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THE UNIVERSITY OF WISCONSIN

THE VARIATIONAL METHOD III -- STEADY STATE

TIME DEPENDENT PERTURBATION THEORY

by

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I WOULD GREATLY APPRECIATE YOUR CRITICISMS, COMMENTS, AND

SUGGESTIONS CONCERNING THE CONTENT AND ORGANIZATION OF THESE LECTURES

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XXII. Steady State Time-dependent Perturbation Theory

Thus far in our discussion, the Hamiltonian has been explicitly independent of time. Now we wish to discuss the response of a system (atom or molecule) to a time dependent external field. Thus we wish to solve the time dependent Schroedinger equation

$$\mathcal{H}\Psi \equiv (H + \mu W)\Psi = i\frac{\partial \Psi}{\partial t} \tag{XXII-1}$$

where H is the time independent internal Hamiltonian of the isolated system (we therefore assume we can separate off the center of mass motion) and μW represents the effect of the external field. In particular we will be concerned with situations in which the external field is sufficiently weak so that a straight forward perturbation approach is appropriate (since we have included only one order of perturbation in (1) our formlism will be strictly applicable only in the case of a time dependent electric field. However, the formal modification needed to incorporate a magnetic field should be quite obvious).

We will be particularly interested in situations in which μW is simple harmonic in time with frequency ω and in which initially $\Psi = \psi_0$, where ψ_0 is the normalized ground state wave function for H :

$$H\psi_0 = E_0\psi_0 \tag{XXII-2}$$

$$(\psi_0, \psi_0) = 1 \tag{XXII-3}$$

Also we will treat $\overset{\prime}{E}_0$ as non degenerate. That is either it is non

degenerate or, for reasons of symmetry, μW does not mix ψ_0 with the

other degenerate eigenfunctions. To make the problem realistic we must

specify how μW is "turned on". The kind of phenomena which result

can often depend in detail on this information. Because of its in-

trinsic interest in connection with the index of refraction for dilute

gases, and because it is the natural extension of our earlier discussion

of stationary states, i.e. energy of eigenstates, we will largely con-

fine our attention to the <u>steady state response</u> of the system to the

simple harmonic perturbation. (The generalization to several fre-

quencies again should be obvious in low orders.)

This however raises a problem. For a real system the total re-

sponse consists of a transient response plus a steady state response,

and the transient response, which depends very much on how μW is

turned on, dies away in time because of some natural damping mechanism.

Thus, whatever the initial condition, one can isolate the steady state

response simply by waiting long enough. However, in our model of an

isolated system in a given external field, there is no natural damping

-- no collisions, no quanta, no reaction on the sources of the field.

Thus in order to isolate the steady state response it behooves us to

try and eliminate the transients. Fortunately the method is well

known. One imagines the field to be turned on very slowly ("adiabati-

cally"), starting at $t = -\infty$. Thus for a simple harmonic perturba-

tion we take μW to be of the form

$$W = W_+ \, e^{i\omega t} + W_- \, e^{-i\omega t} \quad , t > 0$$

$$W = \left(W_+ \, e^{i\omega t} + W_- \, e^{-i\omega t} \right) e^{\alpha t} \quad , t < 0 \tag{XXII-4}$$

with $\alpha > 0$, and we will be interested in the response for $t > 0$. At the end of the calculations we will let $\alpha \to +0$. Note that for W to be Hermitian we must have

$$W_- = (W_+)^\dagger \tag{XXII-5}$$

where W_+ may depend on the coordinates spin and momenta of the particles. In particular, in a spatially uniform electric field $\vec{\mathcal{E}} = \vec{\mathcal{E}}_0 \cos \omega t$

$$W_+ = W_- = -\tfrac{1}{2} \sum_s e_s \, \vec{R}_s \cdot \vec{\mathcal{E}}_0 \tag{XXII-6}$$

where e_s is the charge of the s'-th particle and $\vec{R}_s$ is its position vector referred to some fixed origin.

For a neutral system note that the r.h.s. of (6) is translationally invariant and therefore depends only on internal coordinates. For a non-neutral system we would include only the internal part of $\vec{D} \equiv \sum_s e_s \vec{R}_s$ in W. Problem: Consider an atomic ion. Using the usual coordinates (center of mass, nucleus, electrons relative to nucleus) find the internal part of $\vec{D}$. Do the same for a diatomic molecular ion using some suitable coordinate system.

Problem: Consider a neutral atom in a spatially uniform magnetic field. Find the internal perturbation (see E. Breitenberger, J.O.S.A. 58, 1314 (1968)).

To this prescription for W we then append the "initial" condition

$$\Psi \underset{t \to -\infty}{\longrightarrow} \psi_0 \, e^{-i E_0 t} \tag{XXII-7}$$

which then completes the specification of our problem.

At this point one might well question the relevance of our problem to the real world. Since we have no damping we should expect, and will find, infinite response at certain values for ω. In this regard we will say only that our treatment, though clearly invalid near a resonance, is quite adequate well away from the resonances. [For a realistic treatment see N. M. Kroll in "Quantum Optics and Electronics" page 41, et. seq., C. de Witt et al. ed., Gordon and Breach (1965). The fact that (Ψ, Ψ) is conserved (see next section) does supply some "damping". However, it is not really effective in a straightforward perturbation treatment. We will have more comments on this point later.]

XXIII. Two General Theorems -- Conservation of Normalization and the Time Dependent Hellman-Feynman Theorem

Before proceeding to a discussion of the solution of our problem, it will be useful to prove two general theorems, analogous to the sort of theorems we have discussed earlier for the time independent case. In Sec. XXVII we will discuss various other theorems.

(A) Conservation of Normalization

Using the fact that $\mathcal{H}$ is Hermitian it is easy to show (Problem: Do this) that if Ψ and Ψ' are two solutions of (XXII-1) then

$$\frac{\partial}{\partial t} (\Phi, \Phi') = 0 \qquad \text{(XXIII-1)}$$

Thus in particular normalization is preserved in time and so is orthogonality. From (XXII-3) and (XXII-7) then this means that for our problem

$$(\Phi, \Phi) = 1 \qquad \text{(XXIII-2)}$$

(B) Time Dependent Hellmann-Feynman Theorem

Consider again the case of a spatially uniform electric field. Then the quantity of physical interest in determining index of refraction phenomena is the induced dipole moment of the system and, evidently, from (XXII-6), this will be proportional to

$$(\Phi, w\Phi) = (\Phi, \frac{\partial H}{\partial \mu} \Phi)$$

We now use the Schroedinger equation to write this in another form. First of all we have the identity, with σ an arbitrary real parameter which could be μ in particular,

$$\frac{\partial}{\partial \sigma} (\Phi, H\Phi) = (\frac{\partial \Phi}{\partial \sigma}, H\Phi) + (\Phi, H\frac{\partial \Phi}{\partial \sigma}) + (\Phi, \frac{\partial H}{\partial \sigma} \Phi)$$

which, from the Schroedinger equation, we can rewrite as

$$\frac{\partial}{\partial \sigma} (\Phi, H\Phi) = i (\frac{\partial \Phi}{\partial \sigma}, \frac{\partial \Phi}{\partial t}) - i (\frac{\partial \Phi}{\partial t}, \frac{\partial \Phi}{\partial \sigma}) + (\Phi, \frac{\partial H}{\partial \sigma} \Phi) \qquad \text{(XXIII-3)}$$

On the other hand we can also use the Schroedinger equation before we differentiate with respect to σ and write

$$\frac{\partial}{\partial \sigma} (\Phi, H\Phi) = i \frac{\partial}{\partial \sigma} (\Phi, \frac{\partial \Phi}{\partial t}) = i (\frac{\partial \Phi}{\partial \sigma}, \frac{\partial \Phi}{\partial t}) + i (\Phi, \frac{\partial^2 \Phi}{\partial \sigma \partial t}) \qquad \text{(XXIII-4)}$$

Equating the right hand sides of (3) and (4) then we have

$$\left(\Psi, \frac{\partial \mathcal{H}}{\partial \sigma}\Psi\right) = i\left(\Psi, \frac{\partial^2 \Psi}{\partial \sigma \partial t}\right) + i\left(\frac{\partial \Psi}{\partial t}, \frac{\partial \Psi}{\partial \sigma}\right)$$

or

$$\left(\Psi, \frac{\partial \mathcal{H}}{\partial \sigma}\Psi\right) = i\frac{\partial}{\partial t}\left(\Psi, \frac{\partial \Psi}{\partial \sigma}\right) \qquad \text{(XXIII-5)}$$

which is the time dependent Hellmann-Feynman theorem (Hayes and Parr, J. Chem. Phys. 43, 1831 (1961).)

Problem: Show that in the static case, and Ψ an energy eigenfunction, this reduces to the Hellmann-Feynman theorem.

XXIV. Direct Solution -- The Method of Variation of Constants

With all this behind us it is now easy to see, at least formally, how to solve our problem. If we expand Ψ in a perturbation series

$$\Psi = \Psi^{(0)} + \mu \Psi^{(1)} + \mu^2 \Psi^{(2)} + \cdots \qquad \text{(XXIV-1)}$$

then from (XXII-1) we evidently find

$$\left(H - i\frac{\partial}{\partial t}\right)\Psi^{(0)} = 0 \qquad \text{(XXIV-2)}$$

$$\left(H - i\frac{\partial}{\partial t}\right)\Psi^{(1)} + W\Psi^{(0)} = 0 \qquad \text{(XXIV-3)}$$

$$\left(H - i\frac{\partial}{\partial t}\right)\Psi^{(2)} + W\Psi^{(1)} = 0 \qquad \text{(XXIV-4)}$$

etc.

Since condition (XXII-7) is independent of μ it then follows that

$$\Psi^{(0)} = \psi_0 \, e^{-i \, \varepsilon_0 t} \tag{XXIV-5}$$

To solve the remaining equations we write,

$$\Psi^{(n)} = \sum_k a_k^{(n)} \psi_k \, e^{-i \, \varepsilon_k t} \tag{XXIV-6}$$

where the $a_k^{(n)}$ are functions of time, the ψ_k are the time-independent complete orthonormal set of eigenfunctions of H, and the ε_k are the eigenvalues:

$$H \psi_k = \varepsilon_k \psi_k$$

$$\tag{XXIV-7}$$

$$(\psi_k, \psi_L) = \delta_{kL}$$

(As is customary we have used a discrete notation.) To satisfy the initial condition we then require that

$$a_k^{(n)} \xrightarrow[t \to -\infty]{} 0 \qquad n \neq 0 \tag{XXIV-8}$$

Inserting (6) into the n'th equation of the sequence (2) - - - and using (7)   One readily finds

$$i \, \frac{d a_k^{(n)}}{dt} = \sum_L (\psi_k, w \psi_L) e^{i (\varepsilon_k - \varepsilon_L) t} \, a_L^{(n-1)}$$

whence, using (8) we have

$$i \, a_k^{(n)} = \int_{-\infty}^{t} dt' \sum_L (\psi_k, w \psi_L) e^{i (\varepsilon_k - \varepsilon_L) t'} \, a_L^{(n-1)}(t') \; , \; n > 0 \tag{XXIV-9}$$

Thus starting with

$$a_L^{(0)} = \delta_{L,0}$$

we may integrate sequentially and, at least formally, solve our problem.

Problem: Write $\psi = \sum_k a_k \psi_k e^{-i\varepsilon_k t}$ (*) and derive

$$a_k = \delta_{k,0} - i \int_{-\infty}^{t} dt' \sum_L (\psi_k, W\psi_L) e^{i(\varepsilon_k - \varepsilon_L)t'} a_L(t')$$

and hence derive (9) by expanding a_L in a perturbation series. If $W \geq 0$ then the form (*), with the a_k constant, yields the general solution of (XXII-1). Hence the name "variation of constants".

However this approach is unsatisfactory on two accounts. First of all it yields the solution in a "sum over state form" whence unless the sum terminates, we have only a formal solution of the sort which we have discussed in connection with the analogous formulation of stationary state perturbation theory. More important, although carrying out the time integrations is in principle straightforward, it can become very messy even in the simple harmonic case where only simple functions appear. In the next section we will discuss an alternate approach in which, for the simple harmonic case, we essentially guess the time dependence of the $\psi^{(m)}$ and then are left with differential equations to solve for the spatial dependence, differential equations much like those we have discussed in connection with stationary state problems and to which we may apply all the techniques developed there.

XXV.   Simple Harmonic Perturbation -- Solution by Ansatz

What we are going to do here is quite analogous to what one does in solving a classical forced oscillation problem -- we are going to write down a particular solution of our differential equation for $t > 0$, a solution describing oscillations with frequency ω and multiples thereof superposed on the natural frequency E_0 with the expectation that this solution in fact represents the steady state behavior we are after. In Appendix A we will check this approach through second order by explicitly carrying through the procedure described in the preceding section. Thus after all our talk about adiabatic turn on, we are going to ignore it.

Returning now to the sequence of equations (XIV-2) etc. we again put

$$\Phi^{(0)} = \psi_0\, e^{-i E_0 t}$$

Note however, that we can no longer argue for this on the grounds of initial conditions because, in general, a particular solution will not satisfy the initial conditions. More to the point is the remark that this is the exact solution of our problem for $\mu = 0$.

We now turn to the first order equation. Inserting (XXII-4) it then reads for $t > 0$

$$\left(H - i \frac{\partial}{\partial t}\right) \Phi^{(1)} + \left(W_+ e^{i\omega t} + W_- e^{-i\omega t}\right) \psi_0 e^{-i E_0 t} = 0 \quad \text{(XXV-1)}$$

The "ansatz"

$$\Phi^{(1)} = \psi_+^{(1)} e^{-i(E_0 - \omega)t} + \psi_-^{(1)} e^{-i(E_0 + \omega)t} \quad \text{(XXV-2)}$$

where $\psi_{\pm}^{(1)}$ are independent of time, is then evidently suggested, and we see that indeed this is a consistent choice in that by inserting (2) into (1) and equating terms with like time dependence we are led to the time independent differential equations

$$(H - E_0 \pm \omega) \psi_{\pm}^{(1)} + W_{\pm} \psi_0 = 0 \tag{XXV-3}$$

whose formal solutions are clearly

$$\psi_{\pm}^{(1)} = - \sum_{k} \psi_{k} \frac{(\psi_{k}, W_{\pm} \psi_0)}{E_{k} - E_0 \pm \omega} \tag{XXV-5}$$

(Problem: Derive (3) and (5).) Note that with $\psi_{\phi}^{(1)}$ given by (5), ψ is normalized through first order. (Problem: Prove this.) Note also that the general solution of (1) is $(2) + \sum_{k} A_k \psi_{k} e^{-i E_k t}$ where the A_k are constants. The presence of terms with $k \neq 0$ would evidently imply that the system has made some sort of transition, and hence are part of the transient response. The term with $k = 0$ can simply be absorbed in a phase factor if we require that ψ be normalized.

