- BesselI(1/3,x^(3/2)) + BesselI(-1/3,x^(3/2))):
> plot(g(x),x=0..4,numpoints=100):
> h := piecewise(x<0,g(-x), x>0, f(x)):
> plot(h,x=-4..20);
```



You see the perfect match through the turning point, the expo decay on the left and the increasing sine frequency on the right as we move away from the turning point. Here we assumed $k^2 = x$ everywhere so $k^{-1/2} = x^{-1/4}$ which is the leading factor. The next factor is just $\xi^{1/2}$ and I have not show the constant 2/3 in $\xi = \sqrt{C}\ (2/3)\ x^{3/2}$. Notice how close the curve is to the simple Visio plot shown earlier, except the amplitude decreases as we move to the right, an effect of the Bessel J function. Presumably if we were to allow k(x) to vary from its value $k^2 = x$ as we move off to the right, the curve would have this same general appearance, but sure, the waves would be shifted left or right somehow. You are not far off saying that the wavefunction in the well is sine-like at the turning point and roughly penetrates 1/8 wave.

Comment on the steep wall problem: this is modeled by large C in $k^2 = Cx$. In the plot above, you still get the 1/8 wave extension notion in ξ space, but in x space penetration is basically 0 as C gets very large. In the limit there is no penetration at all, as in our friendly particle in a box problem.

The **connection formula** shown in 34.17 is what we used above to deal with the linear turning point. This just shows the limits of the sum solution Bessel functions in the two directions. Schiff's remarks about the arrows I think relates to error issues if you are doing numerical work. Page 276 shows a typical potential well bound state problem as we dealt with above. Here he handles the two turning points as I have done above, and then if you force them to match phase "out in the middle", you get the quantization rule shown in 34.21 or 34.22. This rule is basically the Bohr-Sommerfeld thing, but is also providing a way to find the eigenenergies! You keep raising E until you get a multiple as shown and then that E will be an eigenenergy of the problem. Schiff comments on some of the special turning points, like the well or infinite wall, and also mentions that the entire technique can be applied to a SE radial equation. His closing section discusses α decay as a tunneling problem and some interesting results are given. See raw notes for more on this last subject, including something on the Gamov Factor.

35. Methods for Time-dependent Problems (279)

1. Time Dependent Perturbation theory, emphasis on first order (280)

The first step is to recast the SE in terms of the $a_k(t)$ coefficients. $\psi = \Sigma_k\ a_k(t)\ u_k(r)\ e^{-iEkt/\hbar}$. We then interpret $a_k(t) = \langle k|\psi_I(t)\rangle$ where $|\psi_I(t)\rangle$ is an interaction (Dirac) picture ket. It is moved not by the full H, but just by H'_I. This is just an interpretation and does not much enter calculations. The SE in terms of the $a_k(t)$ is given in 35.5 as $\dot{a}_k(t) = \Sigma_n\ (\lambda H'_{kn})\ a_n(t)\ \exp(i\omega_{kn}t) / i\hbar$. If we then expand $a_k = \Sigma_{s=0}\ a_k^{(s)}\lambda^s$, we

get a set of ladder equations as shown in 35.8: $\dot{a}_k^{(s+1)}(t) = \Sigma_n (H'_{kn}) a_n^{(s)}(t) \exp(i\omega_{kn}t) / i\hbar$ and also we get $\dot{a}_k^{(0)}(t) = 0$. This let's us compute our coefficients $a_k(t)$ systematically to any order, but it is the first order that is most important. We assume system is in some particular state m so that $a_k^{(0)} = \delta_{km}$ and our 35.8 with s=0 becomes $\dot{a}_k^{(1)}(t) = (H'(t)_{km}) \exp(i\omega_{km}t) / i\hbar$ which we integrate to get 35.9:

$$a_k^{(1)}(t) = \int_{-\infty}^{t} dt \ (H'(t')_{km}) \exp(i\omega_{km}t') / i\hbar$$

We next assume that H'(t') goes as 2 $H'_{km}\sin(\omega t)$ and do the above integral from t=0 to t=t_0 to get 35.11 where we see a resonance at $\omega = \omega_{km}$. Assuming we are near this value of ω, we discard the first term and square to get 35.12. We can then use this fact, a representation of the delta function,

$$\lim_{a\to 0} [(a/\pi x^2) \sin^2(x/a)] = \delta(x) \quad \text{or} \quad \lim_{b\to\infty} [(1/\pi b x^2) \sin^2(bx)] = \delta(x)$$

Set $b = t_0$ and $x = \Delta\omega/2$ and this says [$\Delta\omega = \omega_{km} - \omega$]

$$| a_k^{(1)}(t) |^2 = |H'_{km}|^2 t_0 \, 2\pi \, \delta(\omega - \omega_{km}) = |H'_{km}|^2 t_0 \, 2\pi/\hbar \, \delta(E - E_{km}) \qquad \text{for large } t_0$$

and we see the idea that this probability grows linearly with t_0 which is the duration during which we allow our sine perturbation to act. So we define a transition rate dw

$$dw = | a_k^{(1)}(t) |^2/t_0 = (2\pi/\hbar) |H'_{km}|^2 \delta(E - E_{km}) \qquad E = \hbar\omega$$

into a single final state E_k . Then we assume some $\rho(E_k)dE_k$ as a final density of states if we transition into a continuum and we get

$$w = \int (2\pi/\hbar) |H'_{km}|^2 \delta(E - E_{km}) \rho(E_k)dE_k = (2\pi/\hbar) |H'_{km}|^2 \rho(E_k)$$

and this is the famous **Golden Rule #2** of 35.14. **Golden Rule #1** is the corresponding formula in second order perturbation theory if there is no coupling in first order between our two states k and m.

