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DEGENERATE R-S PERTURBATION THEORY

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## ABSTRACT

A concise, systematic procedure is given for determining the Rayleigh-Schrödinger energies and wavefunctions of degenerate states to arbitrarily high orders even when the degeneracies of the various states are resolved in arbitrary orders. The procedure is expressed in terms of an iterative cycle in which the energy through the (2n+1)st order is expressed in terms of the partially determined wavefunction through the n-th order. Both a direct and an operator derivation are given. The two approaches are equivalent and can be transcribed into each other. The direct approach deals with the wavefunctions (without the use of formal operators) and has the advantage that it resembles the usual treatment of non-degenerate perturbations and maintains close contact with the basic physics. In the operator approach, the wavefunctions are expressed in terms of infinite order operators which are determined by the successive resolution of the space of the zeroth order functions. The operator

treatment has some similarity to that of Choi (1969), but it is more closely related to that of either Hirschfelder (1969) or Silverstone-Holloway (1971). The operator expressions are useful for: double perturbations, expectation values of physical properties, and problems involving finite dimensional Hilbert space (for example, wavefunctions approximated by linear basis sets). The use of variational principles for degenerate perturbation problems is discussed.

The object of this article is to provide a practical method for systematically determining the n-th order Rayleigh-Schrodinger energies $\varepsilon_q^{(n)}$ and wavefunctions $\psi_q^{(n)}$ of perturbed degenerate states q to arbitrarily high orders, even when the degeneracies of the various states are resolved in arbitrary orders.

We start with a set of solutions $\underset{\sim}{\phi}_{[0]q}^{(0)}$ to the zeroth order equation. Next the $\underset{\sim}{\phi}_{[0]q}^{(0)}$ are used to help us find $\underset{\sim}{\phi}_{[1]q}^{(0)}$ and $\underset{\sim}{\phi}_{[1]q}^{(1)}$, a set of particular solutions to the zeroth and first order perturbation equations which correspond to the energies $\varepsilon_q^{(0)}$ and $\varepsilon_q^{(1)}$ and make the first order equation consistent. Then we use these particular solutions to help us find $\underset{\sim}{\phi}_{[2]q}^{(0)}$, $\underset{\sim}{\phi}_{[2]q}^{(1)}$, and $\underset{\sim}{\phi}_{[2]q}^{(2)}$, a new set of particular solutions which correspond to $\varepsilon_q^{(0)}$, $\varepsilon_q^{(1)}$, and $\varepsilon_q^{(2)}$ and make the first and second order perturbation equations consistent. In this way we proceed in an iterative fashion. We call the relationship between the particular solutions of the first n equations to the particular solutions of the first (n-1) equations the <u>magic formula</u>. Once it was discovered, the completion of the formulation became relatively easy. In the early stages of the iterative process, the $\psi_q^{(n)}$ are only partially determined. At a later stage, after the degeneracies have been resolved, the $\psi_q^{(n)}$ become completely determined. However, at all stages of the calculations the particular solutions of the first n equations suffice to determine the energy through the (2n+1)st order (in accordance with Wigner's rule which states that if the error in the wavefunction is $0(\lambda^{n+1})$ then the error in the energy is $0(\lambda^{2n+2})$ ).

Let us explain the contents of this paper. In Section I, those features of Rayleigh-Schrodinger theory are presented which are common to both the degenerate and non-degenerate problems. The equations and concepts developed in Section I are used in the formulation of the degenerate treatment. In Section II, the special notation and concepts required for the degenerate problems are discussed. The detailed treatment of the first and second order perturbations of degenerate states is given in Section III. The basic iterative pattern which appears in the treatment of these low orders is then generalized in Section IV to apply to the n-th order. This basic cycle is then proved by induction. In Section V, it is shown how to achieve greater solutional economy by calculating the energy through the (2n+1)st order after calculating the $\underset{\sim}{\phi}$'s through the n-th order. How both the basic and the (2n+1) procedures can be incorporated into cycles, suitable for computer programming, is shown in Section VI. The special simplifications which occur in orders higher than the one in which the degeneracy is completely resolved are given in Section VII. Up to this point, it has been assumed that all of the perturbation equations are solved exactly. In Section VIII, the use of variational principles and/or fixed linear basis sets to approximate the $\underset{\sim}{\phi}$'s and determine approximate energies is discussed. Finally, Section IX is devoted to deriving the formal operator treatment of degenerate perturbations in a form such that our $\underset{\sim}{\phi}$'s and energies can be expressed in terms of the formal operators $Q_n^{(m)}$ and the resolvents $R^{(-n)}$ which have been used in previous papers of Hirschfelder[1] and Silverstone and Holloway[2]. These operator relations should be useful in developing interchange-type relations to use in the determination of physical properties.

Those readers who are interested in the solution of the perturbation equations but are not concerned with the derivations are advised to read Section II, then skip to Section VI.

Our original intention was to improve the operator treatment given in Reference (1). In this respect, we succeeded in deriving the operator formalism given in Section IX which is not inituitive and is more concise and easier to use than Reference (1). In the first part of the operator treatment, the Hilbert space is first compacted into the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ space to give the familiar "infinite order" perturbation relations. Then, by successive resolutions, the Hilbert space is further compacted to the space of the $\underset{\sim}{\phi}^{(0)}_{[n]q}$ . At this point, our treatment resembles the implicit formulation of Choi[3]. In order to make further progress, we focus our attention on the iterative cycle of starting with the relations after (n-1) resolutions; determining $\varepsilon^{(n)}_{[n]\ell}$ and $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ ; and then satisfying the consistency equation which leads to the n-th resolution. In this phase, our operator approach, except for a number of significant improvements, has a very strong resemblance (including notation) to that of Reference (1). However, it became apparent that if we defined $\underset{\sim}{\phi}^{(m)}_{[n]\ell} = G^{(m)}_{n+1}\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ (where $G^{(m)}_{n+1}$ is one of our operators), we could transcribe our operator treatment into the direct formalism in which the only operators involved are the Hamiltonian and the resolvent. The direct treatment has the advantage of having a very close resemblance to the usual treatment of non-degenerate problems and it maintains a close contact with the basic physics. On the other hand, the formal operators may be useful in their own right since they can be split up in many different ways and their Hermitean components may be moved around to form a variety of identities, such as the interchange-type relations which arise in connection with double perturbations. The formal operators may also be convenient when the wavefunctions are approximated by fixed linear basis sets [see Section VIII].

We believe that this paper is more complete and easier to use than previous formalisms. However, our treatment is not basically new since it represents a restructuring (by algebraic manipulations) of the work of Van Vleck[4], Lennard-Jones[5], Brillouin[6], Kato[7], Bloch[8], Löwdin[9], Primas[10], Morita[11], Epstein[12], des Cloizeaux[13], Kirtman[14], Klein[15], Sack[16], Chong[17], Silverstone[2], Choi[3], and many others[18-22]. Indeed, there have been a great many implicit treatments (where the energy is embedded in the operators); and there have been a great many explicit treatments of degenerate perturbations. All of them are really different ways of saying the same thing. Thus, Klein[15] has made an extensive review of the explicit formulations and shown how they are interrelated. Then, too, des Cloizeaux[13] has shown how the implicit developments are related to the explicit. Sack[16] goes even farther in showing how all of the operator developments are related to the Lagrangian expansion of implicitly defined variables and then he discusses the many interesting mathematical properties of the Lagrangian expansions. Thus, there is nothing basically new to be discovered in the Rayleigh-Schrodinger treatment of degenerate perturbations. As Einstein said of such problems, "It is simple, it is just hard to do". Degenerate perturbations are very complex. However, as Abell[23] said, "A complexity is nothing more than a disarrangement of simplicities". Thus, we hope that we have succeeded in rearranging the disarrangement.

After we had recast our development into its present direct form (without the use of formal operators) we discovered many points of similarity with a preliminary research note given to us by Sambé and Roothaan[18]. Their approach is similar in viewpoint to the Chong and Larcher[17] method of "contrained secular equations". The Sambé and Roothaan "wavefunctions" are really our particular solutions, the $\underset{\sim}{\phi}$'s, but they lacked the relationship between the $\underset{\sim}{\phi}$'s and the true wavefunctions. They discovered the magic formula (quite independent of us) and their relations for the energies, including the (2n+1) development, are similar to ours. We hope that our paper will not detract from theirs.

## I. GENERAL FEATURES OF R-S THEORY WHICH APPLY TO BOTH DEGENERATE AND NON-DEGENERATE PERTURBATIONS.

In Rayleigh-Schrödinger perturbation theory we seek the solutions to the perturbed Schrödinger equations

$$[H(\lambda) - E_\ell(\lambda)]\psi_\ell(\lambda) = 0 , \tag{1}$$

where the Hamiltonian $H$ (assumed to be Hermitean), the wavefunction $\psi_\ell$ , and the energy $E_\ell$ are assumed to be expressible as power series in the perturbation parameter,

$$\begin{aligned} H &= H^{(0)} + \sum_{n=1} \lambda^n H^{(n)} \\ \psi_\ell &= \psi_\ell^{(0)} + \sum_{n=1} \lambda^n \psi_\ell^{(n)} \\ E_\ell &= \varepsilon_\ell^{(0)} + \sum_{n=1} \lambda^n \varepsilon_\ell^{(n)} . \end{aligned} \tag{2}$$

The unperturbed Hamiltonian $H^{(0)}$ is assumed to possess a complete set of eigensolutions

$$[H^{(0)} - \varepsilon_\ell^{(0)}]\phi_{\ell\alpha}^{(0)} = 0 , \quad 1 \le \alpha \le g_\ell , \tag{3}$$

where the $\phi_{\ell\alpha}^{(0)}$ are a $g_\ell$-fold ortho-normal set of degenerate eigenfunctions corresponding to the energy level $\varepsilon_\ell^{(0)}$ . The zeroth order wavefunction $\psi_\ell^{(0)}$ (which is defined as the limit of $\psi_\ell(\lambda)$ as $\lambda$ tends to zero) is a linear combination of the $\phi_{\ell\alpha}^{(0)}$ .

In the present paper we fix our attention on a particular state $q$ which arises from the perturbation of the degenerate $(g_q > 1)$ energy level $\varepsilon_q^{(0)}$. However, our results also apply to non-degenerate $(g_q = 1)$ cases. As a matter of fact, the following expressions for the perturbation equations, the perturbation energies, the perturbed wavefunctions, and the normalization are all equally applicable to degenerate or non-degenerate problems.

The Perturbation Equations.

Substituting the power series expansions (2) into the Schrödinger equation (1) for the state $q$ yields

$$\sum_{n=0} \lambda^n \sum_{t=0}^{n} \bar{H}^{(t)} \psi_q^{(n-t)} = 0 , \tag{4}$$

where we use the notation

$$\bar{H}^{(n)} = H^{(n)} - \varepsilon_q^{(n)} . \tag{5}$$

Assuming that Eq. (4) is valid for all values of $\lambda$ within the radius of convergence of the series (2), the coefficient of each power of $\lambda$ in Eq. (4) must vanish. Thus, the n-th order Rayleigh-Schrodinger perturbation equation is[24]

$$(H^{(0)} - \varepsilon_q^{(0)})\psi_q^{(n)} = -\sum_{t=1}^{n} \bar{H}^{(t)}\psi_q^{(n-t)} . \tag{6}$$

In this manner the original Schrödinger Eq. (1) is resolved into an infinite number of inhomogeneous perturbation equations.

In order that Eq. (6) be mathematically consistent, its right-hand side must be orthogonal to each of the $g_q$ eigenfunctions $\phi_{q\alpha}^{(0)}$. One of these conditions is used to determine the n-th order energy; the other $(g_q - 1)$ conditions are used in the determination of the $\psi_q^{(0)}$, $\psi_q^{(1)},\ldots,\psi_q^{(n-1)}$.

The second feature of Eq. (6) to observe is that insofar as the n-th order perturbation equation is concerned, $\psi_q^{(n)}$ is the sum of a particular solution plus an arbitrary linear combination of the $\phi_{\ell\alpha}^{(0)}$. However, such extra terms in $\psi_q^{(n)}$ affect the mathematical consistency of the higher order perturbation equations and the determination of the higher order wavefunctions.