Now let us turn to the second order equation. Using (2) it reads

$$(H - i \frac{\partial}{\partial t}) \Phi^{(2)} + (W_+ e^{i\omega t} + W_- e^{-i\omega t})(\psi_+^{(1)} e^{-i(E_0 - \omega)t} + \psi_-^{(1)} e^{-i(E_0 + \omega)t}) = 0 \tag{XXV-6}$$

which clearly suggests the ansatz

$$\psi^{(2)} = \psi_+^{(2)} e^{-i(E_0 - 2\omega)t} + \psi_0^{(2)} e^{-i E_0 t} + \psi_-^{(2)} e^{-i(E_0 + 2\omega)t} \tag{XXV-7}$$

and this seems to work in that we are led to the time independent differential equations

$$(H - E_0 + 2\omega)\, \psi_+^{(2)} + W_+ \psi_+^{(1)} = 0 \qquad \text{(XXV-8)}$$

$$(H - E_0 - 2\omega)\, \psi_-^{(2)} + W_- \psi_-^{(1)} = 0 \qquad \text{(XXV-9)}$$

$$(H - E_0)\, \psi_0^{(2)} + (W_+ \psi_-^{(1)} + W_- \psi_+^{(1)}) = 0 \qquad \text{(XXV-10)}$$

However now we see a difficulty. Namely equations (8) and (9) are perfectly consistent inhomogeneous differential equations with formal solutions

$$\psi_\pm^{(2)} = -\sum_K \frac{\psi_K (\psi_K, W_\pm \psi_\pm^{(1)})}{E_K - E_0 \pm 2\omega} \qquad \text{(XXV-11)}$$

however (10) as it stands is __inconsistent__. Namely, viewed as inhomogeneous differential equations there is an essential difference between (8) and (9) on the one hand and (10) on the other -- the homogeneous part of (10) has ψ_0 as a solution, while (except for very special values which we will avoid -- they yield the resonances mentioned earlier) the homogeneous part of (8) and (9) have no solutions (more precisely no acceptible solutions) since $E_0 \pm 2\omega$ will not be an eigenvalue.

If now we take the scalar product of (10) with ψ_0 we then derive the well known result that when the homogeneous equations has a solution, then the inhomogeneous part must be orthogonal to that solution:

$$(\psi_0, W_+ \psi_-^{(1)} + W_- \psi_+^{(1)}) = 0 \qquad \text{(XXV-12)}$$

which is certainly impossible since from (5) the left hand side is

$$- \sum_{k} \frac{(\psi_0, W_+ \psi_k)(\psi_k, W_- \psi_0)}{E_k - E_0 - \omega} - \sum_{k} \frac{(\psi_0, W_- \psi_k)(\psi_k, W_+ \psi_0)}{E_k - E_0 + \omega}$$

which, remembering that $W_- = (W_+)^\dagger$, we can write as

$$- \sum_{k} \frac{|(\psi_0, W_+ \psi_k)|^2}{E_k - E_0 - \omega} - \sum_{k} \frac{|(\psi_0, W_- \psi_k)|^2}{E_k - E_0 + \omega} \qquad \text{(XXV-13)}$$

which in general won't vanish.

Evidently something has gone wrong with our ansatz. The clue to seeing how to rescue the situation is to consider the static limit $\omega \to 0$. What do we expect there? The answer is given by the famous adiabatic theorem: In the steady state starting from a normalized non-degenerate eigenfunction of H, Ψ will become the corresponding (in the sense of perturbation theory) normalized eigenfunction of $H + \mu W$ c.e,

$$\Psi = \psi \, e^{-i E t} \qquad t > 0 \qquad \text{(XXV-14)}$$

where

$$(H + \mu W)\psi = E\psi \quad , \quad (\psi, \psi) = 1 \qquad \text{(XXV-15)}$$

and

$$\psi = \psi_0 + \mu \psi^{(1)} + \mu^2 \psi^{(2)} + - - \qquad \text{(XXV-16)}$$

$$E = E_0 + \mu E^{(1)} + \mu^2 E^{(2)} + - - \qquad \text{(XXV-17)}$$

Now expanding (14) in powers of μ we see that there are terms linear

in t, quadratic in t, etc. representing the energy shift brought about by the perturbation. Now the point is that we may expect similar "permanent" energy shifts even with non zero frequency -- the so-called "lamp shift". [See for example Jones and Verschueren, Phys. Rev. 176, 42 (1968).] Most naively suppose we (incorrectly) apply the stationary states energy formula

$$E = E_0 + \mu (\psi_0, W \psi_0) - \mu^2 \sum_{k}' \frac{|(\psi_0, W \psi_k)|^2}{E_k - E_0}$$

to a time dependent W. Then we see that in addition to oscillating terms there appear, first in second order, terms which are independent of t (terms which don't vanish on averaging over a period) arising from cross terms involving as many W_+ as W_-; terms therefore which are suggestive of a permanent energy shift brought about by the perturbation μW.

This line of argument then suggests that we amend our ansatz (7) to read

$$\Psi^{(2)} = \psi_+^{(2)} e^{-i(E_0 - 2w)t} + \psi_0^{(2)} e^{-i E_0 t} + \psi_-^{(2)} e^{-i(E_0 + 2w)t} - i \epsilon t \psi_0 e^{-i E_0 t}$$

where ϵ is some constant which is to be determined. Inserting this we then find (8) and (9) as before, but now instead of (10) we find (__Problem__: Derive this)

$$(H - E_0) \psi_0^{(2)} + (W_+ \psi_-^{(1)} + W_- \psi_+^{(1)}) - \epsilon \psi_0 = 0 \qquad \text{(XXV-18)}$$

whence we will have consistency if

$$\epsilon = (\psi_0, W_+ \psi_-^{(1)}) + (\psi_0, W_- \psi_+^{(1)}) \qquad \text{(XXV-19)}$$

[Note that from (13) it follows that $\in$ is real]. The formal solution of (18) is evidently

$$\psi_0^{(2)} = -\sum_{k \neq 0} \frac{\psi_k \, (\psi_k, W_+ \psi_-^{(1)} + W_- \psi_+^{(1)})}{E_k - E_0} + C \psi_0 \qquad (XXV\text{-}20)$$

where the real part of the constant C can be found by requiring that Ψ be normalized through second order. (Problem: Show that by Appropriate choice of Re C, Ψ will be normalized through second order).

Problem: Compare $\in$ with the time independent term in $E^{(2)}$ above.

Problem: Show that the imaginary part of C does not contribute to expectation values through second order.

XXVI.   The Static Limit and a New Ansatz

Let us again consider the static limit $\omega \to 0$ and for simplicity let us put $W_+ = W_- = \frac{1}{2} W$. Then from (13) we see that

$$\in = \frac{1}{2} E^{(2)}$$

This raises the question, where does the rest of $E^{(2)}$ come from? Also where is $E^{(1)}$? The answer to the latter question can be seen from (XXV-5). Namely in the limit $\omega \to 0$ we see that

$$\psi_+^{(1)} e^{i\omega t} + \psi_-^{(1)} e^{-i\omega t} \longrightarrow$$

$$-i \, (\psi_0, W \psi_0) \, t \psi_0 - \sum_{k \neq 0} \frac{\psi_k \, (\psi_k, W \psi_0)}{E_k - E_0}$$

$$= -i \, E^{(1)} t \psi_0 + \psi^{(1)}$$

and the rest of $E^{(2)}$ arises in a similar way from $\Psi^{(2)}$. (Problem:
Derive this result and also "find" the rest of $E^{(2)}$.)

Now formally at least it would be nice if the static limit could be
approached in a simpler way, without the need for being careful about
limiting behavior as $\omega \to 0$. In a practical way this would also be
useful since the presence of potentially singular terms can be a source
of numerical difficulties if one is interested in low frequences.

We now note that the bothersome terms, the $\frac{1}{\omega}$ terms in Ψ , the
terms in $t , t^{\sim} \ldots$ can be thought of as arising from the expansion
of a factor in Ψ which is of the form exp-i (real function of t only)
[Problem: Show that the $1/\omega$ terms in $\Psi^{(2)}$ can be thought of as arising
in this way], hence this suggests writing

$$\Psi = \chi \, e^{-i\theta} \qquad \qquad \text{(XXVI-1)}$$

where χ depends on space spin and time, and where θ is a real function
of time only. Having done this we would then try to deal separately with
χ and with θ , expanding each in power series in ρ , but not further
expanding $e^{-i\theta}$. Further since θ is real, only χ is needed to
compute expectation values.

However just to write (1) does not get us very far since given Ψ ,
χ and θ are not specified uniquely. However, here our desires for
a simple static limit suggest a prescription, namely write

$$\Psi = \frac{\phi}{(\phi,\phi)^{1/2}} \, e^{-i\theta} \qquad \qquad \text{(XXVI-2)}$$

which ensures that Ψ is normalized, and then impose the additional
requirement that

$$(\psi_0, \phi) = 1 \qquad\qquad \text{(XXVI-3)}$$

or, alternatively, since (3) then implies

$$(\psi_0, \chi) = (\phi, \phi)^{-1/2}$$

we may require

$$\text{Im}\,(\psi_0, \chi) = 0$$

To see that this will probably do the job we now note the following. First of all given a normalized Ψ this certainly specifies ϕ and θ uniquely since from (3) it follows that

$$(\psi_0, \Psi) = \frac{1}{(\phi, \phi)^{1/2}} e^{-i\theta}$$

whence

$$(\phi, \phi)^{1/2} = |(\psi_0, \Psi)|^{-1}$$

and

$$-\theta = \text{phase of } (\psi_0, \Psi) \qquad\qquad \text{(XXVI-4)}$$

Further, since in the static limit we know that

$$\Psi = \psi\, e^{-iEt}$$

we see from (4) that in this limit

$$\theta = Et - \text{phase of } (\psi_0, \psi) = Et + \text{constant} \qquad \text{(XXVI-5)}$$

so that in this limit θ does include <u>all</u> of the energy (including E_0).

Thus we can expect that in the nonstatic case ϕ will contain neither $\frac{1}{\omega}$ terms nor terms involving t, t^2 etc. Finally note that in the static limit

$$\Phi = \frac{\psi}{(\psi_0, \psi)}$$

i.e., ϕ becomes the energy eigenfunction in intermediate normalization.

We will now show that, by use of the Schroedinger equation, that we can determine θ in terms of ϕ and be left with an equation for ϕ alone, an equation which we will then solve by a perturbation expansion. We will then show subsequently that, in accord with the above remarks, we will encounter no inconsistencies when we make the obvious ansatz that the ϕ involve only periodic terms, i.e. terms of the form $e^{\pm i n \omega t}$ with $n = 0, 1, 2 \ldots$

To determine θ and derive the equation for ϕ we write (2) as

$$\Phi = N \, \phi \, e^{-i\theta} \tag{XXVI-6}$$

where $N = (\phi, \phi)^{-1/2}$. Then

$$\frac{\partial \Phi}{\partial t} = \frac{dN}{dt} \phi e^{-i\theta} + N \frac{\partial \phi}{\partial t} e^{-i\theta} - i \frac{d\theta}{dt} N \phi e^{-i\theta}$$

whence

$$H \Phi = i \frac{\partial \Phi}{\partial t}$$

yields

$$H\Phi = i \frac{\partial \Phi}{\partial t} + i \left(\frac{1}{N} \frac{dN}{dt} - i \frac{d\theta}{dt} \right) \Phi \tag{XXVI-7}$$

Now we take the scalar product of (7) with ψ_0 and use $(\psi_0, \Phi) = 1$, and hence $(\psi_0, \frac{\partial \Phi}{\partial t}) = 0$, to find

$$(\psi_0, \mathcal{H} \Phi) = i \left(\frac{1}{N} \frac{\partial N}{\partial t} - i \frac{d\theta}{dt} \right) = i \frac{d}{dt} (\ln N - i\theta) \qquad \text{(XXVI-8)}$$

Now $\mathcal{H} = H + \mu W$ so

$$(\psi_0, \mathcal{H} \Phi) = E_0 + (\psi_0, \mu W \Phi) \qquad \text{(XXVI-9)}$$

whence we may integrate (8) to find

$$i (\ln N - i\theta) = E_0 t + \int_{-\infty}^{t} (\psi_0, \mu W \Phi) dt' \qquad \text{(XXVI-10)}$$

and therefore

$$\Phi = \Phi e^{-i \left[E_0 t + \int_{-\infty}^{t} (\psi_0, \mu W \Phi) dt' \right]} \qquad \text{(XXVI-11)}$$

$$\theta = E_0 t + \text{Re} \int_{-\infty}^{t} (\psi_0, \mu W \Phi) dt'$$

where we have _implicitly_ invoked the adiabatic turn on in order to ensure that the integral exists and where our choice of constant of integration in (10) has been such that the initial condition on Φ is now simply

$$\Phi \xrightarrow[t \to -\infty]{} \psi_0 \qquad \text{(XXVI-12)}$$

Finally from (7), (8), and (9) must also satisfy the differential equation

$$\mathcal{H} \Phi - \left[E_0 + \mu (\psi_0, W \Phi) \right] \Phi = i \frac{\partial \Phi}{\partial t} \qquad \text{(XXVI-13)}$$

Note that this equation does not require that $(\psi_0, \Phi) = 1$ but it

guarantees that if $(\psi_0, \Phi) = 1$ initially, as it does from (12), then it will stay equal to 1. (Problem: Prove this. Also discuss the static limit of (13).)

Also note that although we used the adiabatic turn on in deriving (12), eq. (13) involves only instantaneous quantities, hence it still allows the particular solution approach which we used before and it is to this that we now turn.

Making the perturbation expansion

$$\Phi = \psi_0 + \mu \, \Phi^{(1)} + \mu^2 \, \Phi^{(2)} + \cdots \qquad \text{(XXVI-14)}$$

and using (9) we readily derive the sequence of equations

$$(H - E_0) \, \Phi^{(1)} + \left[W - (\psi_0, W \psi_0) \right] \psi_0 = i \, \frac{\partial \Phi^{(1)}}{\partial t} \qquad \text{(XXVI-17)}$$

$$(H - E_0) \, \Phi^{(2)} + \left[W - (\psi_0, W \psi_0) \right] \Phi^{(1)} - (\psi_0, W \Phi^{(1)}) \, \psi_0 = \qquad \text{(XXVI-18)}$$

$$i \, \frac{\partial \Phi^{(2)}}{\partial t}$$

etc. Further, the condition $(\psi_0, \Phi) = 1$ becomes

$$(\psi_0, \Phi^{(n)}) = 0 \qquad n \neq 0 \qquad \text{(XXVI-19)}$$

Inserting (XXII-4), (17) then suggests that for $t > 0$

$$\Phi^{(1)} = \phi_+^{(1)} \, e^{i\omega t} + \phi_-^{(1)} \, e^{-i\omega t} \qquad \text{(XXVI-20)}$$

which in turn leads to

$$(H - E_0 \pm \omega) \, \phi_\pm^{(1)} + \left(W_\pm - (\psi_0, W_\pm \psi_0) \right) \psi_0 \qquad \text{(XXVI-21)}$$

whose formal solution is

$$\phi_{\pm}^{(1)} = - \sum_{k \neq 0} \frac{\psi_k (\psi_k, w_{\pm} \psi_0)}{E_k - E_0 \pm \omega} \qquad \text{(XXVI-22)}$$

which, as expected, differs from $\psi_{\pm}^{(1)}$ only in that the $\frac{1}{\omega}$ terms have been removed.

It is now in interest to note that this solution also automatically satisfies $(\psi_0, \Phi^{(n)}) = 0$. Actually this could have been anticipated from the structure of (13). Namely, taking its scalar product with ψ_0 we find

$$(\psi_0, \mathcal{H} \Phi) - E_0 (\psi_0, \Phi) - \mu (\psi_0, w \Phi)(\psi_0, \Phi) = i \frac{d}{dt} (\psi_0, \Phi) \qquad \text{(XXVI-23)}$$

or

$$\mu (\psi_0, w \Phi) [1 - (\psi_0, \Phi)] = i \frac{d}{dt} (\psi_0, \Phi)$$

whence it follows that if we have satisfied the condition $1 - (\psi_0, \Phi) = 0$ through (n-1)st order then

$$\frac{d}{dt} (\psi_0, \Phi^{(n)}) = 0 \qquad \text{(XXVI-24)}$$

whence any oscillating terms in $\Phi^{(n)}$ will automatically be orthogonal to ψ_0 as required. However, this will not be the case for the time independent terms. Such terms first appear in $\Phi^{(n)}$ as we will see in a moment. Further this result also shows that the time independent terms in $\Phi^{(n)}$ will always yield consistent equations (recall that with $\psi^{(n)}$ it was the term $\psi_0^{(n)} e^{-iE_0 t}$ which led to difficulties and that in the present discussion the E_0 has been absorbed into $\mathcal{H}$.) Namely $\Phi^{(n)}$ satisfies an equation of the form

$$(H - E_0) \Phi^{(n)} + X^{(n)} = i \frac{\partial \Phi^{(n)}}{\partial t}$$

whence it follows from (24) that

$$(\psi_0, X^{(n)}) = 0 \qquad \text{(XXVI-25)}$$

Now the part of $\Phi^{(n)}$ which is independent of time will satisfy

$$(H - E_0) \Phi_0^{(n)} + X_0^{(n)} = 0 \qquad \text{(XXVI-26)}$$

whence since (25) evidently implies that $(\psi_0, X_0^{(n)}) = 0$, it follows that (26) is a consistent equation.