2. Application of First Order TDPT to Hydrogen Ionization by an E field

We apply a sin(ωt) E field to an H atom in its ground state, and we just imagine we could do this with a capacitor, although we are talking X-ray frequencies. We ignore the Coulomb wave functions and put the final state continuum as plane waves with box normalization. He computes the $\rho(E_k)$ density of these final plane wave states, computes the matrix element H'_{km} on page 287, and we get the result 35.20 which shows the differential rate of ionization into solid angle dΩ. The result depends on the E field, on the Bohr radius, on the final energy $E_k = \hbar^2k^2/2\mu$, and we find $dw/d\Omega$ = stuff ($\cos^2\theta$) where θ is the polar angle away from the E field direction which we select as $\hat{z}$. We expect electrons to be kicked off in the $\pm\hat{z}$ direction because the kicking E field points in that direction (making a classical force on the electron in that direction). Other directions have less force by $\cos^2\theta$.

3. Second Order Perturbation Theory.

This would start off like this (where now t lies in 0 to t_0)

$$a_k^{(1)}(t) = \int_0^t dt\ (H'(t')_{km}) \exp(i\omega_{km}t') / i\hbar \approx + H'_{km}\ (e^{i\Delta\omega t} - 1)/(i\hbar\Delta\omega) \qquad // 35.11$$

$$\dot{a}_k^{(2)}(t) = \Sigma_n (H'_{kn}(t))\, a_n^{(1)}(t) \exp(i\omega_{kn}t) / i\hbar$$

$$= \Sigma_n (H'_{kn}(t))\{ H'_{km}\ (e^{i\Delta\omega t} - 1)/(i\hbar\Delta\omega) \} \exp(i\omega_{kn}t) / i\hbar$$

$$= \Sigma_n (2H'_{kn})\{ H'_{km}\ (e^{i\Delta\omega t} - 1)/(i\hbar\Delta\omega) \} \sin(\omega t) \exp(i\omega_{kn}t) / i\hbar$$

When we integrate this thing, we have resonance at new places, like $\omega = 2\omega_{kn}$, and this tells us that we are talking about "two photon processes" somehow. Schiff does not pursue this at all, just comments. I think Saxon might do more of this. We are warned that you get artifact terms from turning on suddenly at t = 0.

4. Adiabatic Approximation.

The idea here is this: suppose your Hamiltonian H(t) varies only very slowly. Then at any instant of time, you have a "TISE" 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.

To verify that this gut feeling is right subject to certain slowness conditions, Schiff defines some $a_k(t)$ in a slightly different manner than done for TDPT, see 35.23. He recasts the SE as 35.26. He then assumes we start off in some state "m" when we turn on our slow changes, and he computes the amplitude to be in some other state "k", which amplitude is just $a_k(t)$. The result is 35.27, and if the factors shown there are small, you see that $a_k(t)$ is small for all time, and this is the condition for our gut feeling. However, if you insist on having your system change in time in a manner that is resonance with a pair of energy levels, the assumption breaks down and you get that linear time growth we found in TDPT.

5. Sudden Approximation.

Suppose at t = 0 we make a sudden change in a QM system. Before the change we have H_0 and $|n\rangle$ and a_n, and after the change we have H_1 and $|\mu\rangle$ and b_μ. We come into the change at t=0 in some state "m" of H_0. The wave function must be continuous at t = 0 so we conclude that after the change, $b_\mu = \Sigma_n a_n \langle\mu|n\rangle$ and in our case this is $b_\mu = \langle\mu|n\rangle$. So we start in a single state, but we end up in a mix of states with these amplitudes b_μ. Most of this section discusses the triple situation of H_0 then some H_i then some H_1 so we can develop a condition for how fast a change has to be so it is "sudden" and our formula here is justified.

6. Harmonic Oscillator Examples for Adiabatic and Sudden Approximations

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 in 1D 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). Since a(t) appears in the Hamiltonian, we are changing the Hamiltonian.

We find the following: If we start the HO in its ground state and if we move the board at a velocity that is small compared to the effective KE velocity of the HO ground state, we meet the adiabatic condition and our system stays in the ground state.

In the sudden case, we jerk the board horizontally a distance a and watch what happens. In this case we start in the ground state and end up in some high classical state region since the HO is now doing major classical motion. The claim made is that we have to jerk the board in a time that is small compared to the a certain multiple of the classical oscillator period. Notice that energy is not conserved because we added energy in our sudden jerk of the system.