<u>The Perturbation Energies.</u>

The n-th order energy is obtained by multiplying Eq. (6) by $\psi_q^{(0)*}$ and integrating,[24]

$$\varepsilon_q^{(n)} = \langle\psi_q^{(0)}|H^{(n)}|\psi_q^{(0)}\rangle + \sum_{t=1}^{n-1} \langle\psi_q^{(0)}|\bar{H}^{(t)}|\psi_q^{(n-t)}\rangle . \qquad (7)$$

Here the $\varepsilon_q^{(n)}$ is expressed in terms of the wavefunction through the (n-1)st order. For $n \geq 3$, equivalent expressions requiring the knowledge of lower order wavefunctions can be obtained by algebraic manipulations making use of the Hermitean property of the $H^{(t)}$ and repeated use of the perturbation equations (6). Thus, for $0 \leq k \leq n-1$,

$$\varepsilon_q^{(n)} = \langle\psi_q^{(0)}|H^{(n)}|\psi_q^{(0)}\rangle + \sum_{s=0}^{k}{}' \sum_{t=0}^{n-k-1}{}' \langle\psi_q^{(s)}|\bar{H}^{(n-s-t)}|\psi_q^{(t)}\rangle \qquad (8)$$

where <u>the primed summations mean that the term $s = t = 0$ is omitted.</u> In accordance with the Wigner (2n+1) rule, $\varepsilon_q^{(2n)}$ and $\varepsilon_q^{(2n+1)}$ can be expressed in terms of the wavefunction through $\psi_q^{(n)}$ by using Eq. (8) with n replaced by 2n and $k = n - 1$, or with n replaced by (2n+1) and $k = n$. Thus,

$$\varepsilon_q^{(2n)} = \langle\psi_q^{(0)}|H^{(2n)}|\psi_q^{(0)}\rangle + \sum_{s=0}^{n-1}{}' \sum_{t=0}^{n}{}' \langle\psi_q^{(s)}|\bar{H}^{(2n-s-t)}|\psi_q^{(t)}\rangle, \quad (9)$$

and

$$\varepsilon_q^{(2n+1)} = \langle\psi_q^{(0)}|H^{(2n+1)}|\psi_q^{(0)}\rangle + \sum_{s=0}^{n}{}' \sum_{t=0}^{n}{}' \langle\psi_q^{(s)}|\bar{H}^{(2n+1-s-t)}|\psi_q^{(t)}\rangle . \quad (10)$$

Although Eqs. (7)-(10) apply to degenerate, as well as to non-degenerate, perturbation problems, they are not directly useable until the calculations have proceeded to a sufficiently high order that the degeneracy is resolved and the $\psi_q^{(0)},\ldots,\psi_q^{(n)}$ are known.

<u>The Perturbed Wavefunctions.</u>

The n-th order wavefunction can be expressed as a linear combination of the complete ortho-normal set of eigenfunctions of $H^{(0)}$,

$$\psi_q^{(n)} = \sum_k{}' \sum_\alpha \phi_{k\alpha}^{(0)}\langle\phi_{k\alpha}^{(0)}|\psi_q^{(n)}\rangle + \sum_\alpha \phi_{q\alpha}^{(0)}\langle\phi_{q\alpha}^{(0)}|\psi_q^{(n)}\rangle , \quad (11)$$

where the prime indicates that $k \neq q$. Substituting (11) into the n-th order perturbation Eq. (6),

$$\sum_k{}' \sum_\alpha (\varepsilon_q^{(0)} - \varepsilon_k^{(0)})\phi_{k\alpha}^{(0)}\langle\phi_{k\alpha}^{(0)}|\psi_q^{(n)}\rangle = \sum_{t=1}^{n} \bar{H}^{(t)}\psi_q^{(n-t)}, \quad (12)$$

so that

$$\langle\phi_{k\alpha}^{(0)}|\psi_q^{(n)}\rangle = [\varepsilon_q^{(0)} - \varepsilon_k^{(0)}]^{-1}\langle\phi_{k\alpha}^{(0)}|\sum_{t=1}^{n} \bar{H}^{(t)}|\psi_q^{(n-t)}\rangle . \quad (13)$$

Thus,

$$\psi_q^{(n)} = R^{(0)} \sum_{t=1}^{n} \bar{H}^{(t)}\psi_q^{(n-t)} + \sum_\alpha \phi_{q\alpha}^{(0)}\langle\phi_{q\alpha}^{(0)}|\psi_q^{(n)}\rangle , \tag{14}$$

where $R^{(0)}$ is the resolvent

$$R^{(0)} = \sum_k{}' \, [\varepsilon_q^{(0)} - \varepsilon_k^{(0)}]^{-1} \sum_\alpha |\phi_{k\alpha}^{(0)}\rangle\langle\phi_{k\alpha}^{(0)}| . \tag{15}$$

The resolvent has the property that if $F$ is any function

$$-(H^{(0)} - \varepsilon_q^{(0)})R^{(0)}F = F - \sum_\alpha \phi_{q\alpha}^{(0)}\langle\phi_{q\alpha}^{(0)}|F\rangle . \tag{16}$$

Thus, if we know the function $F$, we can determine $R^{(0)}F$ by solving Eq. (16).[25] In this manner, if we know the wavefunction through the (n-1)st order, we can determine the part of $\psi_q^{(n)}$ which is orthogonal to the $\phi_{q\alpha}^{(0)}$. The coefficients $\langle\phi_{q\alpha}^{(0)}|\psi_q^{(n)}\rangle$ must be determined from the normalization and the consistency conditions.

The Normalization.

The normalization of the wavefunctions is not determined by the perturbation equations and remains arbitrary. In the present paper we adopt intermediate normalization so that

$$\langle\psi_q^{(0)}|\psi_q\rangle = 1 \quad \text{and} \quad \langle\psi_q^{(0)}|\psi_q^{(n)}\rangle = \delta_{n,0} . \tag{17}$$

However, it is easy to convert our results to any other type of normalization. A perturbed wavefunction $\chi_q(\lambda)$ corresponding to a different normalization scheme differs from our $\psi_q(\lambda)$ by a constant factor. Thus, $\chi_q(\lambda) = \psi_q(\lambda)C_q(\lambda)$ . Expanding the constant in powers of $\lambda$ , $C_q(\lambda) = \sum_{n=0} \lambda^n C_q^{(n)}$ , it follows that the n-th order wavefunction corresponding to $\chi_q(\lambda)$ is[26]

$$\chi_q^{(n)} = \sum_{s=0}^{n} \psi_q^{(s)} C_q^{(n-s)} . \tag{18}$$

For degenerate wavefunctions Eq. (18) can be expressed in the form of Eq. (36).

Solution of the Perturbation Equations.

The Rayleigh-Schrödinger perturbation theory is an iterative procedure for determining $\psi_q$ and $E_q$ to any desired precision. We begin with the solutions to the unperturbed problem, Eq. (3), and proceed recursively to solve the perturbation eqations (6), together with the normalization conditions (17), to successively higher orders of perturbation. The details of how this is done depends upon whether the state q under consideration is non-degenerate or degenerate:

(1) The Non-Degenerate Case.

For the case that $\varepsilon_q^{(0)}$ is non-degenerate, the unperturbed Schrödinger Eq. (3) has only one independent solution $\phi_{q1}^{(0)}$ . Thus, $\psi_q^{(0)} = \phi_{q1}^{(0)}$ is known. As a result of the normalization condition (17), the n-th order wavefunction (14) can be expressed in terms of the lower order wavefunctions

$$\psi_q^{(n)} = R^{(0)} \sum_{t=1}^{n} \bar{H}^{(t)} \psi_q^{(n-t)} . \tag{19}$$

The explicit determination of $\psi_q^{(n)}$ then requires the solution of a partial differential equation of the Eq. (16) type.[25] Eq. (19) together with the Eqs. (9) and (10) for $\varepsilon_q^{(2n)}$ and $\varepsilon_q^{(2n+1)}$ then forms the basis for the recursive procedure.

(2) The Degenerate Case.

For the case that $\varepsilon_q^{(0)}$ is degenerate, $\psi_q^{(0)}$ is usually not known at the beginning of the calculation. The functions $\phi_{q\alpha}^{(0)}$ provide a basis for the $\psi_q^{(0)}$ so that

$$\psi_q^{(0)} = \sum_\alpha \phi_{q\alpha}^{(0)} \langle \phi_{q\alpha}^{(0)} | \psi_q^{(0)} \rangle \ . \tag{20}$$

Similarly, according to Eq. (14), the $\psi_q^{(n)}$ involves $g_q$ unknown expansion coefficients $\langle \phi_{q\alpha}^{(0)} | \psi_q^{(n)} \rangle$ . For each order $n$ , starting with $n = 0$ , the normalization condition (17) provides one condition upon the expansion coefficients. The other $(g_q - 1)$ conditions are provided by the mathematical consistency conditions for each order of the perturbation equations. Before discussing exactly how these equations are made consistent and solved, it is best that we introduce our notation and concepts.

Symmetry Considerations

In some cases, $\psi_q^{(0)}$ can be completely or partially determined by group theoretic considerations.[9] The unperturbed Hamiltonians have symmetry groups $G^{(0)}$ and $G$ respectively. The functions $\phi_{q\alpha}^{(0)}$ are bases for the irreducible representations of $G^{(0)}$ ; whereas, $\psi_q^{(0)}$ and $\psi_q$ transform according to the irreducible representation $D^{(q)}$ of $G$ . Thus, if $A_q$ is the projector of $D^{(q)}$ , then $A_q\psi_q = \psi_q$ .

If, now, $A_q$ commutes with $H^{(0)}$ as well as with $H(\lambda)$, then: (1) The set of functions $\bar{\phi}_{q\alpha}^{(0)} = A_q \phi_{q\alpha}^{(0)}$ are solutions to the zeroth order Schrodinger equation and are orthogonal to the functions $\hat{\phi}_{q\alpha}^{(0)} = (1-A_q)\phi_{q\alpha}^{(0)}$. (2) All of the energy and overlap matrix elements vanish which link the states arising from the $\bar{\phi}_{q\alpha}^{(0)}$ with those which arise from the $\hat{\phi}_{q\alpha}^{(0)}$. (3) Thus, in determining $E_q$ and $\psi_q$, only the zeroth order functions $\bar{\phi}_{q\alpha}^{(0)}$ need to be considered and the functions $\hat{\phi}_{q\alpha}^{(0)}$ can be ignored. The hydrogen atom Stark effect provides a good example where $A_q$ commutes with both $H^{(0)}$ and $H(\lambda)$. Here $H^{(0)}$ has spherical or parabolic symmetry while $H(\lambda)$ has only parabolic symmetry. Thus $A_q$ corresponds to a particular set of parabolic quantum numbers and $A_q \phi_{q\alpha}^{(0)}$ is one particular linear combination of the hydrogen orbitals for a particular value of the principal quantum number. Thus, if one treats the hydrogen Stark effect in parabolic coordinates, the other degenerate functions $(1-A_q)\phi_{q\alpha}^{(0)}$ can be ignored and the problem becomes equivalent to a non-degenerate perturbation.

Even if $A_q$ does not commute with $H^{(0)}$, symmetry considerations may be useful if there exists a subgroup $G_1$ which is common to both $G^{(0)}$ and $G$. The irreducible representations of $G$ are then subduced[27] (or decomposed) into irreducible representations of its subgroups. The functions $\psi_q$ and $\psi_q^{(0)}$ belong to irreducible representations $D_1^{(q)}$ of the common subgroup $G_1$. If $A_{q1}$ is the projector corresponding to $D_1^{(q)}$, then $A_{q1}$ commutes with both $H^{(0)}$ and $H(\lambda)$. Thus $A_{q1}\psi_q = \psi_q$ and the functions $A_{q1}\phi_{q\alpha}^{(0)}$ play the role of the $\bar{\phi}_{q\alpha}^{(0)}$ in the previous paragraph. Furthermore, the quantum number associated with $A_{q1}$ remains unaffected by the perturbation (an example would be the magnetic quantum number in the Stark effect).

If all of the $\phi_{\sim q\alpha}^{(0)}$ belong to the same $g_q$-dimensional irreducible representation of $G^{(0)}$, the degeneracy is symmetry-related and not "accidental". If $\psi_q^{(0)}$ and $\psi_q$ belong to an m-dimensional irreducible representation of $G$, then the block of states containing $q$ will remain m-fold degenerate even after an infinite order of perturbation.

## II. NOTATION FOR DEGENERATE STATES.

A clear, concise, and consistent notation is very important for treating degenerate perturbation problems where the pattern of degeneracy splitting cannot be predicted beforehand. The set of degenerate states having the zeroth order energy $\varepsilon_q^{(0)}$ splits into subsets characterized by the first order energies $\varepsilon_{qi}^{(1)}$ [where we might number $\varepsilon_{q1}^{(1)} < \varepsilon_{q2}^{(1)} < \ldots$]. These subsets are further split in second order into smaller subsets characterized by $\varepsilon_{qij}^{(2)}$. After calculating the energy through the n-th order, the states are split into subsets corresponding to the energies $\varepsilon_q^{(0)}$, $\varepsilon_{qi}^{(1)}$, $\varepsilon_{qij}^{(2)}$, ..., $\varepsilon_{qij\ldots t}^{(n)}$. Thus, a particular state can be characterized by the "genealogy" qij...t... of its energy through the order in which its degeneracy is resolved. The degeneracy is resolved if either its subset is reduced so that it contains only one state, or else, no further splittings occur in higher orders[27].

In calculating the energy and wavefunctions of a set of perturbed degenerate states it may be necessary to use this complete genealogical nomenclature. However, in the development of the theory, our concern is with a particular state which we denote by $q$ rather than by its full genealogical characterization. In addition, we use:

$[n]q$ labels subsets having $\varepsilon_q^{(0)}, \varepsilon_q^{(1)}, \ldots \varepsilon_q^{(n)}$.

$[n]k$ labels subsets having the same energy as $q$ through (n-1)st order but $\varepsilon_k^{(n)} \neq \varepsilon_q^{(n)}$. Such states comprise the n-th class with respect to $q$.

$[n]\ell$ labels subsets having the same energy as $q$ through (n-1)st order but $\varepsilon_\ell^{(n)}$ may be either equal or not equal $\varepsilon_q^{(n)}$.

To make our notation more concise, we adopt a vector notation with a set of functions denoted by a row vector. Thus, for example, the set $\phi_{q\alpha}^{(0)}$ with $1 \leq \alpha \leq g_q$ is denoted by $\underset{\sim}{\phi}_{[0]q}^{(0)}$.