Turning now to second order the obvious ansatz

$$\Phi^{(2)} = \phi_+^{(2)} e^{2i\omega t} + \phi_0^{(2)} + \phi_-^{(2)} e^{-2i\omega t} \qquad \text{(XXVI-27)}$$

then yields the consistent set of equations

$$(H - E_0 \pm 2\omega) \phi_{\pm}^{(2)} + [W_{\pm} - (\psi_0, W_{\pm} \psi_0)] \phi_{\pm}^{(1)}$$

$$- (\psi_0, W_{\pm} \phi_{\pm}^{(1)}) \psi_0 = 0 \qquad \text{(XXVI-28)}$$

$$(H - E_0) \phi_0^{(2)} + [W_+ - (\psi_0, W_+ \psi_0)] \phi_-^{(1)}$$

$$\qquad \text{(XXVI-29)}$$

$$+ [W_- - (\psi_0, W_- \psi_0)] \phi_+^{(1)} - (\psi_0, W_+ \phi_-^{(1)}) \psi_0 - (\psi_0, W_- \phi_+^{(1)}) \psi_0 = 0$$

From (28) it then follows, in accord with our general argument above, that $(\psi_0, \phi_{\pm}^{(2)}) = 0$, while in (29) the inhomogeneous term is ortho- (Problem: show this) gonal to ψ_0 as required. This of course leaves $(\psi_0, \phi_0^{(2)})$ undeter- mined, however, we may then impose our requirement that this vanishes to fix $\phi_0^{(2)}$ uniquely. (Problem: Write down the formal solutions to (28)

and (29).) Before turning to a discussion of the solution of these equations it will be useful first to talk a bit more about what we are actually interested in calculating.

XXVII. A Quantity of Interest -- The Average Polarization

Consider again the spatially uniform simple harmonic electric field. Then we have seen that

$$W_+ - W_- = \frac{1}{2} \vec{D} \cdot \vec{\mathcal{E}}_0$$

where $\vec{D}$ is (proportional to) the internal dipole moment operator of the system. Now for the purpose of computing the index of refraction the quantity of interest is precisely the expectation value of

$$\frac{(\Psi, \vec{D}\,\Psi)}{(\Psi,\Psi)} = \frac{(\Phi, \vec{D}\,\Phi)}{(\Phi,\Phi)}$$

and a similar remark applies in other cases. For our purposes however it proves more useful to consider the expectation value of W from which we may then readily extract the expectation value of $\vec{D}$. We will now write out this quantity through terms of fourth order

For another use for $\Phi^{(n)}$ -- calculation of two photon absorption -- see Honig and Jortner, J. Chem. Phys. 47, 3698 (1967), and references given there.

First of all we have

$$(\Phi, W\Phi) = (\Psi_0, W\Psi_0)$$
$$+ \mu\left[(\Psi_0, W\Phi^{(1)}) + (\Phi^{(1)}, W\Psi_0)\right]$$
$$+ \mu^2\left[(\Psi_0, W\Phi^{(2)}) + (\Phi^{(2)}, W\Psi_0) + (\Phi^{(1)}, W\Phi^{(1)})\right]$$
$$+ \mu^3\left[(\Psi_0, W\Phi^{(3)}) + (\Phi^{(3)}, W\Psi_0) + (\Phi^{(1)}, W\Phi^{(2)}) + (\Phi^{(2)}, W\Phi^{(1)})\right]$$
$$+ \mu^4\left[(\Psi_0, W\Phi^{(4)}) + (\Phi^{(4)}, W\Psi_0) + (\Phi^{(1)}, W\Phi^{(3)}) + (\Phi^{(3)}, W\Phi^{(1)}) + (\Phi^{(2)}, W\Phi^{(2)})\right]$$
$$+ \cdots$$

Then, using $(\Psi_0, \Phi^{(n)}) = 0$ we have

$$(\Phi, \Phi) = 1$$
$$+ \mu^2 (\Phi^{(1)}, \Phi^{(1)})$$
$$+ \mu^3 \left[(\Phi^{(1)}, \Phi^{(2)}) + (\Phi^{(2)}, \Phi^{(1)}) \right]$$
$$+ \mu^4 \left[(\Phi^{(1)}, \Phi^{(3)}) + (\Phi^{(3)}, \Phi^{(1)}) + (\Phi^{(2)}, \Phi^{(2)}) \right]$$
$$+ \cdots$$

Putting this together we then have

$$\frac{(\Phi, W\Phi)}{(\Phi, \Phi)} = (\Psi_0, W\Psi_0)$$
$$+ \mu \left[(\Psi_0, W\Phi^{(1)}) + (\Phi^{(1)}, W\Psi_0) \right]$$
$$+ \mu^2 \left[(\Psi_0, W\Phi^{(2)}) + (\Phi^{(2)}, W\Psi_0) + (\Phi^{(1)}, W\Phi^{(1)}) - (\Psi_0, W\Psi_0)(\Phi^{(1)}, \Phi^{(1)}) \right]$$

$$+ \mu^3 \left[(\Psi_0, W\Phi^{(3)}) + (\Phi^{(3)}, W\Psi_0) + (\Phi^{(1)}, W\Phi^{(2)}) + (\Phi^{(2)}, W\Phi^{(1)}) \right.$$

$$- (\Phi^{(1)}, \Phi^{(1)}) \left\{ (\Psi_0, W\Phi^{(1)}) + (\Phi^{(1)}, W\Psi_0) \right\}$$

$$\left. - \left\{ (\Phi^{(1)}, \Phi^{(2)}) + (\Phi^{(2)}, \Phi^{(1)}) \right\} (\Psi_0, W\Psi_0) \right]$$

$$+ \mu^4 \left[(\Psi_0, W\Phi^{(4)}) + (\Phi^{(4)}, W\Psi_0) + (\Phi^{(1)}, W\Phi^{(3)}) + (\Phi^{(3)}, W\Phi^{(1)}) \right.$$

$$+ (\Phi^{(2)}, W\Phi^{(2)}) - (\Phi^{(1)}, \Phi^{(1)}) \left\{ (\Psi_0, W\Phi^{(2)}) + (\Phi^{(2)}, W\Psi_0) + (\Phi^{(1)}, W\Phi^{(1)}) \right\}$$

$$\left. - \left\{ (\Phi^{(1)}, \Phi^{(2)}) + (\Phi^{(2)}, \Phi^{(1)}) \right\} \left\{ (\Psi_0, W\Phi^{(1)}) + (\Phi^{(1)}, W\Psi_0) \right\} \right]$$

$$+ \mu^5 \cdots$$

$$\equiv W_0 + \mu W^{(1)} + \mu^2 W^{(2)} + \cdots \qquad \text{(XXVII-1)}$$

where of course,

$$W = W_+ e^{i\omega t} + W_- e^{-i\omega t}$$
(XXVII-2)

$$\Phi^{(1)} = \phi_+^{(1)} e^{i\omega t} + \phi_-^{(1)} e^{-i\omega t}$$
(XXVII-3)

$$\Phi^{(2)} = \phi_+^{(2)} e^{2i\omega t} + \phi_0^{(2)} + \phi_-^{(2)} e^{-2i\omega t}$$
(XXVII-4)

$$\Phi^{(3)} = \phi_+^{(3)} e^{3i\omega t} + \phi_{+1}^{(3)} e^{i\omega t} + \phi_{-1}^{(3)} e^{-i\omega t} + \phi_-^{(3)} e^{-3i\omega t}$$
(XXVII-5)

$$\Phi^{(4)} = \phi_+^{(4)} e^{4i\omega t} + \phi_{+2}^{(4)} e^{2i\omega t} + \phi_0^{(4)} + \phi_{-2}^{(4)} e^{-2i\omega t} + \phi_-^{(4)} e^{-4i\omega t}$$
(XXVII-6)

Problem: Verify (5) and (6).

Of particular formal interest to us, though not necessarily of
greatest physical interest, will be the terms in W which are time independent.
As we will begin to see in this section, they have properties much
like the terms in the energy expansion of stationary state perturbation
theory and eventually (Sec. XXXIII) we will show that we can derive
them from a variational principle, that is that we can hope to calcu-
late them approximately with an error of second order.

Let us then look at these terms. In W_0 there clearly are none,
nor are there any in $W^{(2)}$ or in $W^{(4)}$. (Problem: Show that there are
no such terms in $W^{(n)}$ with n even.) On the other hand there are such
terms in $W^{(1)}$ and $W^{(3)}$, namely

$$\langle W^{(1)} \rangle_T = 2\text{Re}\left[(\psi_0, W_+ \phi_-^{(1)}) + (\psi_0, W_- \phi_+^{(1)}) \right] \qquad \text{(XXVII-7)}$$

and

$$\langle W^{(3)} \rangle_T = 2\text{Re}\left[(\psi_0, W_+ \phi_{-1}^{(3)}) + (\psi_0, W_- \phi_{+1}^{(3)}) \right]$$

$$\qquad \text{(XXVII-8)}$$

$$+ 2\text{Re}\left[(\phi_+^{(1)}, [W_+ - (\psi_0, W_+ \psi_0)]\phi_0^{(2)}) + (\phi_-^{(1)}, [W_- - (\psi_0, W_- \psi_0)]\phi_0^{(2)}) \right]$$

$$+ 2\text{Re}\left[(\phi_+^{(1)}, [W_- - (\psi_0, W_- \psi_0)]\phi_+^{(2)}) + (\phi_-^{(1)}, [W_+ - (\psi_0, W_+ \psi_0)]\phi_-^{(2)}) \right]$$

$$\qquad + \text{ terms which involve } \phi_\pm^{(1)} \text{ and } \psi_0 \text{ only}$$

where $\langle \ \rangle_T$ can be understood to indicate an average over a period, $T = 2\pi/\omega$

> **Problem:** Prove that in fact $(\psi_0, W_+ \phi_-^{(1)})$ and $(\psi_0, W_- \phi_+^{(1)})$ are real. How about the terms in $\langle W^{(3)} \rangle_T$?

To evaluate $\langle W^{(1)} \rangle_T$ we need ψ_0 and $\phi_\pm^{(1)}$ while to evaluate $\langle W^{(3)} \rangle_T$ we apparently also need $\phi_\pm^{(2)}$, $\phi_0^{(2)}$ and $\phi_\pm^{(3)}$. We will now show that in fact we don't need $\phi_\pm^{(3)}$. As we will see later, this result is analogous to the fact that in time independent perturbation theory, that to evaluate $E^{(4)}$ we need only $\psi_0, \psi^{(1)}$ and $\psi^{(2)}$ and don't need $\psi^{(3)}$ or $\psi^{(4)}$, and indeed the proof proceeds in a similar way. Namely we have the following equations

$$(H - E_0 \pm \omega)\phi_\pm^{(1)} + (W_\pm - (\psi_0, W_\pm \psi_0))\psi_0 = 0 \qquad \text{(XXVII-9)}$$

and

$$(H - E_0 \pm w) \phi_{\pm 1}^{(3)} + (W_\pm - (\psi_0, W_\pm \psi_0)) \phi_0^{(2)} + (W_\mp - (\psi_0, W_\mp \psi_0)) \phi_\pm^{(2)}$$

$$- (\psi_0, W_\pm \phi_\pm^{(1)}) \phi_\mp^{(1)} - [(\psi_0, W_\mp \phi_-^{(1)}) + (\psi_0, W_- \phi_\mp^{(1)})] \phi_\pm^{(1)} \qquad \text{(XXVII-10)}$$

$$- [(\psi_0, W_\pm \phi_0^{(2)}) + (\psi_0, W_\mp \phi_\pm^{(2)})] \psi_0 = 0$$

Now the terms in $\langle W^{(3)} \rangle_\mp$ which involve $\phi_\mp^{(3)}$ can be written

$$(\psi_0, [W_\mp - (\psi_0, W_\mp \psi_0)] \phi_{-1}^{(3)}) + (\psi_0, [W_- - (\psi_0, W_- \psi_0)] \phi_{+1}^{(3)})$$

$$= ([W_- - (\psi_0, W_- \psi_0)] \psi_0, \phi_{-1}^{(3)}) + ([W_+ - (\psi_0, W_+ \psi_0)] \psi_0, \phi_{+1}^{(3)})$$

where we have used $(\psi_0, \phi_{\pm 1}^{(3)}) = 0$. Now from (9) this equals

$$= -(\phi_-^{(1)}, (H - E_0 - w) \phi_{-1}^{(3)}) - (\phi_+^{(1)}, (H - E_0 - w) \phi_{+1}^{(3)})$$

which from (10), using $(\phi_\pm^{(1)}, \psi_0) = 0$, can be written as

$$(\phi_-^{(1)}, [W_- - (\psi_0, W_- \psi_0)] \phi_0^{(2)}) + (\phi_-^{(1)}, [W_+ - (\psi_0, W_+ \psi_0)] \phi_-^{(2)})$$

$$+ (\phi_+^{(1)}, [W_+ - (\psi_0, W_+ \psi_0)] \phi_0^{(2)}) + (\phi_+^{(1)}, [W_- - (\psi_0, W_- \psi_0)] \phi_+^{(2)})$$

$$+ \text{terms involving only } \phi_\pm^{(1)} \text{ and } \psi_0$$

and hence we see that as announced

$$\langle W^{(3)} \rangle_T = 4 Re \left[(\phi_+^{(1)}, [w_+ - (\psi_0, w_+ \psi_0)] \phi_0^{(2)}) \right.$$

$$+ (\phi_-^{(1)}, [w_- - (\psi_0, w_- \psi_0)] \phi_0^{(2)})$$

$$+ (\phi_+^{(1)}, [w_- - (\psi_0, w_- \psi_0)] \phi_+^{(2)}) \tag{XXVII-11}$$

$$\left. + (\phi_-^{(1)}, [w_+ - (\psi_0, w_+ \psi_0)] \phi_-^{(2)}) \right]$$

$$+ \text{terms involving only } \phi_{\pm}^{(1)} \text{ and } \psi_0$$

Problem: Can you make a similar reduction in the time dependent terms in $W^{(3)}$? Can you eliminate $\phi_{+,-,0}^{(2)}$ in favor of $\phi_{\pm}^{(1)}$ in $W^{(4)}$?