In terms of our vector notation, we can discuss the resolution of the degeneracies more precisely. In the first order, the function set $\underset{\sim}{\phi}_{[0]q}^{(0)}$ is split into the set $\underset{\sim}{\phi}_{[1]q}^{(0)}$ and the sets $\underset{\sim}{\phi}_{[1]k}^{(0)}$. Similarly, in the n-th order, the function set $\underset{\sim}{\phi}_{[n-1]q}^{(0)}$ is split into the set $\underset{\sim}{\phi}_{[n]q}^{(0)}$ and the sets $\underset{\sim}{\phi}_{[n]k}^{(0)}$. The new functions $\underset{\sim}{\phi}_{[n]\ell}^{(0)}$ are ortho-normal linear combinations of the $\underset{\sim}{\phi}_{[n-1]q}^{(0)}$. Thus,

$$\underset{\sim}{\phi}_{[n]\ell}^{(0)} = \underset{\sim}{\phi}_{[n-1]q}^{(0)} \langle \underset{\sim}{\phi}_{[n-1]q}^{(0)} | \underset{\sim}{\phi}_{[n]\ell}^{(0)} \rangle , \qquad (21)$$

and

$$\langle \underset{\sim}{\phi}_{[n]\ell}^{(0)} | \underset{\sim}{\phi}_{[n]\ell'}^{(0)} \rangle = \delta_{\ell,\ell'} \underset{\approx}{1} . \qquad (22)$$

Since the ortho-normal $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ functions span the same space as the ortho-normal $\underset{\sim}{\phi}^{(0)}_{[n-1]q}$ functions,

$$\underset{\sim}{\phi}^{(0)}_{[n-1]q} = \underset{\sim}{\phi}^{(0)}_{[n]q}\langle\underset{\sim}{\phi}^{(0)}_{[n]q}|\underset{\sim}{\phi}^{(0)}_{[n-1]q}\rangle + \sum_{k} \underset{\sim}{\phi}^{(0)}_{[n]k}\langle\underset{\sim}{\phi}^{(0)}_{[n]k}|\underset{\sim}{\phi}^{(0)}_{[n-1]q}\rangle . \quad (23)$$

Furthermore, the projector onto the $\underset{\sim}{\phi}^{(0)}_{[n-1]q}$ basis has the resolution

$$|\underset{\sim}{\phi}^{(0)}_{[n-1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[n-1]q}| = |\underset{\sim}{\phi}^{(0)}_{[n]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[n]q}| + \sum_{k} |\underset{\sim}{\phi}^{(0)}_{[n]k}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[n]k}| . \quad (24)$$

And the projector onto the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ basis has the resolution

$$|\underset{\sim}{\phi}^{(0)}_{[0]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[0]q}| = |\underset{\sim}{\phi}^{(0)}_{[n]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[n]q}| + \sum_{s=1}^{n} \sum_{k} |\underset{\sim}{\phi}^{(0)}_{[s]k}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[s]k}| . \quad (25)$$

<u>If $n > n'$</u>, then by the repeated use of Eq. (21),

$$\underset{\sim}{\phi}^{(0)}_{[n]\ell} = \underset{\sim}{\phi}^{(0)}_{[n']q}\langle\underset{\sim}{\phi}^{(0)}_{[n']q}|\underset{\sim}{\phi}^{(0)}_{[n'+1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[n'+1]q}|\cdots|\underset{\sim}{\phi}^{(0)}_{[n-1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[n-1]q}|\underset{\sim}{\phi}^{(0)}_{[n]\ell}\rangle . \quad (26)$$

As a result of Eqs. (22) and (26), <u>for all values of $n$ and $n'$</u>,

$$\langle\underset{\sim}{\phi}^{(0)}_{[n']\ell'}|\underset{\sim}{\phi}^{(0)}_{[n]\ell}\rangle = \delta_{n,n'}\delta_{\ell,\ell'}\underset{\approx}{1} . \quad (27)$$

Our conception is that the $\underset{\sim}{\phi}^{(0)}_{[n]q}$ is a linear combination of the zeroth order wavefunctions of <u>all</u> of the states which have the energy $E_q$ through the n-th order. Thus, the $\underset{\sim}{\phi}^{(0)}_{[n]q}$ is a basis for expressing $\psi^{(0)}_q$,

$$\psi^{(0)}_q = \underset{\sim}{\phi}^{(0)}_{[n]q}\langle\underset{\sim}{\phi}^{(0)}_{[n]q}|\psi^{(0)}_q\rangle . \quad (28)$$

Since zeroth order wavefunctions corresponding to different states are orthogonal,

$$<\underset{\sim}{\phi}^{(0)}_{[n]k}|\psi^{(0)}_{q}> = 0 . \qquad (29)$$

The other notational convention which we adopt is to define $\psi^{(0)}_{[n]q}$, $\psi^{(0)}_{[n]k}$, and $\psi^{(0)}_{[n]\ell}$ as the zeroth order wavefunction of <u>any</u> of the perturbed states whose energy genealogy corresponds to $[n]q$, $[n]k$, or $[n]\ell$. Thus, the functions $\underset{\sim}{\phi}^{(0)}_{[n]k}$ are linear combinations of <u>all</u> of the functions $\psi^{(0)}_{[n]k}$.

## III. THE LOW ORDER DEGENERATE PERTURBATIONS.

Having discussed the general features of the Rayleigh-Schrödinger theory, as well as the special notation and concepts required for degenerate problems, we are ready to proceed with the iterative process beginning with the zeroth order.

### A. <u>The Zeroth Order.</u>

We can write the zeroth order perturbation equation either in terms of the functions $\underset{\sim}{\phi}^{(0)}_{[0]q}$ which we know,

$$\bar{H}^{(0)}\underset{\sim}{\phi}^{(0)}_{[0]q} = 0 , \qquad (30)$$

or in terms of the "correct zeroth order wavefunctions" $\psi^{(0)}_{[0]q}$,

$$\bar{H}^{(0)}\psi^{(0)}_{[0]q} = 0 . \qquad (31)$$

Both the $\psi^{(0)}_{[0]q}$ and the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ are taken to be ortho-normal,

$$<\underset{\sim}{\phi}^{(0)}_{[0]q}|\underset{\sim}{\phi}^{(0)}_{[0]q}> = \underset{\approx}{1} . \qquad (32)$$

All that we can conclude by comparing Eqs. (30) and (31) is that each of the $\psi^{(0)}_{[0]q}$ can be expressed as a linear combination of the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ ,

$$\psi^{(0)}_{[0]q} = \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(0)}_{[0]q} \rangle \ . \qquad (33)$$

B. <u>The First Order.</u>

Each of the functions $\psi^{(0)}_{[0]q}$ can also be expressed by the notation $\psi^{(0)}_{[1]\ell}$ where, at this point in our development, the energy $\varepsilon^{(1)}_{[1]\ell}$ is not determined. The first order perturbation Eq. (6) can be written

$$\bar{H}^{(0)} \psi^{(0)}_{[1]\ell} + [H^{(1)} - \varepsilon^{(1)}_{[1]\ell}] \psi^{(0)}_{[1]\ell} = 0 \ . \qquad (34)$$

But $\psi^{(0)}_{[1]\ell}$ is a linear combination of the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ ,

$$\psi^{(0)}_{[1]\ell} = \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(0)}_{[1]\ell} \rangle \ . \qquad (35)$$

Substituting (35) into Eq. (34),

$$\bar{H}^{(0)} \psi^{(1)}_{[1]\ell} + [H^{(1)} - \varepsilon^{(1)}_{[1]\ell}] \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(0)}_{[1]\ell} \rangle = 0 \ . \qquad (36)$$

(1) <u>The $\underset{\sim}{\phi}^{(0)}_{[0]q}$ Consistency; $\varepsilon^{(1)}_{[1]\ell}$ and $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$</u> .

Before solving Eq. (36), we must guarantee that it is consistent. In order to do this, we multiply the equation by $\underset{\sim}{\phi}^{(0)*}_{[0]q}$ and integrate. This results in the eigenvalue-eigenvector equation

$$[\underset{\approx}{\varepsilon}^{(1)}_{[0]q} - \varepsilon^{(1)}_{[1]\ell} \underset{\approx}{1}] \langle \phi^{(0)}_{[0]q} | \psi^{(0)}_{[1]\ell} \rangle = 0 \ , \qquad (37)$$

where

$$\underset{\approx}{\varepsilon}^{(1)}_{[0]q} = \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | H^{(1)} | \underset{\sim}{\phi}^{(0)}_{[0]q} \rangle \ . \qquad (38)$$

Our attention shifts to the properties of the Hermitean matrix $\underset{\approx}{\varepsilon}^{(1)}_{[0]q}$. It has a set of eigenvalues $\varepsilon^{(1)}_{[1]\ell}$ which are determined by solving the secular equation

$$|\underset{\approx}{\varepsilon}^{(1)}_{[0]q} - \varepsilon^{(1)}_{[1]\ell}\underset{\approx}{1}| = 0 . \qquad (39)$$

We designate $<\underset{\sim}{\phi}^{(0)}_{[0]q}|\underset{\sim}{\phi}^{(0)}_{[1]\ell}>$ to be the eigenvectors corresponding to a particular value of $\varepsilon^{(0)}_{[1]\ell}$. They are defined by the matrix equation

$$[\underset{\approx}{\varepsilon}^{(1)}_{[0]q} - \varepsilon^{(1)}_{[1]\ell}\underset{\approx}{1}]<\underset{\sim}{\phi}^{(0)}_{[0]q}|\underset{\sim}{\phi}^{(0)}_{[1]\ell}> = 0 . \qquad (40)$$

Since $\underset{\approx}{\varepsilon}^{(1)}_{[0]q}$ is Hermitean, we can arrange so that these eigenvectors are orthogonal and have unit length. Furthermore, we can define the new set of functions $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$ as the linear combination of the $\underset{\sim}{\phi}^{(0)}_{[0]q}$

$$\underset{\sim}{\phi}^{(0)}_{[1]\ell} = \underset{\sim}{\phi}^{(0)}_{[0]q}<\underset{\sim}{\phi}^{(0)}_{[0]q}|\underset{\sim}{\phi}^{(0)}_{[1]\ell}> . \qquad (41)$$

The dimensionality of the $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$ is the same as the degree of degeneracy of the $\varepsilon^{(1)}_{[1]\ell}$. Because of Eq. (32) and the ortho-normality of the eigenvectors, the functions $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$ are ortho-normal in the sense that

$$<\underset{\sim}{\phi}^{(0)}_{[1]\ell}|\underset{\sim}{\phi}^{(0)}_{[1]\ell'}> = \delta_{\ell,\ell'}\underset{\approx}{1} . \qquad (42)$$

Making use of Eq. (41), Eq. (40) can be restated

$$<\underset{\sim}{\phi}^{(0)}_{[0]q}|\bar{H}^{(1)}|\underset{\sim}{\phi}^{(0)}_{[1]\ell}> = (\varepsilon^{(1)}_{[1]\ell} - \varepsilon^{(1)}_{q})<\underset{\sim}{\phi}^{(0)}_{[0]q}|\underset{\sim}{\phi}^{(0)}_{[1]\ell}> . \qquad (43)$$

Or using Eqs. (41) and (42),

$$<\underset{\sim}{\phi}^{(0)}_{[1]\ell}|\bar{H}^{(1)}|\underset{\sim}{\phi}^{(0)}_{[1]\ell}> = (\varepsilon^{(1)}_{[1]\ell} - \varepsilon^{(1)}_{q})\delta_{\ell,\ell'} . \qquad (44)$$

At this point we select one particular value of $\varepsilon^{(1)}_{[1]\ell}$ to call $\varepsilon^{(1)}_{q}$ ; the other values of $\varepsilon^{(1)}_{[1]\ell}$ are designated as $\varepsilon^{(1)}_{[1]k}$ . Then we must consider two possible cases:

(a) If $\varepsilon^{(1)}_{[1]\ell}$ is non-degenerate, comparing Eqs. (37) and (40), it follows that $\underset{\sim}{\phi}^{(0)}_{[1]\ell} = \psi^{(0)}_{[1]\ell}$ . Furthermore, the eigenvector $\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi^{(0)}_{[1]\ell}\rangle$ is <u>uniquely</u> determined by the eigenvector of Eq. (37) or (40). Thus, $\psi^{(0)}_{[1]\ell}$ is completely determined by Eq. (35).

(b) If $\varepsilon^{(1)}_{[1]\ell}$ is degenerate, then comparing Eqs. (37) and (40), it follows that $\psi^{(0)}_{[1]\ell}$ must be some linear combination of the functions $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$ . Thus,

$$\psi^{(0)}_{[1]\ell} = \underset{\sim}{\phi}^{(0)}_{[1]\ell}\langle\underset{\sim}{\phi}^{(0)}_{[1]\ell}|\psi^{(0)}_{[1]\ell}\rangle , \tag{45}$$

where the expansion coefficients $\langle\underset{\sim}{\phi}^{(0)}_{[1]\ell}|\psi^{(0)}_{[1]\ell}\rangle$ are not yet determined.

(2) <u>The First Order Equation;</u> $\underset{\sim}{\phi}^{(1)}_{[1]\ell}$ .

Now we are ready to return to first order perturbation equation. Substituting Eq. (45) into Eq. (34),

$$\bar{H}^{(0)}\psi^{(1)}_{[1]\ell} + [H^{(1)} - \varepsilon^{(1)}_{[1]\ell}]\underset{\sim}{\phi}^{(0)}_{[1]\ell}\langle\underset{\sim}{\phi}^{(0)}_{[1]\ell}|\psi^{(0)}_{[1]\ell}\rangle = 0 . \tag{46}$$

On the basis of Eq. (43), Eq. (46) is consistent. Thus we can proceed to solve it. According to Eq. (14), the first order wavefunction can be expressed in the form

$$\psi^{(1)}_{[1]\ell} = R^{(0)}H^{(1)}\psi^{(0)}_{[1]\ell} + \underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi^{(1)}_{[1]\ell}\rangle , \tag{47}$$

which, with the help of Eq. (45), we can rewrite as

$$\psi^{(1)}_{[1]\ell} = \underset{\sim}{\phi}^{(1)}_{[1]\ell} \langle \underset{\sim}{\phi}^{(0)}_{[1]\ell} | \psi^{(0)}_{[1]\ell} \rangle + \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(1)}_{[1]\ell} \rangle \; , \tag{48}$$

where $\underset{\sim}{\phi}^{(1)}_{[1]\ell}$ is defined to be

$$\underset{\sim}{\phi}^{(1)}_{[1]\ell} = R^{(0)} H^{(1)} \underset{\sim}{\phi}^{(0)}_{[1]\ell} \; . \tag{49}$$

From Eq. (16), it is clear that $\underset{\sim}{\phi}^{(1)}_{[1]\ell}$ is completely specified by the equation

$$\bar{H}^{(0)} \underset{\sim}{\phi}^{(1)}_{[1]\ell} + [H^{(1)} - \varepsilon^{(1)}_{[1]\ell}] \underset{\sim}{\phi}^{(0)}_{[1]\ell} = 0 \tag{50}$$

subject to the condition that

$$\langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \underset{\sim}{\phi}^{(1)}_{[1]\ell} \rangle = 0 \; . \tag{51}$$

To verify that Eq. (48) is indeed the solution of Eq. (46), it is only necessary to substitute (48) into (46) and remember Eq. (50). However, we should note that in Eq. (47) the expansion coefficients $\langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(1)}_{[1]\ell} \rangle$, as well as the $\langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi^{(0)}_{[1]\ell} \rangle$, are <u>not</u> determined by the first order equation.

C. <u>The Second Order.</u>

Each of the functions $\psi^{(0)}_{[1]q}$ can also be expressed by the notation $\psi^{(0)}_{[2]\ell}$ where, at this point, the energy $\varepsilon^{(2)}_{[2]\ell}$ is not yet determined. The second order perturbation Eq. (6) can be written

$$\bar{H}^{(0)} \psi^{(2)}_{[2]\ell} + \bar{H}^{(1)} \psi^{(1)}_{[2]\ell} + [H^{(2)} - \varepsilon^{(2)}_{[2]\ell}] \psi^{(0)}_{[2]\ell} = 0 \; . \tag{52}$$

And since Eqs. (45) and (48) apply to <u>any</u> function $\psi_{[1]\ell}$ including those which we label $\psi_{[2]\ell}$ ,

$$\psi^{(0)}_{[2]\ell} = \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi^{(0)}_{[2]\ell} \rangle \tag{53}$$

and

$$\psi^{(1)}_{[2]\ell} = \underset{\sim}{\phi}^{(1)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi^{(0)}_{[2]\ell} \rangle + \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(1)}_{[2]\ell} \rangle \ . \tag{54}$$

Substituting (53) and (54) into Eq. (52),

$$\bar{H}^{(0)}\psi^{(2)}_{[2]\ell} + [\bar{H}^{(1)}\underset{\sim}{\phi}^{(1)}_{[1]q} + (H^{(2)} - \varepsilon^{(2)}_{[2]\ell})\underset{\sim}{\phi}^{(0)}_{[1]q}] \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi^{(0)}_{[2]\ell} \rangle$$

$$+ \bar{H}^{(1)}\underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(1)}_{[2]\ell} \rangle = 0 \ . \tag{55}$$

First we must insure that Eq. (55) is mathematically consistent with respect to the functions $\underset{\sim}{\phi}^{(0)}_{[0]q}$ . However, the function space of the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ is spanned by the $\underset{\sim}{\phi}^{(0)}_{[1]q}$ together with the $\underset{\sim}{\phi}^{(0)}_{[1]k}$ for all values of k . Thus, we divide the problem into two parts: first, to obtain consistency with respect to the $\underset{\sim}{\phi}^{(0)}_{[1]q}$ and then consistency with respect to the $\underset{\sim}{\phi}^{(0)}_{[1]k}$ .

(1) <u>The $\underset{\sim}{\phi}^{(0)}_{[1]q}$ Consistency; $\varepsilon^{(2)}_{[2]\ell}$ and $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$</u> .

Multiplying Eq. (55) by $\underset{\sim}{\phi}^{(0)*}_{[1]q}$ and integrating,

$$[\underset{\approx}{\varepsilon}^{(2)}_{[1]q} - \varepsilon^{(2)}_{[2]\ell}\underset{\approx}{1}] \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi^{(0)}_{[2]\ell} \rangle = 0 \tag{56}$$

where

$$\underset{\approx}{\varepsilon}^{(2)}_{[1]q} = \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \bar{H}^{(1)}\underset{\sim}{\phi}^{(1)}_{[1]q} + H^{(2)}\underset{\sim}{\phi}^{(0)}_{[1]q} \rangle \ . \tag{57}$$

Note that as a result of Eq. (43), the last term in Eq. (55) does not contribute to Eq. (56). As a result of Eq. (49), $\underset{\approx}{\varepsilon}^{(2)}_{[1]q}$ is Hermitean so that

$$\underset{\approx}{\varepsilon}^{(2)}_{[1]q} = \langle \bar{H}^{(1)} \underset{\sim}{\phi}^{(1)}_{[1]q} + H^{(2)} \underset{\sim}{\phi}^{(0)}_{[1]q} | \underset{\sim}{\phi}^{(0)}_{[1]q} \rangle \quad . \tag{58}$$

The matrix $\underset{\approx}{\varepsilon}^{(2)}_{[1]q}$ has the set of eigenvalues $\varepsilon^{(2)}_{[2]\ell}$ which are determined by solving the secular equation

$$|\underset{\approx}{\varepsilon}^{(2)}_{[1]q} - \varepsilon^{(2)}_{[2]\ell} \underset{\approx}{1}| = 0 \quad . \tag{59}$$

We designate $\langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \underset{\sim}{\phi}^{(0)}_{[2]\ell} \rangle$ to be the eigenvectors corresponding to a particular value of $\varepsilon^{(2)}_{[2]\ell}$ . They are defined by the matrix equation

$$[\underset{\approx}{\varepsilon}^{(2)}_{[1]q} - \varepsilon^{(2)}_{[2]\ell} \underset{\approx}{1}] \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \underset{\sim}{\phi}^{(0)}_{[2]\ell} \rangle = 0 \quad . \tag{60}$$

Since $\underset{\approx}{\varepsilon}^{(2)}_{[1]q}$ is Hermitean, we can arrange so that these eigenvectors are orthogonal and have unit length. Furthermore, we can define the new set of functions $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$ as the linear combination of the $\underset{\sim}{\phi}^{(0)}_{[1]q}$ such that

$$\underset{\sim}{\phi}^{(0)}_{[2]\ell} = \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \underset{\sim}{\phi}^{(0)}_{[2]\ell} \rangle \quad ; \tag{61}$$

Because of Eq. (42) and the ortho-normality of the eigenvectors,

$$\langle \underset{\sim}{\phi}^{(0)}_{[2]\ell} | \underset{\sim}{\phi}^{(0)}_{[2]\ell'} \rangle = \underset{\approx}{1} \, \delta_{\ell,\ell'} \quad . \tag{62}$$

Making use of Eqs. (58) and (61), Eq. (60) becomes

$$\langle \bar{H}^{(1)} \underset{\sim}{\phi}^{(1)}_{[1]q} + (H^{(2)} - \varepsilon^{(2)}_{[2]\ell}) \underset{\sim}{\phi}^{(0)}_{[1]q} | \underset{\sim}{\phi}^{(0)}_{[2]\ell} \rangle = 0 \tag{63}$$

At this point we select one particular value of $\varepsilon^{(2)}_{[2]\ell}$ to call $\varepsilon^{(2)}_{q}$ ; the other values of $\varepsilon^{(2)}_{[2]\ell}$ are designated as $\varepsilon^{(2)}_{[2]k}$ . Then we must consider two possible cases:

(a) If $\varepsilon^{(2)}_{[2]\ell}$ is non-degenerate, comparing Eqs. (56) and (60), it follows that $\underset{\sim}{\phi}^{(0)}_{[2]\ell} = \psi^{(0)}_{[2]\ell}$ . Furthermore, the eigenvector $\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi^{(0)}_{[2]\ell}\rangle$ is <u>uniquely</u> determined by Eq. (56) or (60). Thus $\psi^{(0)}_{[2]\ell}$ is completely determined by Eq. (54).

(b) If $\varepsilon^{(2)}_{[2]\ell}$ is degenerate, then comparing Eqs. (56) and (60), it follows that $\psi^{(0)}_{[2]\ell}$ must be some linear combination of the functions $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$ . Thus,

$$\psi^{(0)}_{[2]\ell} = \underset{\sim}{\phi}^{(0)}_{[2]\ell}\langle\underset{\sim}{\phi}^{(0)}_{[2]\ell}|\psi^{(0)}_{[2]\ell}\rangle \ . \tag{64}$$

(2) <u>The $\underset{\sim}{\phi}^{(0)}_{[1]k}$ Consistency;</u> $\underset{\sim}{\phi}^{(1)}_{[2]\ell}$ .

Multiplying Eq. (55) by $\underset{\sim}{\phi}^{(0)*}_{[1]k}$ and integrating gives, as the result of Eq. (43),

$$\langle\underset{\sim}{\phi}^{(0)}_{[1]k}|\bar{H}^{(1)}\underset{\sim}{\phi}^{(1)}_{[1]q} + \bar{H}^{(2)}\underset{\sim}{\phi}^{(0)}_{[1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi^{(0)}_{[2]\ell}\rangle$$

$$+ (\varepsilon^{(1)}_{[1]k} - \varepsilon^{(1)}_{q})\langle\underset{\sim}{\phi}^{(0)}_{[1]k}|\psi^{(1)}_{[2]\ell}\rangle = 0 \ . \tag{65}$$

And, if we let

$$\mathcal{E}^{(-1)}_{k} = [\varepsilon^{(1)}_{q} - \varepsilon^{(1)}_{[1]k}]^{-1} \ , \tag{66}$$

the consistency conditions (65) become

$$\langle\underset{\sim}{\phi}^{(0)}_{[1]k}|\psi^{(1)}_{[2]\ell}\rangle = \mathcal{E}^{(-1)}_{k}\underset{\approx}{A}^{(2)}_{[1]k}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi^{(0)}_{[2]\ell}\rangle \ , \tag{67}$$

where we have defined

$$\underset{\approx}{A}^{(2)}_{[1]\ell} = \sum_{t=1}^{2} \langle \underset{\sim}{\phi}^{(0)}_{[1]\ell} | \bar{H}^{(t)} | \underset{\sim}{\phi}^{(2-t)}_{[1]q} \rangle . \quad (68)$$

Let us now express $\psi^{(1)}_{[2]\ell}$ in terms of the $[2]\ell$ functions. Making use of Eq. (64) in the first term of Eq. (54), and using Eq. (25) to project the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ functions onto the $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$ subspaces, and then using Eq. (67), we obtain

$$\psi^{(1)}_{[2]\ell} = \underset{\sim}{\phi}^{(1)}_{[2]\ell} \langle \underset{\sim}{\phi}^{(0)}_{[2]\ell} | \psi^{(0)}_{[2]\ell} \rangle + \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi^{(1)}_{[2]\ell} \rangle , \quad (69)$$

where we have defined

$$\underset{\sim}{\phi}^{(1)}_{[2]\ell} = \{ \underset{\sim}{\phi}^{(1)}_{[1]q} + \sum_{k} \underset{\sim}{\phi}^{(0)}_{[1]k} \mathcal{E}^{(-1)}_{k} \underset{\approx}{A}^{(2)}_{[1]k} \} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \underset{\sim}{\phi}^{(0)}_{[2]\ell} \rangle . \quad (70)$$

In Eq. (69) the functions $\underset{\sim}{\phi}^{(0)}_{[1]q}$ and $\underset{\sim}{\phi}^{(1)}_{[2]\ell}$ are completely specified whereas the coefficients $\langle \underset{\sim}{\phi}^{(0)}_{[2]\ell} | \psi^{(0)}_{[2]\ell} \rangle$ and $\langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi^{(1)}_{[2]\ell} \rangle$ are as yet undetermined.

An alternate definition of the $\underset{\sim}{\phi}^{(1)}_{[2]\ell}$ is that they satisfy the equation

$$\bar{H}^{(0)} \underset{\sim}{\phi}^{(1)}_{[2]\ell} + \bar{H}^{(1)} \underset{\sim}{\phi}^{(0)}_{[2]\ell} = 0 , \quad (71)$$

which follows from Eq. (50), subject to the orthogonality condition

$$\langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \underset{\sim}{\phi}^{(1)}_{[2]\ell} \rangle = 0 , \quad (72)$$

which follows from Eqs. (51) and (70). A physical explanation of Eq. (72) is that up to this point in the development, the functions $\psi_{[2]\ell}$ are indistinguishable from the $\underset{\sim}{\phi}_{[2]\ell}$ . Thus, Eq. (69) must remain valid if we replace the $\underset{\sim}{\phi}_{[2]\ell}$ by the corresponding $\psi_{[2]\ell}$ functions. The orthogonality relation (72) makes this substituted Eq. (69) a trivial identity.