Now let us turn to a more detailed examination of $W^{(1)}$ in the case of a uniform electric field

$$w = \vec{D} \cdot \vec{\mathcal{E}}_0 \cos \omega t$$

$$w_+ = w_- = \frac{1}{2} \vec{D} \cdot \vec{\mathcal{E}}_0$$

Then we have

$$W^{(1)} = \left[(\psi_0, \vec{D} \, \Phi^{(1)}) + (\Phi^{(1)}, \vec{D} \, \psi_0) \right] \cdot \vec{\mathcal{E}}_0 \cos \omega t$$

where from (XXVI-23)

$$\Phi^{(1)} = -\frac{1}{2} \sum_{k \neq 0} \psi_k (\psi_k, \vec{D} \cdot \vec{\mathcal{E}}_0 \psi_0) \left[\frac{e^{i\omega t}}{E_k - E_0 + \omega} + \frac{e^{-i\omega t}}{E_k - E_0 - \omega} \right]$$

Thus one readily finds

$$W^{(n)} = - \sum_{k \neq 0} (\psi_0, \vec{D} \cdot \vec{\mathcal{E}}_0 \psi_k)(\psi_k, \vec{D} \cdot \vec{\mathcal{E}}_0 \psi_0) \Big[$$

$$\Big[\frac{1}{E_k - E_0 + \omega} + \frac{1}{E_k - E_0 - \omega} \Big] \cos^2 \omega t \equiv - \vec{\mathcal{E}} \cdot \overleftrightarrow{\alpha} \cdot \vec{\mathcal{E}}$$

(XXVII-12)

which defines the polarizibility tensor $\overleftrightarrow{\alpha}(\omega)$

$$\overleftrightarrow{\alpha}(\omega) = 2 \sum_{k \neq 0} \frac{(\psi_0, \vec{D} \psi_k)(\psi_k, \vec{D} \psi_0)(E_k - E_0)}{(E_k - E_0)^\nu - \omega^\nu}$$

(XXVII-13)

For $\omega \to 0$ it becomes the static polarizability, and as we know we have

a variational principle for its diagonal elements. The same will

shortly be seen to be true for general ω and will rest on the

observation that

$$\langle W^{(n)} \rangle_T = - \frac{1}{2} \vec{\mathcal{E}}_0 \cdot \overleftrightarrow{\alpha} \cdot \vec{\mathcal{E}}_0$$

(XXVII-14)

Note also that (14) imples that we can recover all of $W^{(b)}$ from $\langle W^{(n)} \rangle_T$

and, as noted earlier, it is for $\langle W^{(n)} \rangle_T$ that we will find a variational

principle. In higher orders however $W^{(m)}$ contains other terms which

cannot be recovered from $\langle W^{(m)} \rangle_T$. Since, as noted earlier,

it is for $\langle W^{(m)} \rangle_T$ that we will find a variational

principle, it follows that we will have no variational principle

for these physically very interesting quantities.

As is clear from (13), if E_0 is the ground state the diagonal

elements of $\overleftrightarrow{\alpha}$ (which are the quantities involved in (12)), are positive,

and that $\overleftrightarrow{\alpha}$ becomes infinite when $\omega = E_k - E_0$. This infinite

response is of course just the behavior we referred to in Sec. XXII.

In light of our subsequent investigation there is one aspect which may

appear odd however -- namely why do the resonances occur at $\omega = E_k - E_0$?

What happened to the "lamp shift"? One answer of course is to say that the shifts are at least of second order and hence yield a higher order effect. However this is really no answer since it should be fairly clear that however far one goes in the perturbation theory resonances will be predicted only at these and similar positions since one will always have denominators of the form

$$E_k - E_v \pm m\omega$$

($m \neq 1$ can be thought of as due to the absorption of m quanta.)
The real point is that to see the shift of the resonances one must really abandon straightforward perturbation theory and use some method which in effect permits a partial re-summing of the perturbation series in order to, so to speak, "put some μ's in the denominator". (For a systematic approach see the Kroll reference in Sec. XXII.)

Problem: Show that through third order $\langle W^{(n)} \rangle_T$ and some of the terms arising from the $\langle (\Phi^{(n)}, \Phi^{(n)}) \, \mathcal{l} \rangle_T$ term in $\langle W^{(3)} \rangle_T$ can be combined to exhibit a shifted resonance $E_k - E_v - \omega \rightarrow E_k - E_v - \Delta - \omega$ What is Δ ? Does it equal $\mathcal{E}$ of Sec. XXV as we expect?

Finally one other point which may be puzzling -- how can a normalized wave function become infinite everywhere? Clearly this is also an artifact of straightforward perturbation theory since for example

$$\frac{(\psi_0 + \chi^{(n)})}{(\psi_0 + \chi^{(n)}, \psi_0 + \chi^{(n)})^{1/2}}$$

stays perfectly finite. However $\chi^{(n)}$ is not the only term which resonates; there are terms in each order, hence to do the job correctly

again calls for a rearrangement of the perturbation series. Also to

include real physical damping one should explicitly include photons in

the theory. For details we again refer to Kroll.

All of this discussion can be summarized by the obvious remark

that straightforward perturbation theory is inadequate near a resonance,

and is also inadequate if the lamp shifts are not small compared with the level spacings.

XXVIII. Exact Solution of the Differential Equations

$\Phi^{(h)}$ is known for hydrogen in a spatially uniform electric field.

However it is sufficiently complicated in structure that we have rele-

gated its discussion to an Appendix. (not involved in this report) The essential difficulty is that

even though one can immediately reduce the problem to a radial problem,

the independent solutions of the homogeneous equations are quite com-

plicated for $\omega \neq 0$. For low frequencies however, the situation be-

comes more transparent in that it is reasonable to expand $\Phi^{(h)}_{\pm}$ in

powers of ω (correspondingly $\alpha(i\omega)$ will be represented as a power

series in ω^2). Thus writing

$$\Phi^{(h)}_{\pm} = \sum_n \omega^n \Phi^{(h,n)}_{\pm}$$

we clearly are let to equations of the form

$$(H - E_0) \, \Phi^{(h,n)}_{\pm} \qquad\qquad = \text{terms involving lower order functions}$$

Such equations are of course exactly of the type which we encountered in

stationary state problems and may be readily delt with in the case of

hydrogen. See Dalgarno and Kingston, Proc. Foy. Soc. A259, 424 (1960)

for details.

The expansion in power of ω requires that $\frac{|\omega|}{E_r - E_D} < 1$ and hence will fail near and above the first resonance, i.e. $|\omega| \gtrsim E_r - E_D$. However one might extend the range by proceeding as follows: First of all, assuming that one knows ψ_1, one can insert the first resonance "by hand" i.e. one can write

$$\phi_{\pm}^{(\omega)} = -\psi_1 \frac{(\psi_1, w_2 \psi_D)}{E_1 - E_D \pm \omega} + \zeta_{\pm}^{(\omega)}$$

Then $\zeta_{\pm}^{(\omega)}$ satisfies

$$(H - E_D \pm \omega)\,\zeta_{\pm}^{(\omega)} + (w_2 - (\psi_D, w_2 \psi_D))\psi_D - (\psi_1, w_2 \psi_D)\psi_1 = 0$$

and one could now expand $\zeta_{\pm}^{(\omega)}$ in powers of ω which will again yield equations of familiar form, or as an alternate one might rearrange the series and expand $\zeta^{(\omega)}$ in power of $\xi \equiv \omega - (E_r - E_D)$. Then one will get the same sort of equation but now with E_D replaced by E_1. i.e.

$$(H - E_1)\,\zeta_{\pm}^{(\xi n)} = \text{known things}$$

Aside from hydrogen however the possibility of exact solutions seems remote and hence one must resort to approximation methods, in particular variational methods. Before discussing these techniques however there is one more topic which we wish to take up.

XXIX. Double Perturbation Theory

Here we will simply refer to Hirschfelder, Brown and Epstein in Adv. in Quan. Chem. I. P. O. Löwdin ed. (1964), pages 323-324. For an application to He see Musulin and Epstein, Phys. Rev. 136, A966 (1964). For an extension to complex frequencies and for other applications see papers by Kestner and collaborators in J. Chem. Phys. 45, 4014 (1966); 49, 3392 (1968); 49, 3398 (1968).

XXX. The Variational Method I

Our approach to the variational method here is going to be exactly opposite to the course we followed in discussing stationary state problems. There we started with the general variational method, made a perturbation analysis, derived the Hylleraas variational functional and its generalization in higher order, and finally noted that we could have written these down directly as the variational functionals which give the equations for $\psi^{(1)}$, $\psi^{(2)}$ etc.

Here we will proceed just the other way around. Thus our first step is to note that equation (XXVI-22) can be derived from

$$\delta \tilde{L}^{(2)}_{\pm} = 0$$

where

$$\tilde{L}^{(2)}_{\pm} = \left(\tilde{\phi}^{(1)}_{\pm}, (H - E_0 \pm \omega) \, \tilde{\phi}^{(1)}_{\pm} \right)$$
$$+ \left(\tilde{\phi}^{(1)}_{\pm}, [W_{\pm} - (\psi_0, W_{\pm} \psi_0)] \, \psi_0 \right) \tag{XXX-1}$$
$$+ \left(\psi_0, [W_{\pm} - (\psi_0, W_{\pm} \psi_0)] \, \tilde{\phi}^{(1)}_{\pm} \right)$$

Similarly the equations for $\phi^{(1)}_{\pm}$ and $\phi^{(2)}_{0}$, namely (XXVI-25) and (XXVI-29) can be derived from

$$\delta \tilde{L}^{(1)}_{\pm} = 0$$

and

$$\delta \tilde{L}^{(1)}_{0} = 0$$

where

$$\tilde{L}_{\pm}^{(4)} = \left(\tilde{\phi}_{\pm}^{(2)}, (H - E_0 \pm 2\omega)\tilde{\phi}_{\pm}^{(2)} \right)$$

$$+ \left(\tilde{\phi}_{\pm}^{(2)}, [W_{\pm} - (\psi_0, W_{\pm}\psi_0)]\phi_{\pm}^{(1)} \right)$$

$$+ \left(\phi_{\pm}^{(1)}, [W_{\mp} - (\psi_0, W_{\mp}\psi_0)]\tilde{\phi}_{\pm}^{(2)} \right)$$

$$- (\psi_0, W_{\pm}\phi_{\pm}^{(1)})(\tilde{\phi}_{\pm}^{(2)}, \psi_0) - (\phi_{\pm}^{(1)}, W_{\mp}\psi_0)(\psi_0, \tilde{\phi}_{\pm}^{(2)})$$

(XXX-2)

and

$$\tilde{L}_{0}^{(4)} = \left(\tilde{\phi}_{0}^{(2)}, (H - E_0)\tilde{\phi}_{0}^{(2)} \right)$$

$$+ \left(\tilde{\phi}_{0}^{(2)}, [W_+ - (\psi_0, W_+\psi_0)]\phi_{-}^{(1)} \right) + \left(\phi_{-}^{(1)}, [W_- - (\psi_0, W_-\psi_0)]\tilde{\phi}_{0}^{(2)} \right)$$

$$+ \left(\tilde{\phi}_{0}^{(2)}, [W_- - (\psi_0, W_-\psi_0)]\phi_{+}^{(1)} \right) + \left(\phi_{+}^{(1)}, [W_+ - (\psi_0, W_+\psi_0)]\tilde{\phi}_{0}^{(2)} \right)$$

$$- \left[(\psi_0, W_+\phi_{-}^{(1)}) + (\psi_0, W_-\phi_{+}^{(1)}) \right] (\tilde{\phi}_{0}^{(2)}, \psi_0)$$

$$- \left[(\phi_{-}^{(1)}, W_-\psi_0) + (\phi_{+}^{(1)}, W_+\psi_0) \right] (\psi_0, \tilde{\phi}_{0}^{(2)})$$

(XXX-3)

Note that analogously to $\tilde{J}_{H}^{(2)}$ and $\tilde{J}_{H}^{(4)}$; in $\tilde{L}_{\pm}^{(2)}$, ψ_0 is the exact function and in $\tilde{L}_{\pm,0}^{(4)}$, ψ_0 and $\phi_{\pm}^{(1)}$ are the exact functions. We now discuss some general properties of these functionals. (<u>Problem</u>: Write down the variational functionals associated with $\psi_{\pm}^{(1)}$ and $\psi_{\pm,0}^{(2)}$ and carry through an analogous discussion for them).

(A) With $\hat{\phi}_{\pm}^{(1)} = \phi_{\pm}^{(1)}$ and $\hat{\phi}_{\pm,0}^{(2)} = \phi_{\pm,0}^{(2)}$ we see that the numerical values of $\hat{L}_{\pm}^{(2)}$ and $\hat{L}_{\pm,0}^{(4)}$ are

$$L_{\pm}^{(2)} = (\psi_0, W_{\mp}\phi_{\pm}^{(1)})$$

(XXX-4)

$$L_{\pm}^{(4)} = (\phi_{\pm}^{h}, [W_{\mp} - (\psi_0, W_{\mp}\psi_0)]\,\phi_{\pm}^{(2)})$$ (XXX-5)

AND

$$L_0^{(4)} = (\phi_-^{h}, [W_{--} - (\psi_0, W_-\psi_0)]\,\phi_d^{(2)}) + (\phi_+^{h}, [W_+ - (\psi_0, W_+\psi_0)]\,\phi_d^{(2)})$$ (XXX-6)

respectively where we have used $(\psi_0, \phi^{(m)}) = 0$

Comparing $L_{\pm}^{(2)}$ with (XXVII-7) we see that given ψ_0, $\hat{L}_{\pm}^{(2)}$ will

yield a variational approximation to $\langle W^{(2)}\rangle_{\mp}$, and comparing $L_{\mp}^{(4)}$ with

(XXVII-11) we see, given ψ_0 and $\phi_{\mp}^{h}$, that $\hat{L}_{\mp}^{(4)}$ will yield a

variational approximation for $\langle W^{(3)}\rangle_{\mp}$. However we do not have a variational

approximation for $W^{(2)}$, for the rest of $W^{(3)}$, etc.

I.e. we have no formulae into which we can substitute approximate

functions and get a result which differs from the exact result by terms

of <u>second</u> order.

(B) If $\Delta\hat{\phi}_{\pm}^{(2)} = \delta\eta\,\hat{\phi}_{\pm}^{(2)}$ with $\delta\eta$ real or pure imaginary are

allowed variations of $\hat{\phi}_{\pm}^{(2)}$ and if $\Delta\hat{\phi}_{\mp}^{(2)} = \delta\eta\,\hat{\phi}_{\mp}^{(2)}$ are allowed

variations of $\hat{\phi}_{\mp}^{(2)}$ then one finds (<u>Problem</u>: Fill in the details) that

$\hat{L}_{\pm}^{(2)}$ and $\hat{L}_{\mp}^{(4)}$ are given by formulae like (4) - (6) but with $\wedge$ in

appropriate places.

(C) If $\Delta\hat{\phi}_{\pm}^{(2)} = \delta\eta\,\psi_0$ is an allowed variation of $\hat{\phi}_{\pm}^{(2)}$ with $\delta\eta$ real or pure imaginary

then we will have $(\psi_0, \hat{\phi}_{\pm}^{(2)}) = 0$. Similarly $\Delta\hat{\phi}_{\mp}^{(2)} = \delta\eta\,\psi_0$

allowed yields $(\psi_0, \hat{\phi}_{\mp}^{(2)}) = 0$. (<u>Problem</u>: Prove all this.)

(D) For E_0 the ground state it is easy to show (<u>Problem</u>: Do this)

that

$$\hat{L}_{+}^{(2)} \geqslant L_{+}^{(2)} \quad \text{AND} \quad \hat{L}_{+}^{(4)} \geqslant L_{+}^{(4)}$$

For all positive ω, while

$$\hat{L}_-^{(\omega)} \geqslant L^{(\omega)}$$

only if $\omega < E' - E_0$ where E' is the lowest excited state which can appear in $\Phi^{(1)}$, and

$$\hat{L}_-^{(\omega)} \geqslant L^{(\omega)}$$

only for $2\omega < E'' - E_0$

where E'' is the first excited state which can appear in $\Phi^{(2)}$.

Since from (XXVII-7), (XXVII-12), and (4) we know that $-(\hat{L}_+^{(\omega)} + \hat{L}_-^{(\omega)})$ yields a variational approximation to the diagonal component of α , it now further follows that we have a variational lower bound for this quantity for frequencies below the first resonance.