A useful property of $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$ and $\underset{\sim}{\phi}^{(1)}_{[2]\ell}$ results from Eqs. (70) and (68),

$$<\underset{\sim}{\phi}^{(0)}_{[1]k}|\bar{H}^{(1)}|\underset{\sim}{\phi}^{(1)}_{[2]\ell}> + <\underset{\sim}{\phi}^{(0)}_{[1]k}|H^{(2)}|\underset{\sim}{\phi}^{(0)}_{[2]\ell}> = 0 . \qquad (73)$$

The second order eigenvalue Eq. (60) can be restated in terms of $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$ and $\underset{\sim}{\phi}^{(1)}_{[2]\ell}$ by using Eqs. (70) and (44).

$$\underset{\approx}{A}^{(2)}_{[1]q} = (\varepsilon^{(2)}_{[2]\ell} - \varepsilon^{(2)}_{q})<\underset{\sim}{\phi}^{(0)}_{[1]q}|\underset{\sim}{\phi}^{(0)}_{[2]\ell}> , \qquad (74)$$

where we used the definition (68) with $\ell = q$ .

(2) <u>The Second Order Equation;</u>

At this point we are ready to reconsider the solution of the second order perturbation equation. Substituting Eqs. (64) and (69) into Eq. (52),

$$\bar{H}^{(0)}\psi^{(2)}_{[2]\ell} + [\bar{H}^{(1)}\underset{\sim}{\phi}^{(1)}_{[2]\ell} + (H^{(2)} - \varepsilon^{(2)}_{[2]\ell})\underset{\sim}{\phi}^{(0)}_{[2]\ell}]<\underset{\sim}{\phi}^{(0)}_{[2]\ell}|\psi^{(0)}_{[2]\ell}>$$

$$+ \bar{H}^{(1)}\underset{\sim}{\phi}^{(0)}_{[1]q}<\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi^{(1)}_{[2]\ell}> = 0 . \qquad (75)$$

Using Eqs. (44), (74), and (73), it is easy to verify that Eq. (75) is consistent both with respect to $\underset{\sim}{\phi}^{(0)}_{[1]q}$ and with respect to the $\underset{\sim}{\phi}^{(0)}_{[1]k}$ . Thus, we seek a solution. According to Eq. (14), the second order wave-function can be expressed in the form

$$\psi^{(2)}_{[2]\ell} = R^{(0)}[\bar{H}^{(1)}\psi^{(1)}_{[2]\ell} + (H^{(2)} - \varepsilon^{(2)}_{[2]\ell})\psi^{(0)}_{[2]\ell}]$$

$$+ \underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi^{(2)}_{[2]\ell}\rangle \; . \tag{76}$$

Using Eqs. (49), (64), and (69), Eq. (76) becomes

$$\psi^{(2)}_{[2]\ell} = \underset{\sim}{\phi}^{(2)}_{[2]\ell}\langle\underset{\sim}{\phi}^{(0)}_{[2]\ell}|\psi^{(0)}_{[2]\ell}\rangle + \underset{\sim}{\phi}^{(1)}_{[1]q}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi^{(1)}_{[2]\ell}\rangle$$

$$+ \underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi^{(2)}_{[2]\ell}\rangle \; , \tag{77}$$

where the $\underset{\sim}{\phi}^{(2)}_{[2]\ell}$ is defined to be

$$\underset{\sim}{\phi}^{(2)}_{[2]\ell} = R^{(0)}[\bar{H}^{(1)}\underset{\sim}{\phi}^{(1)}_{[2]\ell} + (H^{(2)} - \varepsilon^{(2)}_{[2]\ell})\underset{\sim}{\phi}^{(0)}_{[2]\ell}] \; . \tag{78}$$

From Eq. (16) it is clear that $\underset{\sim}{\phi}^{(2)}_{[2]\ell}$ is completely specified by the equation

$$\bar{H}^{(0)}\underset{\sim}{\phi}^{(2)}_{[2]\ell} + \bar{H}^{(1)}\underset{\sim}{\phi}^{(1)}_{[2]\ell} + (H^{(2)} - \varepsilon^{(2)}_{[2]\ell})\underset{\sim}{\phi}^{(0)}_{[2]\ell} = 0 \; , \tag{79}$$

subject to the condition that

$$\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\underset{\sim}{\phi}^{(2)}_{[2]\ell}\rangle = 0 \; . \tag{80}$$

In line with the remark after Eq. (72), if the $\psi_{[2]\ell}$ functions in Eq. (77) were replaced by corresponding $\underset{\sim}{\phi}_{[2]\ell}$ functions, then both Eqs. (72) and (80) would be required in order to make this a trivial identity.

## IV. THE BASIC ITERATIVE PATTERN.

Most of the basic iterative pattern is developed in the first and second order treatments. The remaining features appear in the third order and were confirmed by considering the fourth and fifth orders. However, there is no need to present the third and higher orders here, since we prove by induction that the pattern applies to all orders. By pattern, we mean all of the relationships which are found in carrying out the general n-th order iterative step.

In the n-th order iterative step, the n-th order energies $\varepsilon^{(n)}_{[n]\ell}$ and the new sets of functions $\underset{\sim}{\phi}^{(0)}_{[n]\ell}, \underset{\sim}{\phi}^{(1)}_{[n]\ell}, \ldots, \underset{\sim}{\phi}^{(n)}_{[n]\ell}$ are determined. Any zeroth order wavefunction $\psi^{(0)}_{[n]\ell}$ which corresponds to a state having the energy genealogy $[n]\ell$ is a linear combination of the functions $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$,

$$\psi^{(0)}_{[n]\ell} = \underset{\sim}{\phi}^{(0)}_{[n]\ell} \langle \underset{\sim}{\phi}^{(0)}_{[n]\ell} | \psi^{(0)}_{[n]\ell} \rangle . \qquad (81)$$

The first $n$ orders of $\psi_{[n]\ell}$ are related to the $\underset{\sim}{\phi}_{[n]\ell}$ and the functions determined in the previous steps by the relations

$$\psi^{(m)}_{[n]\ell} = \sum_{t=0}^{m-1} \underset{\sim}{\phi}^{(t)}_{[n-m+t]q} \langle \underset{\sim}{\phi}^{(0)}_{[n-m+t]q} | \psi^{(m-t)}_{[n]\ell} \rangle + \underset{\sim}{\phi}^{(m)}_{[n]\ell} \langle \underset{\sim}{\phi}^{(0)}_{[n]\ell} | \psi^{(0)}_{[n]\ell} \rangle , \quad 1 \leq m \leq n . \qquad (82)$$

In this equation, the functions $\underset{\sim}{\phi}$ are completely specified but the expansion coefficients are not determined unless the degeneracy has been completely resolved.

The $\underset{\sim}{\phi}_{[n]\ell}$ are the particular solutions to the first $n$ orders of the Rayleigh-Schrödinger perturbation equations

$$\sum_{t=0}^{m} \bar{H}^{(t)} \underset{\sim}{\phi}^{(m-t)}_{[n]\ell} + \delta_{m,n} (\varepsilon^{(n)}_{q} - \varepsilon^{(n)}_{[n]\ell}) \underset{\sim}{\phi}^{(0)}_{[n]\ell} = 0 , \quad 0 \leq m \leq n , \qquad (83)$$

which satisfy the orthogonality conditions

$$<\underset{\sim}{\phi}^{(0)}_{[n]\ell}|\underset{\sim}{\phi}^{(0)}_{[n]\ell'}> \;=\; \delta_{\ell,\ell'} \;, \tag{84}$$

$$<\underset{\sim}{\phi}^{(0)}_{[n-m]q}|\underset{\sim}{\phi}^{(m)}_{[n]\ell}> \;=\; 0 \;, \qquad 1\leq m\leq n \;. \tag{85}$$

The Eqs. (83)-(85) specify the $\underset{\sim}{\phi}_{[n]\ell}$ to within a unitary transformation of the set $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ .

The wavefunctions $\psi_{[n]\ell}$ are intermediately normalized in accordance with Eq. (17). A wavefunction $\chi_{[n]\ell}$ having a different normalization differs from $\psi_{[n]\ell}$ by a constant factor $C_{[n]\ell}(\lambda)$ . Thus, substituting Eq. (82) into Eq. (18), the n-th order of $\chi_{[n]\ell}$ is

$$\chi^{(m)}_{[n]\ell} \;=\; \underset{\sim}{\phi}^{(m)}_{[n]\ell}<\underset{\sim}{\phi}^{(0)}_{[n]\ell}|\psi^{(0)}_{[n]\ell}>C^{(0)}_{[n]\ell}$$

$$+\sum_{t=0}^{m-1} \underset{\sim}{\phi}^{(t)}_{[n-m+t]q} \sum_{s=t}^{m} <\underset{\sim}{\phi}^{(0)}_{[n-m+t]q}|\psi^{(s-t)}_{[n]\ell}>C^{(m-s)}_{[n]\ell} \;. \tag{86}$$

Since the constants $C^{(n-s)}_{[n]\ell}$ are determined by the normalization scheme, it is easy to convert our wavefunctions into functions having a different normalization.

The new sets of functions $\underset{\sim}{\phi}_{[n]\ell}$ are determined in terms of the previously determined functions by requiring that the n-th order perturbation equation for $\psi_{[n]\ell}$ be mathematically consistent with respect to the complete set of zeroth order degenerate eigenfunctions $\underset{\sim}{\phi}^{(0)}_{[0]q}$ . The function space of the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ is resolved into the subspaces $\underset{\sim}{\phi}^{(0)}_{[n-1]q}, \underset{\sim}{\phi}^{(0)}_{[n-1]k}, \underset{\sim}{\phi}^{(0)}_{[n-2]k}, \ldots,$ and $\underset{\sim}{\phi}^{(0)}_{[1]k}$ . The consistency with respect to each subspace is considered in turn.

The $\underset{\sim}{\phi}^{(0)}_{[n-1]q}$ consistency requirement leads to the secular equation for the n-th order energy $\epsilon^{(n)}_{[n]\ell}$

$$\left|\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} - \varepsilon^{(n)}_{[n]\ell}\underset{\approx}{1}\right| = 0 , \tag{87}$$

where $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ is the Hermitean matrix

$$\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} = \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} \left| \sum_{t=1}^{n-1} \bar{H}^{(t)} \phi^{(n-t)}_{[n-1]q} + H^{(n)} \phi^{(0)}_{[n-1]q} \right\rangle . \tag{88}$$

At this point we must choose which value of $\varepsilon^{(n)}_{[n]\ell}$ to call $\varepsilon^{(n)}_{q}$ , the other values are then designated as $\varepsilon^{(n)}_{[n]k}$ . The eigenvectors of $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ are the expansion coefficients $\langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle$ ,

$$[\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} - \varepsilon^{(n)}_{[n]\ell}\underset{\approx}{1}] \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle = 0 . \tag{89}$$

The new functions $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ are then linear combination of the $\underset{\sim}{\phi}^{(0)}_{[n-1]q}$ ,

$$\underset{\sim}{\phi}^{(0)}_{[n]\ell} = \underset{\sim}{\phi}^{(0)}_{[n-1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle . \tag{90}$$

The $\underset{\sim}{\phi}^{(0)}_{[n-m]k}$ requirement leads to the determination of the functions $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ by means of the <u>magic formula</u>,

$$\underset{\sim}{\phi}^{(m)}_{[n]\ell} = \left[ \underset{\sim}{\phi}^{(m)}_{[n-1]q} + \sum_{k} \sum_{p=0}^{m-1} \underset{\sim}{\phi}^{(p)}_{[n-m+p]k} \mathcal{E}^{(-n+m-p)}_{k} \underset{\approx}{A}^{(n)}_{[n-m+p]k} \right] \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle , \quad 1 \le m \le n-1 , \tag{91}$$

where we have defined the matrices

$$\underset{\approx}{A}^{(n)}_{[s]\ell'} = \sum_{t=1}^{n} \langle \underset{\sim}{\phi}^{(0)}_{[s]\ell'} | \bar{H}^{(t)} | \underset{\sim}{\phi}^{(n-t)}_{[n-1]q} \rangle , \tag{92}$$

and let

$$\mathcal{E}^{(-u)}_{k} = [\varepsilon^{(u)}_{q} - \varepsilon^{(u)}_{[u]k}]^{-1} . \tag{93}$$

We call Eq. (91) the magic formula because it is really the key to the general iterative procedure.

And, finally, the n-th order perturbation equation is solved to obtain

$$\underset{\sim}{\phi}^{(n)}_{[n]\ell} = R^{(0)} \sum_{t=1}^{n} \bar{H}^{(t)} \underset{\sim}{\phi}^{(n-t)}_{[n]\ell} \ . \qquad (94)$$

Eq. (94) is, of course, exactly equivalent to solving Eqs. (83) and (85) with $m = n$. Note that the functions $\underset{\sim}{\phi}^{(n)}_{[n]k}$ are never required in the iterative procedure for determining $\psi_q$.

In our derivations, we make use of the fact that when

<u>$(n-1) \geq s \geq p$</u> ,

$$\underset{\approx}{A}^{(p)}_{[s]\ell'} = \delta_{s,p}(\varepsilon^{(p)}_{[p]\ell'} - \varepsilon^{(p)}_{q})\langle\underset{\sim}{\phi}^{(0)}_{[p]\ell'}|\underset{\sim}{\phi}^{(0)}_{[p-1]q}\rangle \ . \qquad (95)$$

<u>The Inductive Proof of the Iterative Pattern.</u>

Our proof of the iterative scheme is inductive. We <u>know</u> that the pattern corresponding to Eqs. (81)-(95) applies through the first <u>two</u> iterative steps. Assuming that these equations apply for the first (n-1) steps, we prove that they apply to the n-th step.

In treating the n-th order step, we follow the same format which we used for the first two steps. In this section we focus our attention on a $\psi_{[n]\ell}$ which is one of the set of $\psi_{[n-1]q}$. Thus, in the previous order, the equation corresponding to Eq. (82) has n replaced by (n-1) in the subscripts of the functions $\underset{\sim}{\phi}$,

$$\psi^{(m)}_{[n]\ell} = \sum_{t=0}^{m} \underset{\sim}{\phi}^{(t)}_{[n-m-1+t]q}\langle\underset{\sim}{\phi}^{(0)}_{[n-m-1+t]q}|\psi^{(m-t)}_{[n]\ell}\rangle \ , \quad 0 \leq m \leq n-1 \ . \qquad (96)$$

Although the energy $\varepsilon^{(n)}_{[n]\ell}$ remains to be determined, the n-th order perturbation equation (6) can be written

$$\sum_{t=0}^{n-1} \bar{H}^{(t)} \psi^{(n-t)}_{[n]\ell} + (H^{(n)} - \varepsilon^{(n)}_{[n]\ell})\psi^{(0)}_{[n]\ell} = 0 . \tag{97}$$

Substituting Eq. (96) into Eq. (97), we obtain

$$\bar{H}^{(0)}\psi^{(n)}_{[n]\ell} + [\sum_{t=1}^{n-1} \bar{H}^{(t)} \underset{\sim}{\phi}^{(n-t)}_{[n-1]q} + (H^{(n)}-\varepsilon^{(n)}_{[n]\ell})\underset{\sim}{\phi}^{(0)}_{[n-1]g}] \langle \underset{\sim}{\phi}^{(0)}_{[n-1]g} | \psi^{(0)}_{[n]\ell}\rangle$$

$$+ \sum_{s=1}^{n-1} \sum_{t=1}^{n-s} \bar{H}^{(t)} \underset{\sim}{\phi}^{(n-t-s)}_{[n-1-s]g} \langle \underset{\sim}{\phi}^{(0)}_{[n-1-s]g} | \psi^{(s)}_{[n]\ell}\rangle = 0 . \tag{98}$$

At this point, we are ready to assure the consistency of Eq. (98) with respect to the functions $\underset{\sim}{\phi}^{(0)}_{[n-1]q}$ , $\underset{\sim}{\phi}^{(0)}_{[n-1]k}$ , $\underset{\sim}{\phi}^{(0)}_{[n-2]k}$ , ... , $\underset{\sim}{\phi}^{(0)}_{[1]k}$ .

(1) <u>The $\underset{\sim}{\phi}^{(0)}_{[n-1]q}$ Consistency;</u> $\varepsilon^{(n)}_{[n]\ell}$ <u>and</u> $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ .

Multiplying Eq. (98) by $\underset{\sim}{\phi}^{(0)*}_{[n-1]q}$ and integrating,

$$[\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} - \varepsilon^{(n)}_{[n]\ell} \underset{\approx}{1}] \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \psi^{(0)}_{[n]\ell}\rangle = 0 , \tag{99}$$

where the $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ is given by Eq. (88). Because of Eq. (95), the last line of Eq. (98) does not contribute to Eq. (99). By repeated manipulations involving the equations (83) [see Eq. (132) with u=n-1 ]. we can show that $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ is Hermitean and it can also be written in the form

$$\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} = \langle \sum_{t=1}^{n} \bar{H}^{(t)} \underset{\sim}{\phi}^{(n-t)}_{[n-1]q} + H^{(n)} \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n-1]q}\rangle . \tag{100}$$

As explained previously, the $\varepsilon^{(n)}_{[n]\ell}$ are the roots of the secular equation (87) and the corresponding eigenvectors of $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ are the expansion coefficients $<\underset{\sim}{\phi}^{(0)}_{[n-1]q}|\underset{\sim}{\phi}^{(0)}_{[n]\ell}>$ which satisfy Eq. (89). The function $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ is defined by Eq. (90). Since the eigenvectors are orthogonal and taken to have unit length, Eq. (84) is satisfied.

Making use of Eqs. (100) and (90), the conjugate complex of Eq. (88) becomes a new member of the Eq. (95) family,

$$\underset{\approx}{A}^{(n)}_{[n]\ell'} = (\varepsilon^{(n)}_{[n]\ell'} - \varepsilon^{(n)}_{q})<\underset{\sim}{\phi}^{(0)}_{[n]\ell'}|\underset{\sim}{\phi}^{(0)}_{[n-1]q}> .$$

Also

$$\underset{\approx}{A}^{(p)}_{[n]\ell'} = <\underset{\sim}{\phi}^{(0)}_{[n]\ell'}|\underset{\sim}{\phi}^{(0)}_{[n-1]q}>A^{(p)}_{[n-1]q} = 0 , \quad 1\le p\le n-1 \tag{101}$$

Therefore we have proved that if Eq. (95) is valid for $s\leq(n-1)$ , then it is also valid for $s\leq n$ .

(2) <u>The</u> $\underset{\sim}{\phi}^{(0)}_{[n-s]k}$ <u>Consistency</u>.

Multiplying Eq. (98) by $\underset{\sim}{\phi}^{(0)*}_{[n-s]k}$ and integrating, we obtain

$$[\underset{\approx}{A}^{(n)}_{[n-s]k} + (\varepsilon^{(n)}_{q}-\varepsilon^{(n)}_{[n]\ell})<\underset{\sim}{\phi}^{(0)}_{[n-s]k}|\underset{\sim}{\phi}^{(0)}_{[n-1]q}>]<\underset{\sim}{\phi}^{(0)}_{[n-1]q}|\psi^{(0)}_{[n]\ell}>$$

$$+ \sum_{p=1}^{n-1} \underset{\approx}{A}^{(n-p)}_{[n-s]k} <\underset{\sim}{\phi}^{(0)}_{[n-1-p]q}|\psi^{(p)}_{[n]\ell}> = 0 . \tag{102}$$

However, by repeated use of Eq. (90),

$$\underset{\sim}{\phi}^{(0)}_{[n-1]q} = \underset{\sim}{\phi}^{(0)}_{[n-s]q}<\underset{\sim}{\phi}^{(0)}_{[n-s]q}|\underset{\sim}{\phi}^{(0)}_{[n-s+1]q}><\underset{\sim}{\phi}^{(0)}_{[n-s+1]q}|\cdots|\underset{\sim}{\phi}^{(0)}_{[n-1]q}> , \tag{103}$$

so that according to Eq. (84)

$$<\underset{\sim}{\phi}^{(0)}_{[n-s]k} \mid \underset{\sim}{\phi}^{(0)}_{[n-1]q}> = 0 . \tag{104}$$

Also, from Eq. (95),

$$\underset{\approx}{A}^{(n-p)}_{[n-s]k} = 0 \quad , \quad p > s \; , \tag{105}$$

$$\underset{\approx}{A}^{(n-s)}_{[n-s]k} = (\varepsilon^{(n-s)}_{[n-s]k} - \varepsilon^{(n-s)}_{q})<\underset{\sim}{\phi}^{(0)}_{[n-s]k}|\underset{\sim}{\phi}^{(0)}_{[n-s-1]q}> . \tag{106}$$

Thus, since by Eq. (90),

$$<\underset{\sim}{\phi}^{(0)}_{[n-s]k}|\psi^{(s)}_{[n]\ell}> = <\underset{\sim}{\phi}^{(0)}_{[n-s]k}|\underset{\sim}{\phi}^{(0)}_{[n-s-1]q}> <\underset{\sim}{\phi}^{(0)}_{[n-s-1]q}|\psi^{(s)}_{[n]\ell}> , \tag{107}$$

Eq. (102), the $\underset{\sim}{\phi}^{(0)}_{[n-s]k}$ consistency condition, becomes

$$<\underset{\sim}{\phi}^{(0)}_{[n-s]k}|\psi^{(s)}_{[n]\ell}> = \sum_{p=0}^{s-1} \mathcal{E}^{(s-n)}_{k} \; \underset{\approx}{A}^{(n-p)}_{[n-s]k}<\underset{\sim}{\phi}^{(0)}_{[n-1-p]q}|\psi^{(p)}_{[n]\ell}> . \tag{108}$$

In deriving the magic formula, these consistency conditions are used in the following connection. Since,

$$\underset{\sim}{\phi}^{(0)}_{[n-s-1]q} = \underset{\sim}{\phi}^{(0)}_{[n-s]q}<\underset{\sim}{\phi}^{(0)}_{[n-s]q}|\underset{\sim}{\phi}^{(0)}_{[n-s-1]q}>$$

$$+ \sum_{k} \underset{\sim}{\phi}^{(0)}_{[n-s]k}<\underset{\sim}{\phi}^{(0)}_{[n-s]k}|\underset{\sim}{\phi}^{(0)}_{[n-s-1]q}> , \tag{109}$$

it follows that

$$\langle \underset{\sim}{\phi}^{(0)}_{[n-s-1]q} | \psi^{(s)}_{[n]\ell} \rangle = \langle \underset{\sim}{\phi}^{(0)}_{[n-s-1]q} | \underset{\sim}{\phi}^{(0)}_{[n-s]q} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[n-s]q} | \psi^{(s)}_{[n]\ell} \rangle$$

$$+ \sum_k \langle \underset{\sim}{\phi}^{(0)}_{[n-s-1]q} | \underset{\sim}{\phi}^{(0)}_{[n-s]k} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[n-s]k} | \psi^{(s)}_{[n]\ell} \rangle \; . \qquad (110)$$

Thus, using the $\underset{\sim}{\phi}^{(0)}_{[n-s]k}$ consistency condition,

$$\langle \underset{\sim}{\phi}^{(0)}_{[n-s-1]q} | \psi^{(s)}_{[n]\ell} \rangle = \langle \underset{\sim}{\phi}^{(0)}_{[n-s-1]q} | \underset{\sim}{\phi}^{(0)}_{[n-s]q} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[n-s]q} | \psi^{(s)}_{[n]\ell} \rangle$$

$$+ \sum_k \langle \underset{\sim}{\phi}^{(0)}_{[n-s-1]q} | \underset{\sim}{\phi}^{(0)}_{[n-s]k} \rangle \sum_{p=0}^{s-1} \mathcal{E}^{(s-n)}_k \underset{\approx}{A}^{(n-p)}_{[n-s]k} \langle \underset{\sim}{\phi}^{(0)}_{[n-1-p]q} | \psi^{(p)}_{[n]\ell} \rangle \; . \qquad (111)$$

(3) <u>The Proof of the Magic Formula;</u> $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ .

We seek to show that if the magic formula is valid for the determination of all of the $\underset{\sim}{\phi}^{(m')}_{[n']\ell'}$ for $n'<n$ and $m'<n'$ , then it is also valid for the determination of the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ with $m<n$ . We do this by comparing the two expressions for $\psi^{(m)}_{[n]\ell}$ , Eqs. (96) and (82). In Eq. (96), all of the $\underset{\sim}{\phi}^{(m')}_{[n']q}$ which occur correspond to $n'<n$ and therefore we can assume that they are known at this stage of the development. In Eq. (82), except for the $\psi^{(m-t)}_{[n]\ell}$, the only unknown function at this point is $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ . By starting out with Eq. (96) and making repeated use of Eq. (109), we obtain a new equation which agrees with Eq. (82) provided that $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ is defined in accordance with the magic formula (91).