To extend the bound beyond the first resonance one can for example follow procedures analogous to those discussed in Sec. XIX in connection with the applications of the Hylleraas variational principle to excited states. The first approach would simply be to put the lower states into exactly. Thus if there are T states with energies $E_t < E_0 + \omega$ (and which are of appropriate symmetry to appear in $\phi_-^{(\omega)}$) then if we use trial function of the form

$$\tilde{\phi}_-^{(\omega)} = \sum_{t=1}^{T} \hat{a}_t \psi_t + \tilde{\gamma}$$

where $\tilde{\gamma}$ is independent of the $\hat{a}_t$ it will follow (Problem: Prove this) that

$$\hat{L}_-^{(\omega)} \geqslant L^{(\omega)}$$

(XXX-7)

for

$$E_{0+w} < E_{T+1} \qquad\qquad (XXX-8)$$

Alternatively one may ask what will happen if one uses linear trial functions of the form

$$\sum_{K=2}^{M} \tilde{b}_K \gamma_K$$

where

$$(\gamma_K, H\gamma_L) = \epsilon_K \delta_{KL} \quad \text{and} \quad (\gamma_K, \gamma_L) = \delta_{KL}$$

and where there are T of the ϵ_K which are $< E_{0+w}$?

To see the answer we first note that $\tilde{L}^{(w)}_-$ is very similar to $\hat{J}^{(w)}_K$ but has E_{0+w} instead of $E^{(w)}$, H instead of $H^{(w)}$, and W_1 instead of $H^{(w)}$. Thus we can simply take over the discussion of Sec. XIX with appropriate changes in notation. (For an alternative discussion see Kolker, J. Chem. Phys. <u>49</u>, 3106 (1968).) Thus the result following (XIX-6) becomes

$$\tilde{L}^{(w)}_- (M+1) < \tilde{L}^{(w)}_- (M) \quad , \quad \epsilon_T < E_{0+w} < \epsilon'_{T+1} \qquad (XXX-9)$$

[We are assuming here that none of the $(\phi, H\gamma_K)$ vanish. In practice (see Sec. XXXI) this will not be true. However, as was the case in Sec. XIX, this does not affect the general result] Now suppose that we add on one more function. Then we will have, in obvious notation

$$\tilde{L}^{(w)}_- (M+2) < \tilde{L}^{(w)}_- (M+1) \quad ; \quad \epsilon'_T < E_{0+w} < \epsilon''_{T+1}$$

But now ϵ''_{T+1} is $< \epsilon'_{T+1}$ and ϵ'_T is $< \epsilon_T$ so we can combine (9) –
(10) and write

$$\hat{L}^{(\omega)}_-(M+2) < \hat{L}^{(\omega)}_-(M) \quad , \quad \epsilon_T < E_{0+\omega} < \epsilon''_{T+1} \tag{XXX-11}$$

whence as we add on more and more functions we conclude that

$$L^{(\omega)}_- < \hat{L}^{(\omega)}_-(M) \quad , \quad \epsilon_T < E_0 + \omega < E_{T+1} \tag{XXX-12}$$

Thus if there are T of the ϵ_K below $E_{0+\omega}$, then we will have a
lower bound to the diagonal part of $\vec{\alpha}$ in the range $\epsilon_T < E_{0+\omega} < \epsilon_{T+1}$
[Note that to know the range one must know E_{T+1}]. To get some insight
into this result it is useful to look at a graph. $L^{(\omega)}_-$ has the form

$$L^{(\omega)}_- = \sum \frac{|\ |^2}{E_{0+\omega} - E_K}$$

while $\hat{L}^{(\omega)}_-(M)$ has the structure

$$\hat{L}^{(\omega)}_-(M) = \sum_1^M \frac{|\ |^2}{E_{0+\omega} - E_K}$$

whence we have

E_T ϵ_T E_{T+1} ϵ_{T+1}

region of the bound
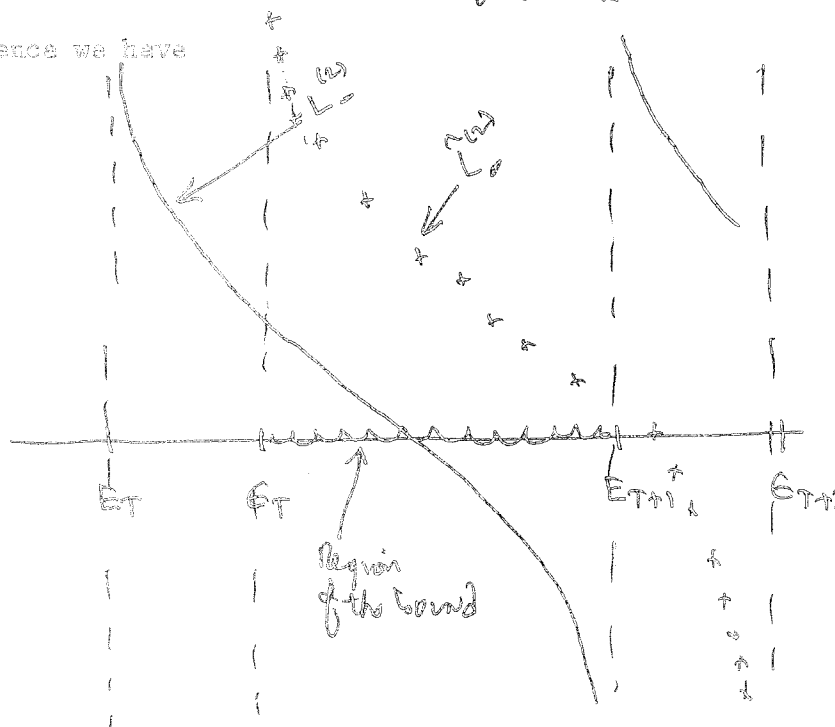
Thus for part of the range the inequality (12) is trivial -- $\tilde{L}^{(2)}_-$ has a pole in the wrong place. However it is not all that trivial since, for example, it does not seem to be true that the inequality is reversed for

$$\epsilon_{T+1} < E_0 + \omega < \epsilon_{T+1}$$

Problem: Evidently, from the work of Sec. XIX it follows that

$$\tilde{L}^{(2)}_-(M) < \tilde{L}^{(2)}_-(M+1) \quad , \quad \epsilon'_{T+1} < E_0 + \omega < \epsilon_{T+1}$$

Can one draw any interesting conclusions from this?

Consider the very special case in which if $\epsilon_1, \epsilon_2 \cdots$ are the states which occur in $L^{(4)}_-$, then $\epsilon_1 < \epsilon_1 < \epsilon_2 < \epsilon_2$ --- . Then the regions in which we have a bound are shown in the following diagram

XXXI. Linear Variational Parameters -- Sum Rules

In the preceding section we noted that $\tilde{L}^{(2)}_\pm$ look just like $\tilde{J}^{(2)}_{\pm q}$ except that $E^{(v)}$ has been replaced by $E_T \pm \omega$ and different symbols are used for the operators. Thus with a suitable change in notation we may take over the discussion of linear variational parameters directly from Sec. XVIII. We will consider $\hat{\Phi}^{(4)}_+$ in detail. A similar discussion of course holds for $\hat{\Phi}^{(4)}_-$. Since, as discussed in Sec. XXX-C, we want $\Delta \hat{\Phi}^{(4)}_\pm = \delta \eta \Psi_0$ to be an allowed variation, we therefore make Ψ_0 a member of the set whence we have from (XVIII-8) that

$$\hat{\phi}_+^{(1)} = -\sum_{k=2}^{M} \gamma_k \frac{(\gamma_k, w_+ \psi_0)}{\epsilon_k - \epsilon_0 + w}$$

and from (XVIII-9) or (XXX-8) that

$$\hat{L}_+^{(2)} = -\sum_{k=2}^{M} \frac{|(\gamma_k, w_+ \psi_0)|^2}{\epsilon_k - \epsilon_0 + w} \tag{XXXI-1}$$

Now as is well know, the exact "generalized oscillator strengths"

$(\epsilon_k - \epsilon_0)|(\psi_k, w_+ \psi_0)|^2$ satisfy various sum rules. For example,

$$\sum_{k=2}^{\infty} |(\psi_k, w_+ \psi_0)|^2 = (\psi_0, w_- w_+ \psi_0)$$

and

$$\sum_{k=0}^{\infty} (\epsilon_k - \epsilon_0)|(\psi_k, w_+ \psi_0)|^2 = (\psi_0, w_- [H, w_+] \psi_0)$$

the latter, in the case of the spatially uniform electric field, being the famous Thomas-Reichs-Kuhn sum rule.

We now ask, do the approximate generalized oscillator strengths

$$(\epsilon_k - \epsilon_0)|(\gamma_k, w_+ \psi_0)|^2$$

satisfy similar rules? That is do we have (recall $\gamma_1 = \psi_0$)

$$\sum_{k=1}^{M} |(\gamma_k, w_+ \psi_0)|^2 = (\psi_0, w_- w_+ \psi_0) \tag{XXXI-2}$$

and

$$\sum_{k=1}^{M} (\epsilon_k - \epsilon_0)|(\psi_k, w_+ \psi_0)|^2 = (\psi_0, w_- [H, w_+] \psi_0) \tag{XXXI-3}$$

In particular since the TRK sum rule is, as is well know, linked

to $xp - px = i\hbar$ one might, in $light$ of the discussion at the

end of Sec. VIII, doubt the validity of (3). We will now show that

(2) and (3) <u>are</u> satisfied if $W_+ \Psi_0$ is in the span of trial functions. Namely

introducing the Π operator of Sec. VIII, we certainly have, for

example, that (<u>Problem</u>: Prove this)

$$\sum_{k=1}^{M} |(\chi_k, W_+ \Psi_0)|^2 = \sum_{k=1}^{M} (\Psi_0, W_- \chi_k)(\chi_k, W_+ \Psi_0) = (\Psi_0, W_- \Pi W_+ \Psi_0)$$

But now to say that $W_+ \Psi_0$ is in the span means that

$$\Pi W_+ \Psi_0 = W_+ \Psi_0$$

whence we have (2). Similarly (<u>Problem</u>: Fill in the details)

$$\sum_{k=1}^{M} (E_k - E_0)|(\chi_k, W_+ \Psi_0)|^2 = \sum_{k=1}^{M} (E_k - E_0)(\Psi_0, W_- \chi_k)(\chi_k, W_- \Psi_0)$$

$$= \sum_{k=1}^{M} (\Psi_0, W_- \chi_k)(\chi_k, [\Pi H \Pi W_+ - W_+ H]\Psi_0)$$

$$= (\Psi_0, W_- \Pi [\Pi H \Pi W_+ - W_+ H]\Psi_0)$$

$$= (\Psi_0, W_- \Pi H \Pi W_+ \Psi_0) - (\Psi_0, W_- \Pi W_+ H \Psi_0)$$

$$= (\Pi W_+ \Psi_0, \Pi W_+ \Psi_0) - (\Pi W_+ \Psi_0, H \Psi_0)$$

which if $\Pi W_+ \Psi_0 = W_+ \Psi_0$ becomes (3)

<u>Problem</u>: Discuss the status of the sum rules involving
$(E_k - E_0)^{\nu}$ and $(E_k - E_0)^2$

So far our discussion of sum rules has been restricted to the case of linear parameters only. If we introduce non-linear parameters as well, then of course, the simple form (i) will be destroyed -- the approximate generalized oscillator strengths will, so to speak, become frequency dependent. However for $L_+^{(2)}$ one has

$$L_+^{(2)} \xrightarrow[\omega \to \infty]{} \frac{\sum |(\psi_k, W_+ \psi_0)|^2}{\omega} + \frac{\sum (E_k - E_0)|(\psi_k, W_+ \psi_0)|^2}{\omega^2}$$

whence we can still ask in a general way whether or not as $\omega \to \infty$ one has

$$L_+^{(2)} \xrightarrow[\omega \to \infty]{} \frac{(\psi_0, W_- W_+ \psi_0)}{\omega} + \frac{(\psi_0, W_- [H, W_+] \psi_0)}{\omega^2} \qquad \text{(XXXI-4)}$$

We will now show that this will almost certainly be the case if

$$\Delta \hat{\phi}_+^{(n)} = \delta \eta \, W_+ \psi_0 \quad , \quad \Delta \hat{\phi}_+^{(n)} = \delta \eta \, \psi_0 \quad \text{and} \quad \Delta \hat{\phi}_+^{(n)} = \delta \eta \, \hat{\phi}_+^{(n)}$$

with $\delta \eta$ real or pure imaginary, are all allowed variations, as was of course true in the linear case which we have just discussed. The point is simply that in order to guarantee that these variations be allowed the space of trial functions will presumably be made up of functions of the form

$$\tilde{a} \, W_+ \psi_0 + \tilde{b} \, \tilde{\chi} + \tilde{c} \, \psi_0$$

where $\tilde{a}$, $\tilde{b}$ and $\tilde{c}$ are arbitrary variational parameters, and where $\tilde{\chi}$ can be anything so long as it does not depend explicitly on $\tilde{a}$, $\tilde{b}$ or $\tilde{c}$. But now with $\tilde{\chi}$ fixed we have a linear space with ψ_0 and $W_+ \psi_0$ members, whence (4) will be satisfied, and since it will be satisfied for any $\tilde{\chi}$ it will also be satisfied by the optimal choice $\hat{\chi}$.

XXXII.   Applications

Here we will content ourselves with citing references and making brief comments. Most of the calculations are concerned with the calculation of $\overleftrightarrow{\alpha}(\omega)$ and since in these cases usually $(\psi_0, \omega_2 \psi_0) \approx 0$ there is no difference between $\psi_2^{\prime}$ and $\phi_2^{\prime\prime}$.

(1)   Karplus and Kolker -- J. Chem. Phys. $\underline{39}$, 1493 (1963). This is a fundamental paper and contains many references to earlier work. The exact solution for hydrogen is derived and the variational approach is tested on hydrogen and on the harmonic oscillator.

(2)   Karplus and Kolker -- J. Chem. Phys. $\underline{39}$, 2997 (1963). Here a kind of uncoupled Hartree-Fock approximation (see Langhoff et. al. J. Chem. Phys. $\underline{44}$, 505 (1966)) is discussed and applied to Helium. That is H is replaced by $H^{(0)} = H_{HF}$ for the isolated atom. ψ_0 is then ψ_{HF} for the isolated atom.

(3)   Chan and Dalgarno, Proc. Phys. Soc. $\underline{86}$, 772 (1965) -- $\alpha(\omega)$ is calculated for the ground state of Helium. H is in effect replaced by the Sternheimer Hamiltonian appropriate to the approximation to ψ_0 which is used. The linear variational method is used and the conditions of the preceding section are met whence the TRK sum rule was found to be satisfied (The Sternheimer H involves only Local potentials which is all that one needs to get TRK). Similar calculations have been made for H_2 by Victor et. al., Proc. Phys. Soc. $\underline{92}$, 42 (1967).

(4)   Victor et. al., Proc. Phys. Soc. $\underline{1}$, 13 (1968). Here various metastable states of H_2 are considered. The linear variational method is

is used however though ψ_0 is again not exact (though hopefully accurate) H is apparently not replaced by the Sternheimer approximation. Nevertheless the results seem quite good, and in particular the TRK sum rule is nearly satisfied.

(5) Stacey and Dalgarno, J. Chem. Phys. 48, 2515 (1968). Here $\alpha(\omega)$ is calculated for the ground state of Li . Probably the Sternheimer approximation is made (the TRK sum rule is well satisfied).

XXXIII. The Variational Method II -- The Heinrichs Variational Principle

(Phys. Rev. 172, 1315 (1968); Erratum 176, 2168 (1968))

Continuing on the path which was outlined at the beginning of Sec. XII, we now want to unify the two variational principles which we have found; to show, so to speak, that they are no accident, that it was no accident that $\phi^{(2)}$ could be eliminated from $\langle w^{(3)}\rangle_t$ etc.