In order to make our derivation less cumbersome, let us define the following functions:

$$f_t(p) = \underset{\sim}{\phi}^{(t)}_{[n-m+t-1]q} + \sum_{u=0}^{p-1} \sum_k \underset{\sim}{\phi}^{(u)}_{[n-m+u]k} \mathcal{E}_k^{(-n+m-u)} \underset{\approx}{A}^{(n-m+t)}_{[n-m+u]k} , \tag{112}$$

$$F_t(p) = f_t(p) \langle \underset{\sim}{\phi}^{(0)}_{[n-m+t-1]q} \mid \psi^{(m-t)}_{[n]\ell} \rangle , \tag{113}$$

and

$$G_t = \underset{\sim}{\phi}^{(t)}_{[n-m+t]q} \langle \underset{\sim}{\phi}^{(0)}_{[n-m+t]q} \mid \psi^{(m-t)}_{[n]\ell} \rangle . \tag{114}$$

We note that, according to the magic formula (91),

$$\underset{\sim}{\phi}^{(t)}_{[n-m+t]\ell'} = f_t(t) \langle \underset{\sim}{\phi}^{(0)}_{[n-m+t-1]q} | \underset{\sim}{\phi}^{(0)}_{[n-m+t]\ell'} \rangle . \tag{115}$$

Then, using Eq. (111) where we take $s=m-t$ and $p=m-u$; also using Eqs. (113) - (115),

$$F_t(t) = G_t + \sum_{u=t+1}^{m} \sum_k \underset{\sim}{\phi}^{(t)}_{[n-m+t]k} \mathcal{E}_k^{(-n+m-t)} \underset{\approx}{A}^{(n-m+u)}_{[n-m+t]k} \langle \underset{\sim}{\phi}^{(0)}_{[n-m-1+u]q} | \psi^{(m-u)}_{[n]\ell} \rangle . \tag{116}$$

In the new notation, Eq. (82) is

$$\psi^{(m)}_{[n]\ell} = \sum_{t=0}^{m-1} G_t + \underset{\sim}{\phi}^{(m)}_{[n]\ell} \langle \underset{\sim}{\phi}^{(0)}_{[n]\ell} | \psi^{(0)}_{[n]\ell} \rangle , \tag{117}$$

and Eq. (96) is

$$\psi^{(m)}_{[n]\ell} = \sum_{t=0}^{m} F_t(0) . \tag{118}$$

Now we are ready to proceed to revise Eq. (118). We start by applying Eq. (116) onto the term $F_0(0)$ . The terms in the Eq. (116) sum provide a contribution to each of the remaining $F_m(0)$ so that the net result of applying Eq. (116) onto $F_0(0)$ is that Eq. (118) becomes

$$\psi^{(m)}_{[n]\ell} = G_0 + \sum_{t=1}^{m} F_t(1) . \tag{119}$$

Applying Eq. (116) upon $F_1(1)$ ; then upon $F_2(2)$ ; ... ; and finally on $F_s(s)$ changes Eq. (119) into

$$\psi^{(m)}_{[n]\ell} = \sum_{v=0}^{s} G_v + \sum_{t=s+1}^{m} F_t(s+1) . \tag{120}$$

When $s=m-1$ , Eq. (120) becomes

$$\psi^{(m)}_{[n]\ell} = \sum_{t=0}^{m-1} G_t + F_m(m) . \tag{121}$$

Comparing Eqs. (117) and (121),

$$\underset{\sim}{\phi}^{(m)}_{[n]\ell} \langle \underset{\sim}{\phi}^{(0)}_{[n]\ell} | \psi^{(0)}_{[n]\ell} \rangle = f_m(m) \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \psi^{(n)}_{[n]\ell} \rangle . \tag{122}$$

Using Eq. (81) [which we have already verified], it follows that

$$\underset{\sim}{\phi}^{(m)}_{[n]\ell} = f_m(m) \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle , \tag{123}$$

where $f_m(m)$ is given by Eq. (112). Eq. (123) is indeed the magic formula! Thus, we have completed the proof.

(4) The m-th Order Perturbation Equations.

According to Eq. (83), the functions $\underset{\sim}{\phi}^{(m')}_{[n-1]q}$ satisfy the perturbation equations

$$\sum_{t=0}^{m} \bar{H}^{(t)} \underset{\sim}{\phi}^{(m-t)}_{[n-1]q} = 0 \quad , \qquad 0 \leq m \leq n-1 \; . \tag{124}$$

Because of Eqs. (91) [which we just proved] and Eq. (124), the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ satisfy the first (n-1)st order perturbation equations (83). And making use of Eq. (91), Eq. (89), and the orthogonality conditions (85) for $\underset{\sim}{\phi}^{(m)}_{[n']\ell}$ with $n'<n$, it follows that Eq. (85) is satisfied by the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$.

(5) The n-th Order Perturbation Equation and $\underset{\sim}{\phi}^{(n)}_{[n]\ell}$.

At this point we are ready to solve the n-th order perturbation equation. Substituting the expressions Eq. (82) for $\psi^{(m)}_{[n]\ell}$ with $m<n$ into Eq. (97),

$$\bar{H}^{(0)}\psi^{(n)}_{[n]\ell} + [\sum_{t=1}^{n} \bar{H}^{(t)}\underset{\sim}{\phi}^{(n-t)}_{[n]\ell} + (\varepsilon^{(n)}_{q} - \varepsilon^{(n)}_{[n]\ell})\underset{\sim}{\phi}^{(0)}_{[n]\ell}]\langle\underset{\sim}{\phi}^{(0)}_{[n]\ell}|\psi^{(0)}_{[n]\ell}\rangle$$

$$+ \sum_{s=1}^{n-1} \sum_{t=1}^{n-s} \bar{H}^{(t)}\underset{\sim}{\phi}^{(n-s-t)}_{[n-s]q} \langle\underset{\sim}{\phi}^{(0)}_{[n-s]q}|\psi^{(s)}_{[n]\ell}\rangle = 0 \; ; \tag{125}$$

Thus, according to Eq. (14),

$$\psi^{(n)}_{[n]\ell} = R^{(0)} \sum_{t=1}^{n} \bar{H}^{(t)}\underset{\sim}{\phi}^{(n-t)}_{[n]\ell}\langle\underset{\sim}{\phi}^{(0)}_{[n]\ell}|\psi^{(0)}_{[n]\ell}\rangle$$

$$+ \sum_{s=1}^{n-1} \sum_{t=1}^{n-s} R^{(0)}\bar{H}^{(t)}\underset{\sim}{\phi}^{(n-s-t)}_{[n-s]q}\langle\underset{\sim}{\phi}^{(0)}_{[n-s]q}|\psi^{(s)}_{[n]\ell}\rangle + \underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi^{(n)}_{[n]\ell}\rangle \; . \tag{126}$$

Thus, if we use the expressions given by Eq. (94) for $\underset{\sim}{\phi}^{(n-s)}_{[n-s]q}$ and define $\underset{\sim}{\phi}^{(n)}_{[n]\ell}$ in accordance with Eq. (94), then $\psi^{(n)}_{[n]\ell}$ is given by Eq. (82). Substituting this expression for $\psi^{(n)}_{[n]\ell}$ into Eq. (125), it follows that the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ satisfy the n-th order equation (83). Since any function of the form $R^{(0)}(\ldots)$ is orthogonal to the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ , it follows from Eq. (94) that $\underset{\sim}{\phi}^{(n)}_{[n]\ell}$ satisfies the orthogonality condition Eq. (85).

(6) Summary.

Thus we have shown that if Eq. (81) - (95) apply through the (n-1)st iterative step, they also apply to the n-th step. Since Eqs. (81) - (95) have been shown to apply through the first two orders, it follows that these relations must hold for all values of n .

## V. THE (2n+1) RULE AND SOLUTIONAL ECONOMY.

The real difficulty of determining the perturbation energies is involved in the solution of the partial differential equations which are required. Thus, there is a very real advantage if we can reduce the number of differential equations necessary to obtain $\varepsilon^{(2n)}_{[2n]\ell}$ or $\varepsilon^{(2n+1)}_{[2n+1]\ell}$ from (2n-1) or 2n to n . This should be possible since Wigner showed that if an approximate wavefunction is accurate through order $\lambda^{n}$ , then the corresponding expectation value for the Hamiltonian should be accurate through order $\lambda^{2n+1}$ . Indeed, for non-degenerate Rayleigh Schrödinger perturbations, the energy through $\varepsilon^{(2n+1)}_{q}$ is determined by the wavefunction through $\psi^{(n)}_{q}$ . We will show in this section, how to do the same thing for degenerate perturbations. This solutional economy is accomplished by means of: (A) The "unwinding and winding" of the $\underset{\approx}{A}^{(n)}_{[s]\ell}$ ; (B) The repeated use of the magic formula to "unwind" the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ ; and (C) The sequential solution of a set of eigenvalue-eigenvector equations.

(A) *The "Unwinding and Winding" of the* $\underset{\approx}{A}^{(n)}_{[s]\ell}$ .

In carrying out the "unwinding and winding" of the $\underset{\approx}{A}^{(n)}_{[s]\ell}$ we shall be concerned with two sets of functions: the $\underset{\sim}{\phi}^{(p)}_{[s]\ell}$ which satisfy the first s perturbation equations (83); and the $\underset{\sim}{\phi}^{(t)}_{[n-1]q}$ which satisfy the first (n-1) perturbation equations (83). Thus, it is obvious that if the first n orders of the Hamiltonian are Hermitean and *if u<s or if we are dealing with* $\underset{\sim}{\phi}^{(p)}_{[s]q}$ *the u=s is also allowed*, then,

$$\sum_{p=0}^{u-1} <\underset{\sim}{\phi}^{(p)}_{[s]\ell}|\bar{H}^{(u-p)}\underset{\sim}{\phi}^{(n-u)}_{[n-1]q}> = - <\underset{\sim}{\phi}^{(u)}_{[s]\ell}|\bar{H}^{(0)}\underset{\sim}{\phi}^{(n-u)}_{[n-1]q}>$$

$$= \sum_{t=0}^{n-u-1} <\underset{\sim}{\phi}^{(u)}_{[s]\ell}|\bar{H}^{(n-u-t)}\underset{\sim}{\phi}^{(t)}_{[n-1]q}> . \tag{127}$$

The $\underset{\approx}{A}^{(n)}_{[s]\ell}$ defined by Eq. (92) can be expressed in the form

$$\underset{\approx}{A}^{(n)}_{[s]\ell} = \sum_{t=0}^{n-1} <\underset{\sim}{\phi}^{(0)}_{[s]\ell}|\bar{H}^{(n-t)}|\underset{\sim}{\phi}^{(t)}_{[n-1]q}> . \tag{128}$$

If we apply onto the term with t=n-1 , the Eq. (127) with the u=1 operation, then we obtain

$$\underset{\approx}{A}^{(n)}_{[s]\ell} = \sum_{t=0}^{n-2} \sum_{p=0}^{1} <\underset{\sim}{\phi}^{(p)}_{[s]\ell}|\bar{H}^{(n-t-p)}|\underset{\sim}{\phi}^{(t)}_{[n-1]q}> . \tag{129}$$

Repeating this operation with u=2 upon the t=n-2 terms in Eq. (129),

$$\underset{\approx}{A}^{(n)}_{[s]\ell} = \sum_{t=0}^{n-3} \sum_{p=0}^{2} \langle \underset{\sim}{\phi}^{(p)}_{[s]\ell} | \bar{H}^{(n-t-p)} | \underset{\sim}{\phi}^{(t)}_{[n-1]q} \rangle . \tag{130}$$

Thus, after repeating this process (u-1) times,

$$\underset{\approx}{A}^{(n)}_{[s]\ell} = \sum_{t=0}^{n-u-1} \sum_{p=0}^{u} \langle \underset{\sim}{\phi}^{(p)}_{[s]\ell} | \bar{H}^{(n-t-p)} | \underset{\sim}{\phi}^{(t)}_{[n-1]q} \rangle \tag{131}$$

where

$$u<s \quad \text{for} \quad \underset{\sim}{\phi}^{(p)}_{[s]k} \quad \text{or} \quad u\leq s \quad \text{for} \quad \underset{\sim}{\phi}^{(p)}_{[s]q} .$$

This "unwinding and winding" of $\underset{\approx}{A}^{(n)}_{[s]\ell}$ has the advantage that instead of requiring $\underset{\sim}{\phi}^{(t)}_{[n-1]q}$ through the (n-1)-st order, it is now only necessary to know it through the (n-u-1)-st order. But it has the disadvantage that now we must know the $\underset{\sim}{\phi}^{(p)}_{[s]\ell}$ through the u-th order. Usually it is best to let $u=(n-1)/2$, or close to it.

(B) <u>The "Unwinding" of the Energy.</u>

Since $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} = \underset{\approx}{A}^{(n)}_{[n-1]q} + \varepsilon^{(n)}_{q}\underset{\approx}{1}$ ; from Eq. (131),

$$\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} = \sum_{t=0}^{n-u-1}{}' \sum_{p=0}^{u}{}' \langle \underset{\sim}{\phi}^{(p)}_{[n-1]q} | \bar{H}^{(n-t-p)} | \underset{\sim}{\phi}^{(t)}_{[n-1]q} \rangle + \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | H^{(n)} | \underset{\sim}{\phi}^{(0)}_{[n-1]q} \rangle \tag{132}$$

where the <u>primes on the summations mean that the term t=p=0 is excluded</u>. By taking u=n-1 , we have demonstrated that $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ is

Hermitean and proved Eq. (100). If in Eq. (132) we replace n by 2n and choose u=n-1, we obtain

$$\underset{\sim}{\varepsilon}^{(2n)}_{[2n-1]q} = \langle \underset{\sim}{\phi}^{(0)}_{[2n-1]q} | H^{(n)} | \underset{\sim}{\phi}^{(0)}_{[2n-1]q} \rangle + \sum_{t=0}^{n}{}' \sum_{p=0}^{n-1}{}' \langle \underset{\sim}{\phi}^{(p)}_{[2n-1]q} | \bar{H}^{(2n-t-p)} | \underset{\sim}{\phi}^{(t)}_{[2n-1]q} \rangle . \tag{133}$$

While if we replace n by 2n+1 and choose u=n, we obtain

$$\underset{\sim}{\varepsilon}^{(2n+1)}_{[2n]q} = \langle \underset{\sim}{\phi}^{(0)}_{[2n]q} | H^{(2n+1)} | \underset{\sim}{\phi}^{(0)}_{[2n]q} \rangle + \sum_{t=0}^{n}{}' \sum_{p=0}^{n}{}' \langle \underset{\sim}{\phi}^{(p)}_{[2n]q} | \bar{H}^{(2n+1-t-p)} | \underset{\sim}{\phi}^{(t)}_{[2n]q} \rangle . \tag{134}$$

These two equations demonstrate the (2n+1) rule for the energies. The $\underset{\sim}{\phi}^{(t)}_{[2n-1]q}$ and $\underset{\sim}{\phi}^{(t)}_{[2n]q}$ with $t \leq n$ in Eqs. (133) and (134) can be expressed in terms of the $\underset{\sim}{\phi}^{(m')}_{[n']\ell}$ with $m' \leq n' \leq n$.