Now in stationary state theory we have a variational principle for the total energy, whereas $\langle w \rangle$ is rather like the expectation value of the perturbation, i.e., part of the energy. In stationary state theory the total energy and the "perturbation energy" can be related via the Hellmann-Feynman Theorem for $\sigma = \mu$, i.e., $\frac{\partial E}{\partial \mu} = (\psi, w\psi)/(\psi,\psi)$. A similar result is true here. [There is also the result $\frac{d}{dt}(\Phi, H\Phi) = (\Phi, \frac{\partial H}{\partial t}\Phi)$, however this isn't especially useful to us]. In Section XVIII we derived the time dependent Hellman-Feynman theorem. The time has come to use it. It reads, for $\sigma = \mu$

$$(\Phi, w\Phi) = i\frac{\partial}{\partial t}(\Phi, \frac{\partial \Phi}{\partial \mu})$$

(XXXIII-1)

Now let us write

$$\Psi = \chi \, e^{-i\theta} \tag{XXXIII-2}$$

without further specifying χ and θ for the moment except to say that θ is a real function of the time alone, and hence that the norm of is independent of time. Then (1) becomes

$$W \equiv \frac{(\chi, w\chi)}{(\chi, \chi)} = \frac{\partial \theta^{\circ}}{\partial \mu} + i \frac{\partial}{\partial t} \left(\chi, \frac{\partial \chi}{\partial \mu}\right) \Big/ (\chi, \chi) \tag{XXXIII-3}$$

where

$$\theta^{\circ} \equiv \frac{\partial \theta}{\partial t}$$

We now confine attention to the simple harmonic case. Then let us further suppose that the split between χ and θ in (2) is such that χ contains only periodic terms. For example this is true of the split we have discussed

$$\chi = \frac{\Phi}{(\Phi, \Phi)^{\chi}} \quad , \quad (\Psi_0, \Phi) = 1$$

however, there are clearly many other possibilities since we may transfer periodic terms from θ to χ. In any case, for such a split, $\left(\chi, \frac{\partial \chi}{\partial \mu}\right)$ will also be periodic, whence if we average (3) over a period we have (remember (χ, χ) is independent of t)

$$\langle W \rangle_T = \frac{\partial}{\partial \mu} \langle \theta^{\circ} \rangle \equiv \frac{\partial \varepsilon}{\partial \mu}$$

We will now exhibit a variational expression for ε. This will then unify the results we have found so far. It immediately explains the fact that we could find variational principles for the $\langle w^{(n)} \rangle$. Further the existence of a variational principle will imply that if we know the

wave function to order μ^n we can calculate $\mathcal{E}$ to order μ^{2n+1} and hence can calculate $\langle w \rangle$ to order μ^{2n} . Thus, as we found, to calculate $\langle w^{(4)} \rangle$ we don't need $\mathcal{E}^{(3)}$. (In Sec. XXXIV we will derive a general μ^{2n+1} theorm.)

Before exhibiting the variational principle there is one point that should be discussed. In the static limit θ° becomes the energy and hence one would think that this would become the usual variational principle for the energy. On the other hand we have found $\langle w^{(n)} \rangle_T = 0$ for n even which means $\mathcal{E}^{(n)} = 0$ for n odd. Thus clearly we won't get the whole variational principle in the static limit. In fact, we will get exactly ^(what we have found so far, namely) the Hylleraas variational principle and its generalizations. The point is simply that where one has oscillating terms

$$\langle \theta^{\circ}(\omega = 0) \rangle_T \quad \neq \quad \langle \theta^{\circ} \rangle_T (\omega = 0)$$

i.e. $\langle e^{i\omega t} \rangle_T = 0$ while $\langle 1 \rangle_T = 1$

To write down the variational principle we note that from the Schroedinger equation and (2) it follows that

$$(H - \theta^{\circ}) \chi = i \frac{\partial \chi}{\partial t} \qquad \text{(XXXIII-5)}$$

whence

$$\theta^{\circ}(\chi, \chi) = (\chi, (H - i \frac{\partial}{\partial t}) \chi)$$

Now consider a trial function $\tilde{\chi}$ which contains only periodic terms and whose norm is constant in time. Then define $\tilde{\theta}^{\circ}$ by

$$\tilde{\theta}^{\circ}(\tilde{\chi}, \tilde{\chi}) \equiv (\tilde{\chi}, (H - i \frac{\partial}{\partial t}) \tilde{\chi}) \qquad \text{(XXXIII-6)}$$

We will now show that $\langle \widehat{\theta'} \rangle_T \equiv \widetilde{\mathcal{E}}$ differs from $\mathcal{E}$ by second order quantities. (Problem: Show that $\widetilde{\theta'}$ is real and periodic.) Thus if we average (6) over a period we will have a variational expression with which to approximate $\mathcal{E}$. To show this we write

$$\widetilde{\chi} = \chi + \Delta$$

Then using (5) we find (Problem: Fill in the details.).

$$\widetilde{\theta'}(\widetilde{\chi}, \widetilde{\chi}) = \theta' \left[(\chi, \chi) + (\Delta, \chi) + (\chi, \Delta) \right] - i \frac{\partial}{\partial t}(\chi, \Delta)$$

$$+ (\Delta, (H - i\frac{\partial}{\partial t})\Delta)$$

$$= \theta'(\chi, \chi) - i \frac{\partial}{\partial t}(\chi, \Delta) + (\Delta, (H - i\frac{\partial}{\partial t} - \theta')\Delta)$$

Now let us average over a period. Since χ and $\widetilde{\chi}$ are both periodic, so therefore is Δ, whence the average of $\frac{\partial}{\partial t}(\chi, \Delta)$ will vanish and we will have, since $(\chi, \widetilde{\chi})$ is constant

$$\widehat{\mathcal{E}} = \mathcal{E} + O(\Delta^2)$$

as announced.

Thus the Heinrich's variational method can be stated as follows: We introduce the functional

$$\widetilde{\mathcal{L}} \equiv \left\langle (\widetilde{\chi}, (H - i\frac{\partial}{\partial t} - \widetilde{\mathcal{E}})\widetilde{\chi}) \right\rangle_T$$

with $\widetilde{\chi}$ periodic and with $\frac{\partial}{\partial t}(\widetilde{\chi}, \widetilde{\chi}) = 0$. Then $\widehat{\chi}$ and $\widehat{\mathcal{E}}$ are determined by

$$\delta \widehat{\mathcal{L}} = 0 \qquad \text{and} \qquad \widehat{\mathcal{L}} = 0$$

<u>Problem</u>: Prove that if the space of trial functions is independent of μ then

$$\frac{\partial \hat{\tilde{E}}}{\partial \mu} = (\hat{\chi}, w\hat{\chi})/(\hat{\chi},\hat{\chi})$$

Introduce a second perturbation and deriving "the prevalence interchange theorems" (See XX $\hat{\chi}$)

Let us now rederive our first order variational principles from this general formulation. To this end we write

$$\hat{\chi} = \psi_0 + \mu \hat{\chi}_+^{(1)} e^{i\omega t} + \mu \hat{\chi}_-^{(1)} e^{-i\omega t}$$
$$+ \mu^2 \hat{\chi}_+^{(2)} e^{2i\omega t} + \mu^2 \hat{\chi}_0^{(2)} + \mu^2 \hat{\chi}_-^{(2)} e^{-2i\omega t} + \cdots \tag{XXXIII-7}$$

and

$$\delta\hat{\chi} = \mu \, \delta\hat{\chi}_+^{(1)} e^{i\omega t} + \mu \, \delta\hat{\chi}_-^{(1)} e^{-i\omega t}$$
$$+ \mu^2 \, \delta\hat{\chi}_+^{(2)} e^{2i\omega t} + \mu^2 \, \delta\hat{\chi}_0^{(2)} + \mu^2 \, \delta\hat{\chi}_-^{(2)} e^{-2i\omega t} + \cdots$$

where of course there must be relations among the $\hat{\chi}^{(n)}$ in order that the norm of $(\hat{\chi},\hat{\chi})$ be constant, but for the moment we ignore them. If now we calculate $(\hat{\chi}, (\hat{H} - i\frac{\partial}{\partial t})\hat{\chi})$ then through second order the only terms independent of time, i.e. the only terms which will survive the averaging over a period, are

$$(\psi_0, H\psi_0) + \mu^2 \left[(\psi_0, w_+ \hat{\chi}_-^{(1)}) + (\psi_0, w_- \hat{\chi}_+^{(1)}) + c.c. \right]$$
$$+ \mu^2 \left[(\hat{\chi}_+^{(1)}, (H+w)\hat{\chi}_+^{(1)}) + (\hat{\chi}_-^{(1)}, (H-w)\hat{\chi}_-^{(1)}) \right]$$
$$+ \mu^2 \left[(\psi_0, H\hat{\chi}_0^{(2)}) + (\hat{\chi}_0^{(2)}, H\psi_0) \right] + O(\mu^4)$$

If now we write

$$\hat{\tilde{E}} = \hat{E}^{(0)} + \mu \hat{E}^{(1)} + \mu^2 \hat{E}^{(2)} + \cdots$$

then since $(\hat{\psi}, \hat{\psi})$ will be made constant we have

$$\hat{\mathcal{E}} \langle (\hat{\psi}, \hat{\psi}) \rangle_T = \hat{\mathcal{E}}^{(0)} (\psi_0, \psi_0) + \mu \, \hat{\mathcal{E}}^{(1)} (\psi_0, \psi_0) + \mu^2 \hat{\mathcal{E}}^{(2)} (\psi_0, \psi_0)$$

$$+ \mu^2 \, \hat{\mathcal{E}}^{(0)} [(\hat{\psi}_+^{(1)}, \hat{\chi}_+^{(1)}) + (\hat{\psi}_-^{(1)}, \hat{\chi}_-^{(1)}) $$

$$+ (\psi_0, \hat{\chi}_0^{(2)}) + (\hat{\psi}_0^{(2)}, \psi_0)]$$

$$+ O(\mu^3)$$

whence through second order we have

$$\hat{\mathcal{J}} = (\psi_0, (H - \hat{\mathcal{E}}^{(0)}) \psi_0) + \mu \, \hat{\mathcal{E}}^{(1)} (\psi_0, \psi_0) + \mu^2 \Big\{$$

$$\Big[(\hat{\psi}_+^{(1)}, (H - \hat{\mathcal{E}}^{(0)} + \omega) \hat{\chi}_+^{(1)}) + (\psi_0, w_- \hat{\chi}_+^{(1)}) + (\hat{\psi}_+^{(1)}, w_+ \psi_0) \Big]$$

$$+ \Big[(\hat{\psi}_-^{(1)}, (H - \hat{\mathcal{E}}^{(0)} - \omega) \hat{\chi}_-^{(1)}) + (\psi_0, w_+ \hat{\chi}_-^{(1)}) + (\hat{\psi}_-^{(1)}, w_- \psi_0) \Big]$$

$$+ \Big[(\psi_0, (H - \hat{\mathcal{E}}^{(0)}) \hat{\chi}_0^{(2)}) + (\hat{\chi}_0^{(2)}, (H - \hat{\mathcal{E}}^{(0)}) \psi_0) \Big] - \hat{\mathcal{E}}^{(2)} (\psi_0, \psi_0) \Big\} + --$$

and we have the conditions

$$\delta \hat{\mathcal{J}} = 0 \qquad \text{and} \qquad \hat{\mathcal{J}} = 0 \quad \text{all } \mu$$

Now the condition that $(\hat{\psi}, \hat{\psi})$ be independent of time requires that $(\psi_0, \hat{\psi}_+^{(1)}) + (\hat{\psi}_-^{(1)}, \psi_0)$ should vanish. (<u>Problem</u>: Prove this.) In accord with our earlier definition of χ which makes $\chi_{\pm}^{(1)} = \psi_{\pm}^{(1)}$ we will strengthen this and require that

$$(\psi_0, \hat{\chi}_{\pm}^{(1)}) = 0 \hspace{4cm} \text{(XXXIII-8)}$$

To implement this one could of course simply restrict the space of trial functions to be orthogonal to ψ_0 . A more flexible procedure is to introduce new constants into $\hat{\ell}$, constants which are to be adjusted in such a way that the optimal $\hat{\chi}_{\pm}^{(1)}$ will satisfy (δ), and which are introduced in such a way that, when (δ) is satisfied, they make no contribution to the numerical value of $\hat{\ell}$. This latter precaution, coupled with the fact that $(\hat{\psi},\hat{\psi})$ will be constant, then leaves undisturbed the statement that $\hat{\xi} - \xi$ is of second order in the error in $\hat{\chi}$. (These constants are usually referred to as Lagrangian multipliers.)

Thus we write

$$\hat{\ell} = (\psi_0, (H - \hat{\xi}^{(0)}) \psi_0) - \mu \hat{\xi}^{(1)}(\psi_0,\psi_0) - \mu^2 \hat{\xi}^{(2)}(\psi_0,\psi_0)$$
$$+ \mu^2 \left[(\psi_0, (H - \hat{\xi}^{(0)})\hat{\chi}_0^{(2)}) + (\hat{\chi}_0^{(2)},(H - \hat{\xi}^{(0)})\psi_0) \right]$$
$$+ \mu^2 [\ ]_+ + \mu^2 [\ ]_- + \cdots$$

where

$$[\ ]_{\pm} = (\hat{\chi}_{\pm}^{(1)}, (H - \hat{\xi}^{(0)} \pm \omega) \hat{\chi}_{\pm}^{(1)}) + (\hat{\chi}_{\pm}^{(1)}, (w_{\pm} - \gamma_{\pm})\psi_0)$$
$$+ (\psi_0, (w_{\mp} - \gamma_{\pm}^*)\hat{\chi}_{\pm}^{(1)})$$

and where $\gamma_{\pm}$ are the constants referred to above. From $\hat{\ell} = 0$ we learn from the zero order terms that as expected

$$\hat{\xi}^{(0)} = (\psi_0, H\psi_0)/(\psi_0,\psi_0) \equiv E_0 \qquad \text{and therefore} \quad (H - \hat{\xi}^{(0)})\psi_0 = 0 \quad,$$

and from the first order terms we learn as expected that
$$\hat{\xi}^{(1)} = 0$$

Then from the second order term we find, using $(\psi_0, \psi_0) = 1$, that

$$\hat{\mathcal{E}}^{(2)} = [\ ]_+ + [\ ]_-$$

(Note that from the Hellmann-Feynman theorem $\langle \hat{w}^{(2)} \rangle = 2\, \hat{\mathcal{E}}^{(2)}$.) Further varying $\hat{\gamma}_0^{(2)}$ in any way yields a contribution to $\delta\hat{f}$ which vanishes identically. ~~Further varying~~ Further varying $\hat{\gamma}_1^{(2)}$ and setting $\delta\hat{f} = 0$ evidently gives us the variational principles which we had before except that $\hat{\gamma}_2$ appears instead of $(\psi_1, w_1 \psi_0)$. However, if $\Delta\hat{\gamma}_2 = \delta\eta\,\psi_0$ are allowed with $\delta\eta$ real or pure imaginary then the requirement that $(\psi_0, \hat{\gamma}_2^{"}) = 0$ yields $\hat{\gamma}_2 = (\psi_1, w_1 \psi_0)$ and we are back where we started from. (Problem: Prove this.)

Suppose that w_e would use, instead of (7),

$$\hat{\gamma} = \hat{\gamma}_0 + \hat{\gamma}_+ e^{i\omega t} + \hat{\gamma}_- e^{-i\omega t}$$

Then evidently we would find

$$\hat{f} = (\hat{\gamma}_0, (H - \hat{\mathcal{E}})\hat{\gamma}_0) + [\ (\hat{\gamma}_+, (H - \hat{\mathcal{E}} + \omega)\hat{\gamma}_+) \ +$$

$$(\hat{\gamma}_+, (\mu W_+ - \hat{\gamma}_+)\hat{\gamma}_0) + (\hat{\gamma}_0, (\mu W_- - \hat{\gamma}_+^*)\hat{\gamma}_+)\ ]$$

For such a $\hat{\gamma}$ one does not in general have $\frac{d}{dt}(\hat{\gamma}, \hat{\gamma}) = 0$ however if $(\hat{\gamma}_0, \hat{\gamma}_1) = 0$ then if we use $\delta\hat{f} = 0, \ \hat{f} = 0$ only for $\underline{\text{small}}$ values of μ , this discrepancy will be of "higher" order. This $\hat{f}$ is essentially the functional discussed and apparently used with success by Chung in his work on Helium (Phys. Rev. $\underline{166}$, 1 (1968). One varies both $\hat{\gamma}_0$ and $\hat{\gamma}_\pm$ and from $\delta\hat{f} = 0, \ \hat{f} = 0$ finds $\hat{\mathcal{E}}$ for a series of small values of μ . The result is fitted to a polynomial in μ and $\hat{\mathcal{E}}(w)$ is extracted. (Note that in general $\hat{\gamma}_0$ will not be independent of μ nor will $\hat{\gamma}_\pm$ be linear in μ).

XXXIV. A General $\int^{2n\gamma)}$ Theorem

We will simply prove the theorem. The applications are very
similar to those discussed in Sec. XVI for the analogous theorem for
stationary states. From $(XXXIII-6)$

$$\tilde{\theta}'\,(\hat{\chi},\hat{\chi}) = (\hat{\chi},\,(\mathcal{H} - i\tfrac{\partial}{\partial t})\hat{\chi}) \tag{XXXIV-1}$$

also

$$\hat{\theta}\,'\,(\hat{\chi},\hat{\chi}) = (\hat{\chi},\,(\mathcal{H} - i\tfrac{\partial}{\partial t})\hat{\chi}) \tag{XXXIV-2}$$

we assume that $\hat{\chi}$ and $\hat{\chi}$ are periodic and that $(\hat{\chi},\hat{\chi})$ and $(\hat{\chi},\hat{\chi})$ are independent of tome.

Now let

$$\hat{\chi} = \hat{\chi} + \delta \tag{XXXIV-3}$$

Then (1) and (2) yield

$$\tilde{\theta}'\,(\hat{\chi},\hat{\chi}) = \hat{\theta}'\,(\hat{\chi},\hat{\chi}) + (\hat{\chi},\,(\mathcal{H} - i\tfrac{\partial}{\partial t})\,\delta)$$
$$+ (\delta,\,(\mathcal{H} - i\tfrac{\partial}{\partial t})\,\hat{\chi})$$
$$+ (\delta,\,(\mathcal{H} - i\tfrac{\partial}{\partial t})\,\delta) \tag{XXXIV-4}$$

But

$$(\tilde{\chi},\tilde{\chi}) = (\hat{\chi},\hat{\chi}) + (\hat{\chi},\delta) + (\delta,\hat{\chi}) + (\delta,\delta)$$

So (4) becomes

$$\tilde{\theta} = \hat{\theta}^{\,\circ} + \frac{\left\{(\hat{\chi}, (\mathcal{H} - i\frac{\partial}{\partial t} - \hat{\theta}^{\,\prime})\delta) + (\delta, (\mathcal{H} - i\frac{\partial}{\partial t} - \hat{\theta}^{\,\prime})\hat{\chi}\right\}}{(\hat{\chi}, \hat{\chi})}$$

$$+ \frac{(\delta, (\mathcal{H} - i\frac{\partial}{\partial t} - \hat{\theta}^{\,\prime})\delta)}{(\hat{\chi}, \hat{\chi})}$$

Now average over a period and remember that $(\hat{\chi}, \hat{\chi})$ is independent of time. Then we see that if

$$\delta = O(\mu^{n+1})$$

then

$$\tilde{\varepsilon} = \hat{\varepsilon} + O(\mu^{2n+2})$$

Provided that the time average of $\{\ \} = O(\mu^{2n+2})$. One now readily sees that even if

$$(\mathcal{H} - i\frac{\partial}{\partial t} - \hat{\theta}^{\,\prime})\hat{\chi} = 0$$

then this will be the case if δ = Allowed variation in the Heinrich's variational principle $+ O(\mu^{2n+2})$.

XXXV. The Variational Method III--The Frenkel Variational Principle

In this section we want to discuss a variational principle which has been widely used, but which, in a sense, is not a variational principle at all, since it cannot be put in the form "variation of something equal to zero". Rather it is more like a method of moments

approach. The principle is simply

$$\left(\delta\hat{\Psi}, \left(\mathscr{H} - i\frac{\partial}{\partial t} \right) \hat{\Psi} \right) + \left(\left(\mathscr{H} - i\frac{\partial}{\partial t} \right) \hat{\Psi}, \delta\hat{\Psi} \right) = 0 \qquad \text{(XXXV-1)}$$

or, if there are no restrictions on reality,

$$\left(\delta\hat{\Psi}, \left(\mathscr{H} - i\frac{\partial}{\partial t} \right) \hat{\Psi} \right) = 0 \qquad \text{(XXXV-2)}$$

which, for $\delta\hat{\Psi}$ completely arbitrary clearly leads to the time dependent Schroedinger equation.

In particular note that (1) can be written

$$\delta\left(\hat{\Psi}, \left(\mathscr{H} - i\frac{\partial}{\partial t} \right) \hat{\Psi} \right) - i\frac{\partial}{\partial t} \left(\hat{\Psi}, \delta\hat{\Psi} \right) = 0 \qquad \text{(XXXV-3)}$$

thus showing fairly convincingly that it is not in the form of "variation of something = 0". On the other hand if we integrate (3) over time and require that $\delta\hat{\Psi}$ vanish at the end points, then we do have a more standard sort of variational principle

$$\delta\int_{t_1}^{t_2} dt \left(\hat{\Psi}, \left(\mathscr{H} - i\frac{\partial}{\partial t} \right) \hat{\Psi} \right) = 0 \qquad ; \quad \delta\hat{\Psi}(t_2) = \delta\hat{\Psi}(t_1) = 0 \qquad \text{(XXXV-4)}$$

which is the one which is usually introduced in connection with discussions of the Schroedinger equation as a field theory. However (4) is not of much use to us. With $t_1 = -\infty$, the condition $\delta\hat{\Psi}(-\infty) = 0$ would make sense — we could require that all our trial functions satisfy the proper initial conditions. However what does one do about t_2 ? A generalization of (4) has however found use in the theory of transition probabilities (see Demkov's book "Variation Principles in the Theory of Collisions" MacMillan 1963).

In the simple harmonic case however, we have exhibited a variational principle -- the Heinrichs variational principle -- and hence it is of interest to see that it is contained in the Frenkel principle under appropriate conditions. Let us insert in (1), the by now familiar form

$$\hat{\Psi} = \hat{\chi} e^{-i\hat{\theta}}$$

$$\delta\hat{\Psi} = \delta\hat{\chi}\, e^{-i\hat{\theta}} - i\,\delta\hat{\theta}\,\hat{\chi}\, e^{-i\hat{\theta}}$$

with $\hat{\theta}$ real, whence (1) becomes

$$\left(\delta\hat{\chi},\ \left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi}\right) + \left(\left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi},\ \delta\hat{\chi}\right)$$

$$+ i\,\delta\hat{\theta}\left[\left(\hat{\chi},\ \left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi}\right) - \left(\left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi},\ \hat{\chi}\right)\right] = 0$$

Now let us suppose that

$$\left(\hat{\chi},\ \left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi}\right) = 0$$

Note that since $\hat{\theta}'$ is real this implies that $(\hat{\chi},\hat{\chi})$ is independent of time. (<u>Problem</u>: Prove this.) Then we have

$$\left(\delta\hat{\chi},\ \left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi}\right) + \left(\left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi},\ \delta\hat{\chi}\right) = 0$$

or

$$\left(\delta\hat{\chi},\ \left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\hat{\chi}\right) + \left(\hat{\chi},\ \left(H - i\frac{\partial}{\partial t} - \hat{\theta}'\right)\delta\hat{\chi}\right)$$

$$+ i\frac{\partial}{\partial t}\left(\hat{\chi},\ \delta\hat{\chi}\right) = 0$$

If now we assume that $\hat{\chi}$ and $\delta\hat{\chi}$ are periodic, then if we average over a period we recover Heinrich's var. prin.

XXXVI. The Time Dependent Linear Variational Method

If we use linear variational parameters

$$\hat{\psi} = \sum_{k=1}^{M} \hat{C}_k(t) \, \phi_k$$

with the ϕ_k independent of time and independent of μ then clearly the Frenkel variational method tells us to solve the

$$\overline{H} + \mu \, \overline{W}$$

problem exactly. In particular in terms of the χ_k, linear combinations of the ϕ_k which are eigenfunctions of $\overline{H}$, the expansions of the results in powers of μ will yield formulae having the same structure as the exact sum over states formulae except that the sums will be finite. (This assumes that as an initial condition one will naturally use $\hat{\psi} \xrightarrow[t \to -\infty]{} e^{-i\varepsilon_1 t} \chi_1$.) I believe that essentially this approach was used by Sitz and Yaris (J. Chem. Phys. 49, 3546 (1968)) in their calculation of higher order suceptibilities for Hydrogen and Helium (in the latter case ϕ_1 is an approximation to ψ_0, but H is effectively replaced by the Sternheimer Hamiltonian so that whatever one uses for $\phi_{2,\cdots}$ still $\chi_1 \equiv \phi_1$).

Incidentally this "finite state" problem has been much studied (particularly for $M=2$) in connection with non steady state behavior. See for example Shirley, Phys. Rev. 135, B979 (1965) and references given there.

XXXVII. Time Dependent Unrestricted Hartree-Fock Theory (TDURHF)

(See Dalgarno review in "Perturbation Theory and its Application in Quantum Mechanics". Wilcox ed. Also Kaveeshavar et. al. Phys. Rev. $\underline{172}$, 35 (1968) and references there.) As for the stationary states, though we could consider an arbitrary determinant, it is convenient to confine attention to normalized determinants formed from orthonormal spin orbitals. Thus we again have

$$(\delta\hat{\Phi}, \hat{\Phi}) + (\hat{\Phi}, \delta\hat{\Phi}) = 0 \qquad (\text{XXXVII-1})$$

whence if we write

$$\delta\hat{\Phi} = A\,\hat{\Phi} + \delta_1\hat{\Phi}$$

where $(\delta_1\hat{\Phi}, \hat{\Phi}) = 0$ then it follows that

$$A + A^* = 0 \qquad (\text{XXXVII-2})$$

which in turn means that the $A\hat{\Phi}$ terms' contribution to the left hand side of (XXXV-1) vanishes identically since that contribution is

$$A^* (\hat{\Phi}, (\mathcal{H} - i\tfrac{\partial}{\partial t})\hat{\Phi}) + A ((\mathcal{H} - i\tfrac{\partial}{\partial t})\hat{\Phi}, \hat{\Phi})$$

$$= (A + A^*)(\hat{\Phi}, (\mathcal{H} - i\tfrac{\partial}{\partial t})\hat{\Phi}) + i A \tfrac{\partial}{\partial t}(\hat{\Phi}, \hat{\Phi})$$

The first term in the bottom line then vanishes from (1) and the second because we have assumed that $\hat{\Phi}$ is normalized.

Thus we may confine attention to $\delta\hat{\Phi}$ which are orthogonal to $\hat{\Phi}$ and further, since we are imposing no further reality conditions, we may use the Frenkel principle in the form (XXXV-2), i.e.

$$(\delta_2 \hat{\Phi}, \ (\mathcal{H} - i \tfrac{\partial}{\partial t}) \ \hat{\Phi} \ ) = 0$$

<div align="right">(XXXVII-3)</div>

For $\delta_2 \hat{\Phi}$ then we insert a Slater determinant which differs from $\hat{\Phi}$ in that one spin-orbital, $\hat{\varphi}_s$ say, has been replaced by a spin-orbital $\delta \hat{\varphi}_s$ which is orthogonal to all the occupied spin-orbitals:

$$(\delta \hat{\varphi}_s, \hat{\varphi}_t) = 0 \qquad t = 1 \cdots N$$

<div align="right">(XXXVII-4)</div>

Evaluating the left hand side of (3) one then finds

$$(\ \delta \hat{\varphi}_s, \ (h_{HF} - i \tfrac{\partial}{\partial t}) \hat{\varphi}_s \ ) = 0$$

which, by comparison with (4), since $\delta \hat{\varphi}_s$ is otherwise arbitrary, implies that

$$(h_{HF} - i \tfrac{\partial}{\partial t}) \ \hat{\varphi}_s = \sum_t \tau_{st} \hat{\varphi}_t$$

<div align="right">(XXXVII-5)</div>

where the τ_{st} are for the moment arbitrary functions of time. (<u>Problem</u>: Fill in the details.) Now to make everything consistent the τ_{st} must be chosen so that the $\hat{\varphi}_s$ are orthonormal, and we see that we can do this most simply by putting $\tau_{st} \equiv 0$. More precisely, under these conditions if $\hat{\varphi}_s$ are chosen to be orthonormal initially they stay orthonormal, (<u>Problem</u>: Prove this.) which, clearly, is as much as we can expect from a differential equation, i.e. <u>we</u> must supply the initial conditions. Thus we have, for the "canonical orbitals"

$$(h_{HF} - i \tfrac{\partial}{\partial t}) \hat{\varphi}_s = 0$$

<div align="right">(XXXVII-6)</div>

Problem: Given the orthonormal set $\hat{e}_i$, we can find many other equivalent sets $\hat{e}'_i = \sum_\gamma U_{S\gamma} \, \hat{e}_\gamma$ where the $U_{S\gamma}$ form a unimodular, possibly time dependent matrix — show that they satisfy an equation of the form (5). *Applications:* (Variation perturbation theory through first order for He, Be, and Ne carried through by Kaveeshwar, et. al. Phys. Rev. <u>172</u>, 35 (1968). He also done by Dalgarno and Victor, Proc. Roy. Soc. <u>A</u> 291 (1966) and by Sengupta and Mukherji, J. Chem. Phys. <u>47</u>, 260 (1967).

<u>XXXVIII</u> <u>Theorems Satisfied by Optimal Trial Functions</u>

(A) Time dependent Hellmann-Feynman Theorem.

If

$$\lambda \hat{\Phi} \;=\; \frac{\partial \hat{\Phi}}{\partial \sigma} \, \delta\sigma \tag{XXXVIII-1}$$

and

$$\lambda \hat{\Phi} = \delta\eta \, \hat{\Phi} \tag{XXXVIII-2}$$

with $\delta\eta$ real and pure imaginary

are allowed then $\hat{\Phi}$ satisfies the time dependent Hellmann-Feynman

theorem. To see this we note that, inserting (1) into (XXXV-1) yields

$$\left(\frac{\partial \hat{\Phi}}{\partial\sigma}, \; \left(H - i\frac{\partial}{\partial t}\right) \hat{\Phi} \right) + \left(\left(H - i\frac{\partial}{\partial t}\right)\hat{\Phi}, \; \frac{\partial \hat{\Phi}}{\partial\sigma} \right) = 0 \tag{XXXVIII-3}$$

while (2) inserted into (XXXV-2) yields

$$\left(\hat{\Phi}, \; \left(H - i\frac{\partial}{\partial t}\right) \hat{\Phi} \right) = 0 \tag{XXXVIII-4}$$

The derivation now follows the pattern of Sec. II. (<u>Problem:</u> Fill in

the details.)

To satisfy all these conditions then one would choose the trial

functions in a σ independent way, and allow them to have arbitrary

(complex) scale. Now the first requirement is met by our TDURHF theory

and thus (3) is satisfied. However, we restricted the norm of our trial functions to be one whence one may wonder about the validity of (4). Indeed it is clear that if we use (XXXVI-6), then (4) won't be satisfied and hence the Hellmann-Feynman theorem won't be satisfied. To see this we need only note that (XXXVI-6) implies that

$$\left(\mathcal{H}_{HF} - i \frac{\partial}{\partial t} \right) \hat{\Phi}_{HF} = 0$$

and we know that

$$\left(\hat{\Phi}_{HF}, \, \mathcal{H}_{HF} \, \hat{\Phi}_{HF} \right) \neq \left(\hat{\Phi}_{HF}, \, \mathcal{H} \, \hat{\Phi}_{HF} \right)$$

when $\mathcal{H}$ includes 2 particle interactions. On the other hand it is clear how to remedy the situation. We will still preserve orthonormality if in (XXXVI-5) we choose $\mathcal{C}_{ts} = \mathcal{C}_t \delta_{ts}$ with $\mathcal{C}_t$ any real functions of time. The new orbitals will then differ from the ones defined by (XXXVI-7) by the time dependent phase factor $e^{-i \int^t \mathcal{C}_t dt'}$ whence the new determinant will differ from the old by an essential phase factor. The new determinant will satisfy (not $\mathcal{H}_{HF}' = \mathcal{H}_{HF}$)

$$\left(\mathcal{H}_{HF} - i \frac{\partial}{\partial t} - \sum \mathcal{C}_s \right) \hat{\Phi}'_{HF} = 0 \qquad \text{(XXXVII-5)}$$

so if we choose

$$\sum \mathcal{C}_s = \left(\hat{\Phi}'_{HF}, \mathcal{H}_{HF} \hat{\Phi}'_{HF} \right) - \left(\Phi'_{HF}, \mathcal{H} \hat{\Phi}'_{HF} \right)$$

$$= \left(\hat{\Phi}_{HF}, \mathcal{H}_{HF} \hat{\Phi}_{HF} \right) - \left(\hat{\Phi}_{HF}, \mathcal{H} \hat{\Phi}_{HF} \right)$$

then (4) will be satisfied and we will have the time dependent Hellmann-Feynman theorem (Problem: Fill in the details.).

or

$$i\left(\hat{\Phi}, U \frac{\partial \hat{\Phi}}{\partial t}\right) + i\left(\frac{\partial \hat{\Phi}}{\partial t}, U \hat{\Phi}\right) + \left(\hat{\Phi}, [H, U]\hat{\Phi}\right) = 0$$

which we can write as

$$\frac{d}{dt}\left(\hat{\Phi}, U \hat{\Phi}\right) = \left(\hat{\Phi}, \frac{\partial U}{\partial t} \hat{\Phi}\right) + i\left(\hat{\Phi}, [H, U]\hat{\Phi}\right) \qquad \text{(XXXVIII-8)}$$

which is the generalized Ehrenfest theorem.

If (XXXV-2) applies then, under the same conditions, we can derive the stronger result

$$\left(\hat{\Phi}, U \mathcal{H} \hat{\Phi}\right) = i\left(\hat{\Phi}, U \frac{\partial \hat{\Phi}}{\partial t}\right) \qquad \text{(XXXVIII-9)}$$

We will now show if U is a one particle operator that (7) and hence (8) hold in the unrestricted Hartree-Fock approximation whatever the choice of the $C_{\lambda s}$ so long as they make the $\hat{\ell}_s$ orthonormal. As in the analogous discussion of hypervirial theorems in the time independent theory it is not clear, from the discussion to date, that (6) is allowed. However, we can argue as follows: $U\hat{\Phi}$ with U a one particle operator (we will omit the subscripts HF) is a sum of Slater determinants, each with one orbital changed from $\hat{\Phi}$. It then follows from (XXXVI-3) that the part of each of these determinants which is orthogonal to $\hat{\Phi}$ will make a zero contribution to the left hand side of (7). Thus we may in effect replace $U\hat{\Phi}$ by

$$\hat{\Phi}\left(\hat{\Phi}, U\hat{\Phi}\right)$$

(remember that $\hat{\Phi}$ is normalized).

If we insert this into the left side of (7) we find

$$(\hat{\Phi}, \cup \hat{\Phi}) \left[-(\hat{\Phi}, (\mathcal{H} - i\frac{\partial}{\partial t})\hat{\Phi}) + ((\mathcal{H} - i\frac{\partial}{\partial t})\hat{\Phi}, \hat{\Phi}) \right]$$

$$= (\hat{\Phi}, \cup \hat{\Phi}) \, i\frac{\partial}{\partial t}(\hat{\Phi}, \hat{\Phi}) = 0 \qquad Q.E.D.$$

Problem: Prove that if the $C_{\Lambda s}$ are chosen as in (6) then (9) is satisfied.

As an application consider the frequency dependent dipole shielding constant for an atom. We will treat the nucleus as infinitely heavy. and ignore velocity dependent forces We bathe the atom in a spatially uniform simple harmonic electric field, and calculate the net field at the nucleus.

The force on the nucleus, if it has charge Z is, as in the static case which we considered earlier (Sec. XI-B)

$$\vec{F}_N = Z\vec{\mathcal{E}} + \vec{F}_{e-N}$$

where $\vec{\mathcal{E}}$ is the electric field and $\vec{F}_{e-N}$ is the force on the nucleus due to the electrons. On the other hand the net force on the electrons, if there are N electrons, is also as before

$$\vec{F}_e = -N\vec{\mathcal{E}} - \vec{F}_{e-N} \qquad \text{(XXXVIII-11)}$$

But now the "force-on-the-electrons" is the average value of the operator $i[\mathcal{H}, \vec{P}]$ where $\vec{P}$ is the total electronic momentum. Thus from Ehrenfest's theorem we have

$$\vec{F}_e = \frac{d}{dt}(\hat{\Phi}, \vec{P}\hat{\Phi})$$

and since $\vec{P}$ is a one electron operator this holds in TDUHF. Further
we have $\vec{P} = i[H, \vec{R}]$ where $\vec{R}$ is the dipole moment. Hence

$$(\hat{\Phi}, \vec{P}\,\hat{\Phi}) = \frac{d}{dt}\,(\hat{\Phi}, \vec{R}\,\hat{\Phi})$$

and since $\vec{R}$ is also a one electron operator this holds in TDUHF.

Thus we finally have the familiar result

$$\vec{F}_e = \frac{d^2}{dt^2}\,(\hat{\Phi}, \vec{R}\,\hat{\Phi})$$

whence to lowest order in the electric field

$$\vec{F}_e = -\overleftrightarrow{\alpha}\cdot\frac{d^2\vec{\mathcal{E}}}{dt^2} = \omega^2\,\overleftrightarrow{\alpha}\cdot\mathcal{E}$$

Returning to (11) we have

$$\vec{F}_{e-N} = -N\vec{\mathcal{E}} - \omega^2\,\overleftrightarrow{\alpha}\cdot\vec{\mathcal{E}}$$

whence, from (10)

$$\vec{F}_N = (Z-N)\,\vec{\mathcal{E}} - \omega^2\,\overleftrightarrow{\alpha}\cdot\vec{\mathcal{E}}$$

$$\equiv Z\vec{\mathcal{E}} - Z\overleftrightarrow{\beta}\cdot\vec{\mathcal{E}}$$

(XXXVIII-12)

which defines the shielding tensor $\overleftrightarrow{\beta}$.

Thus in TDUHF one should find

$$\overleftrightarrow{\beta} = \frac{N}{Z}\,\overleftrightarrow{1} + \frac{1}{Z}\,\omega^2\,\overleftrightarrow{\alpha}(\omega)$$

(XXXVIII-13)

which is a useful check on the calculations and which generalizes the
result we found earlier for static fields $(\omega = 0)$.

Clearly the same result will follow if one requires double spin
occupancy but allows free variation of spatial dependence (i.e. TDSRHF)

because then although (8) will be satisfied only for spin independent one electron operators, $\overrightarrow{P}$ and $\overrightarrow{R}$ are spin independent. (Problem: Prove all this.) Thus TDUHF in general and restricted Hartree-Fock calculations for closed shells and for a half filled shell with all spins aligned outside of closed shells should also yield (13).

(C) Time Dependent Brillouin's Theorem

See Musulin and Epstein, Phys. Rev. 136, A966 (1964) -- Appendix.

XXXIX. Imaginary Frequencies

$\alpha(i\omega)$ for an atom can be used to calculate Van der Waal's forces. Several authors have shown that it is possible to find variational upper and lower bounds to $\alpha(i\omega)$ for all ω [Epstein, J. Chem. Phys. 48, 4716 (1968), Epstein and Epstein, WIS-TCI-297; Goscinski, Int. J. Q. Chem. 2, 761 (1968); P. Robinson (to be published)]. However their results so far seem useless for ab initio calculations -- they involve $(H-E_0)$ to high powers or they involve $(H-E_0)^{-1}$ [perhaps the neatest formulation would use $(H-E_0)^{1/2}$]. Hence we will not discuss them in detail here. Their main use has been to derive bounds for $\alpha(i\omega)$ in terms of its various (exact) derivatives at $\omega=0$ and similar quantities. Such bounds have also been found in other ways by Langhoff and Karplus, Phys. Rev. Lett. 19, 1461 (1967); by Gordon, J. Chem. Phys. 48, 3929 (1968); and by Futrelle and McQuarrie, Chem. Phys. Lett. 2, 223 (1968). See also Weinhold, J. Phys. A. 1 655 (1968).

Problem: Write down the analogue of $\tilde{L}_{\pm}^{(2)}$ for imaginary frequencies (let $\omega_+ \to \omega_-$). Show that it yields a stationary expression for $\alpha(i\omega)$ but in general not a bound.

Appendix A (Sec. XXV)

In this appendix we will present the results which one finds when one carries out the program of Sec. XXIV through the first two orders, and compare them with the ansatz of Sec. XXV. (See also Hammer and Weber, J. Math. Phys. $\underline{6}$, 1591 (1965).) Carrying out the integrations is straightforward but tedious. In first order one finds for $t > 0$

$$i a_k^{(1)} = \frac{(\psi_k, W_+ \psi_0)}{[i(E_k - E_0 + \omega) + \alpha]} - \frac{(\psi_k, W_+ \psi_0)}{[i(E_k - E_0 + \omega)]}$$

$$+ \frac{(\psi_k, W_+ \psi_0) \, e^{i(E_k - E_0 + \omega)t}}{[i(E_k - E_0 + \omega)]}$$

$$+ \text{same thing with } W_+ \rightarrow W_- \text{ and } \omega \rightarrow -\omega.$$

We now let $\alpha \rightarrow +0$ and assume that ω is unequal to any of the $E_k - E_0$, and also that ω is not equal to zero. Then since there are no possible singularities, we can simply put $\alpha = 0$ whence we are left with

If we now insert this in (XXIV-6) we find

$$a_k^{(1)} = - \frac{(\psi_k, W_+ \psi_0)}{E_k - E_0 + \omega} e^{i(E_k - E_0 + \omega)t} - \frac{(\psi_k, W_- \psi_0)}{E_k - E_0 - \omega} e^{i(E_k - E_0 - \omega)t}$$

which is evidently in complete agreement with (XXV-2) and (XXV-5).

Turning now to second order, one finds for $t > 0$

$$-a_K^{(2)} = \sum_L (\psi_K, W_+ \psi_L)(\psi_L, W_+ \psi_0) \left[\left[\frac{1}{[i(E_L - E_0 + w) + \alpha][i(E_K - E_0 + 2w) + 2\alpha]} \right.\right.$$

$$+ \left\{ \frac{e^{i(E_K - E_L + w)t} - 1}{[i(E_K - E_L - w)]} \right\} \left\{ \frac{1}{[i(E_L - E_0 + w) + \alpha]} - \frac{1}{[i(E_L - E_0 + w)]} \right\}$$

$$+ \left\{ \frac{e^{i(E_K - E_0 + 2w)t} - 1}{[i(E_L - E_0 + w)][i(E_K - E_0 + 2w)]} \right\} \left.\right]$$

$$+ \sum_L (\psi_K, W_- \psi_L)(\psi_L, W_+ \psi_0) \left[\left[\frac{1}{[i(E_L - E_0 + w) + \alpha][i(E_K - E_0) + 2\alpha]} \right.\right.$$

$$+ \left\{ \frac{e^{i(E_K - E_L - w)t} - 1}{[i(E_K - E_L - w)]} \right\} \left\{ \frac{1}{[i(E_L - E_0 + w) + \alpha]} - \frac{1}{[i(E_L - E_0 + w)]} \right\}$$

$$+ \left\{ \frac{e^{i(E_K - E_0)t} - 1}{[i(E_L - E_0 + w)][i(E_K - E_0)]} \right\} \left.\right] + \text{Same thing but with}$$

$W_+ \to W_-,\ W_- \to W_+$

and $w \to -w$.

(A-1)

Now for $k \neq 0$ and ω not equal to a resonance value there is no possibility of singular terms and we can freely put $\alpha = 0$ to find, after wholesale cancellation

$$a_k^{(2)} = e^{i(E_k - E_0 + 2\omega)t} \sum_L \frac{(\psi_k, w_+ \psi_L)(\psi_L, w_+ \psi_0)}{(E_k - E_0 + 2\omega)(E_L - E_0 + \omega)}$$

$$(A-2)$$

$$+ e^{i(E_k - E_0)t} \sum_L \frac{(\psi_k, w_- \psi_L)(\psi_L, w_- \psi_0)}{(E_k - E_0)(E_L - E_0 + \omega)}$$

$+$ same thing but with $w_+ \to w_-, \ w_- \to w_+$ and $\omega \to -\omega$

For $k = 0$ we must be more cautious. Noting that $\dfrac{e^{i(E_k - E_0)t} - 1}{i(E_k - E_0)} \to t$ when $E_k \to E_0$ we find, putting $\alpha = 0$ wherever this is no change of a singularity

$$a_0^{(2)} = e^{2i\omega t} \sum_L \frac{(\psi_0, w_+ \psi_L)(\psi_L, w_+ \psi_0)}{2\omega(E_L - E_0 + \omega)}$$

$$+ \sum_L (\psi_0, w_- \psi_L)(\psi_L, w_+ \psi_0) \left[- \frac{1}{2\alpha[i(E_L - E_0 + \omega) + \alpha]} \right.$$

$$\left. + \frac{it}{(E_L - E_0 + \omega)} \right]$$

$+$ same thing but with $w_+ \to w_-, \ w_- \to w_+$ and $\omega \to -\omega$.

Then noting that

$$\frac{1}{2\alpha\,[i\,(E_L-E_0+\omega)+\alpha]} = \frac{1}{2i\alpha\,(E_L-E_0+\omega)} + \frac{1}{2\,(E_L-E_0+\omega)^2} + O(\alpha)$$

we have finally

$$a_0^{(2)} = e^{2i\omega t} \sum_L \frac{(\psi_0, W_+\psi_L)(\psi_L, W_+\psi_0)}{2\omega\,(E_L-E_0+\omega)}$$

$$-\frac{1}{2} \sum_L \frac{(\psi_0, W_-\psi_L)(\psi_L, W_+\psi_0)}{(E_L-E_0+\omega)^2} \qquad (A-3)$$

$$+ i \sum_L \frac{(\psi_0, W_-\psi_L)(\psi_L, W_+\psi_0)}{(E_L-E_0+\omega)} \left(t+\frac{1}{2\alpha}\right)$$

+ same thing but with $W_+ \to W_-$, $W_- \to W_+$ and $\omega \to -\omega$

We leave it as an exercise for the reader to show that (A-2) and (A-3) are in complete agreement with our ansatz

$$\Psi^{(2)} = \psi_+^{(2)}\,e^{-i\,(E_0-2\omega)t} + \psi_0^{(2)}\,e^{-iE_0 t} + \psi_-^{(2)}\,e^{-i(E_0+2\omega)t} - iCt\,\psi_0\,e^{-iE_0 t}$$

where $\psi_\pm^{(2)}$ are given by (XXV-11), C by (XXV-19), and $\psi_0^{(2)}$ by (XXV-20) with the real part of C chosen so as to normalize $\overline{\Psi}$ through second order, and with the imaginary part of C proportional to $\frac{1}{\alpha}$. Thus we have justified our ansatz through second order.