### (C) The Unwinding of the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$

To demonstrate the (2n+1) rule for the wavefunctions, we note that in order to calculate $\underset{\sim}{\phi}^{(m)}_{[n+j]\ell}$ according to the magic formula (91), we require the matrices

$$\underset{\approx}{A}^{(n+j)}_{[n+j-m+p]k} = \langle \underset{\sim}{\phi}^{(0)}_{[n+j-m+p]k} | \underset{\sim}{\phi}^{(0)}_{[n+j-m+p-1]q} \rangle \underset{\approx}{A}^{(n+j)}_{[n+j-m+p-1]q} , \tag{135}$$

which, according to Eq. (92), involves up to (n+j-1) order wavefunctions. However, we may apply Eq. (131) to obtain

$$\underset{\approx}{A}^{(n+j)}_{[n+j-m+p-1]q} = \sum_{t=0}^{n+j-1-u} \sum_{s=0}^{u} \langle \underset{\sim}{\phi}^{(s)}_{[n+j-m+p-1]q} | \bar{H}^{(n+j-t-s)} | \underset{\sim}{\phi}^{(t)}_{[n+j-1]q} \rangle , \tag{136}$$

where $u<(n+j-m+p-1)$ . Thus, we can avoid wavefunctions of higher than n-th order if we choose $u$ so that

$$(j-2) \leq u \leq n \tag{137}$$

For example, taking $u=j-1$,

$$\underset{\approx}{A}^{(n+j)}_{[n+j-m+p-1]q} = \sum_{t=0}^{n} \sum_{s=0}^{j-1} \langle \underset{\sim}{\phi}^{(s)}_{[n+j-m+p-1]q} | \bar{H}^{(n+j-t-s)} | \underset{\sim}{\phi}^{(t)}_{[n+j-1]q} \rangle \; . \tag{138}$$

Of particular interest is the case $j=n$ , which establishes the (2n+1) rule for $\underset{\approx}{\varepsilon}^{(2n)}_{[2n-1]q}$ , and the case $j=n+1$ , which establishes the (2n+1) rule for $\underset{\approx}{\varepsilon}^{(2n+1)}_{[2n]q}$ .

## VI. COMPUTATIONAL PROCEDURES: THE BASIC CYCLE AND THE (2n+1) CYCLE.

There are many ways in which our formalism can be used to calculate the energy and wavefunctions of degenerate states. The optimum procedure depends upon the detailed branching of the energy of these states; whether the wavefunctions as well as the energy are required; whether the energies of all of the degenerate states are being calculated; and to what order should the energies and/or wavefunctions be determined. In arranging the computations, consideration should be given to two types of procedures: the basic cycle and the (2n+1) cycles. In the basic, the $\varepsilon^{(n)}_{[n]\ell}$ is determined from a knowledge of the $\underset{\sim}{\phi}^{(m)}_{[n-1]g}$ where $0\leq m\leq n-1$ . In the (2n+1) , the energy through $\varepsilon^{(2n+1)}_{[2n+1]\ell}$ is determined from a knowledge of the $\underset{\sim}{\phi}^{(s)}_{[2n]q}$ for $s\leq n$ . If the determination of $\underset{\sim}{\phi}^{(s)}_{[s]q}$ requires the solution of a partial differential equation and is therefore a computational bottleneck, then the (2n+1) cycle is beneficial. If, on the other hand, the $\underset{\sim}{\phi}^{(s)}_{[s]q}$ is being approximated by a linear combination of basis functions [see Section VII] and $R^{(0)}$ becomes a finite matrix, then the advantages of the (2n+1) are not obvious. And, finally, if the energy through the $\varepsilon^{(2n+1)}_{[2n+1]\ell}$ is required, then one might choose to use the basic cycle through $\varepsilon^{(n+1)}_{[n+1]\ell}$ and the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ and complete the calculations by a modification of the (2n+1) procedure.

In any case, the $\underset{\sim}{\phi}$'s are related to the wavefunctions by Eq. (82)

$$\psi^{(m)}_{[n]\ell} = \underset{\sim}{\phi}^{(m)}_{[n]\ell} \langle \underset{\sim}{\phi}^{(0)}_{[n]\ell} | \psi^{(0)}_{[n]\ell} \rangle + \sum_{t=0}^{m-1} \underset{\sim}{\phi}^{(t)}_{[n-m+t]q} \langle \underset{\sim}{\phi}^{(0)}_{[n-m+t]q} | \psi^{(m-t)}_{[n]\ell} \rangle , \qquad (82)$$

where the $\psi^{(m)}_{[n]\ell}$ is intermediately normalized. For any other normalization, Eq. (86) should be used in place of Eq. (82).

## The Basic Cycle

The basic cycle consists of the following chain:

$$\ldots \rightarrow \vdots\ \underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} \rightarrow \varepsilon^{(n)}_{[n]\ell} ,\ \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rightarrow \underset{\sim}{\phi}^{(m)}_{[n]\ell} \text{ for } 1 \leq m \leq n-1 \rightarrow \underset{\sim}{\phi}^{(n)}_{[n]\ell}\ \vdots \rightarrow \underset{\approx}{\varepsilon}^{(n+1)}_{[n]q} \rightarrow \ldots .$$

The starting sequence is the regular basic cycle with

$$\underset{\approx}{\varepsilon}^{(1)}_{[0]q} \rightarrow \underset{\approx}{\varepsilon}^{(1)}_{[1]\ell} ,\ \underset{\sim}{\phi}^{(0)}_{[1]\ell} \rightarrow \underset{\sim}{\phi}^{(1)}_{[1]q}\ \vdots \rightarrow \underset{\approx}{\varepsilon}^{(2)}_{[1]q} \rightarrow \underset{\approx}{\varepsilon}^{(2)}_{[2]\ell} ,\ \underset{\sim}{\phi}^{(0)}_{[2]\ell} \rightarrow \underset{\sim}{\phi}^{(1)}_{[2]\ell} \rightarrow \ldots ,$$

The steps in the chain are:

1) The $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ is given by Eq. (88),

$$\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} = \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \sum_{t=1}^{n-1} \bar{H}^{(t)} \underset{\sim}{\phi}^{(n-t)}_{[n-1]q} + H^{(n)} \underset{\sim}{\phi}^{(0)}_{[n-1]q} \rangle \; . \tag{88}$$

2) The $\varepsilon^{(n)}_{[n]\ell}$ is given by Eq. (87),

$$| \underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} - \varepsilon^{(n)}_{[n]\ell} \underset{\approx}{1} | = 0 \; . \tag{87}$$

3) The expansion coefficients $\langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle$ are given as the eigenvectors of $\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q}$ by Eq. (89),

$$[\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} - \varepsilon^{(n)}_{[n]\ell} \underset{\approx}{1}] \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle = 0 \; . \tag{89}$$

The $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ are then given by Eq. (90),

$$\underset{\sim}{\phi}^{(0)}_{[n]\ell} = \underset{\sim}{\phi}^{(0)}_{[n-1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle \; . \tag{90}$$

4) The $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ for $1 \leq m \leq n-1$ are given by Eqs. (91) - (93),

$$\underset{\sim}{\phi}^{(m)}_{[n]\ell} = \left[ \underset{\sim}{\phi}^{(m)}_{[n-1]q} + \sum_{k} \sum_{p=0}^{m-1} \underset{\sim}{\phi}^{(p)}_{[n-m+p]k} \mathcal{E}^{(-n+m-p)}_{k} \underset{\approx}{A}^{(n)}_{[n-m+p]k} \right] \langle \underset{\sim}{\phi}^{(0)}_{[n-1]q} | \underset{\sim}{\phi}^{(0)}_{[n]\ell} \rangle \; , \tag{91}$$

where

$$\underset{\approx}{A}^{(n)}_{[n-m+p]k} = \sum_{t=1}^{n} \langle \underset{\sim}{\phi}^{(0)}_{[n-m+p]k} | \bar{H}^{(t)} | \underset{\sim}{\phi}^{(n-t)}_{[n-1]q} \rangle \; , \tag{92}$$

and

$$\mathcal{E}_k^{(-n+m-p)} = [\, \varepsilon_q^{(n-m+p)} - \varepsilon_{[n-m+p]k}^{(n-m+p)} \,]^{-1} \, . \tag{93}$$

5) The $\underset{\sim}{\phi}_{[n]\ell}^{(n)}$ is the solution of Eq. (83) ,

$$\bar{H}^{(0)} \underset{\sim}{\phi}_{[n]\ell}^{(n)} + \sum_{t=1}^{n-1} \bar{H}^{(t)} \underset{\sim}{\phi}_{[n]\ell}^{(n-t)} + [H^{(n)} - \varepsilon_{[n]\ell}^{(n)}] \underset{\sim}{\phi}_{[n]\ell}^{(0)} = 0 \, , \tag{83}$$

together with the orthogonality requirement of Eq. (85),

$$\langle \underset{\sim}{\phi}_{[0]q}^{(0)} | \underset{\sim}{\phi}_{[n]\ell}^{(n)} \rangle = 0 \, . \tag{85}$$

However, if $\underset{\sim}{\phi}_{[n]\ell}^{(n)}$ is being approximated by a linear combination of fixed basis functions, then $R^{(0)}$ is a matrix [see Eq. (158)] and it is more convenient to determine $\underset{\sim}{\phi}_{[n]\ell}^{(n)}$ by Eq. (94).

## The (2n+1) Cycle

The (2n+1) cycle consists of the following chain:

$$\cdots \underset{\sim}{\phi}_{[n]q}^{(n)} \rightarrow \underset{\sim}{\phi}_{[n+j]\ell}^{(n)} \text{ for } 1 \leq j \leq n-2 \rightarrow \underset{\sim}{\phi}_{[2n-1]\ell}^{(m)} \text{ for } 1 \leq m \leq n$$

$$\underset{\approx}{\varepsilon}_{[2n]q}^{(2n+1)} \leftarrow \underset{\sim}{\phi}_{[2n]\ell}^{(m)} \text{ for } 1 \leq m \leq n \leftarrow \varepsilon_{[2n]\ell}^{(2n)} \, , \, \underset{\sim}{\phi}_{[2n]\ell}^{(0)} \leftarrow \underset{\approx}{\varepsilon}_{[2n-1]q}^{(2n)}$$

$$\rightarrow \varepsilon_{[2n+1]\ell}^{(2n+1)} \, , \, \underset{\sim}{\phi}_{[2n+1]\ell}^{(0)} \rightarrow \underset{\sim}{\phi}_{[n+1]q}^{(n+1)} \rightarrow \cdots$$

The starting sequence is the same as the regular (2n+1) cycle with the following exceptions: In the n=0 cycle, only the (8)-th through

(10)-th steps are performed; in the n=1 cycle, the (2)-nd and (3)-rd steps are omitted; in the n=2 cycle, the (2)-nd step is omitted.

Figure 1 shows the energies and $\underset{\sim}{\phi}$'s which are calculated in each cycle.

The steps in the (2n+1) cycle are:

1) The $\underset{\sim}{\phi}^{(n)}_{[n]q}$ is determined in exactly the same manner as in step (5) of the basic cycle.

2) The $\underset{\sim}{\phi}^{(n)}_{[n+j]\ell}$ for $1 \leq j \leq n-2$ are determined by successive applications (starting with j=1 ) of the following relation (taking m=n ) which is obtained from Eq. (91) with the help of Eqs. (135) and (138),

$$\underset{\sim}{\phi}^{(m)}_{[n+j]\ell} = \left[ \underset{\sim}{\phi}^{(m)}_{[n+j-1]\ell} + \sum_k \sum_{p=0}^{m-1} \underset{\sim}{\phi}^{(p)}_{[n+j-m+p]k} \mathcal{E}_k^{(-n-j+m-p)} \underset{\approx}{A}^{(n+j)}_{[n+j-m+p]k} \right] \langle \underset{\sim}{\phi}^{(0)}_{[n+j-1]q} | \underset{\sim}{\phi}^{(0)}_{[n+j]\ell} \rangle , \qquad (91)$$

where

$$\mathcal{E}_k^{(-n-j+m-p)} = [\varepsilon_q^{(n+j-m+p)} - \varepsilon^{(n+j-m+p)}_{[n+j-m+p]k}]^{-1} , \qquad (93)$$

$$\underset{\approx}{A}^{(n+j)}_{[n+j-m+p]k} = \langle \underset{\sim}{\phi}^{(0)}_{[n+j-m+p]k} | \underset{\sim}{\phi}^{(0)}_{[n+j-m+p-1]q} \rangle \underset{\approx}{A}^{(n+j)}_{[n+j-m+p-1]q} , \qquad (135)$$

and

$$\underset{\approx}{A}^{(n+j)}_{[n+j-m+p-1]q} = \sum_{t=0}^{n} \sum_{s=0}^{j-1} \langle \underset{\sim}{\phi}^{(s)}_{[n+j-m+p-1]q} | \bar{H}^{(n+j-t-s)} | \underset{\sim}{\phi}^{(t)}_{[n+j-1]q} \rangle . \qquad (138)$$

3) The $\underset{\sim}{\phi}^{(m)}_{[2n-1]\ell}$ for $1 \leq m \leq n$ are determined from the same equations, (91), (93), (135), and (138) as occur in step (2) where now j=n-1 .

4) The $\underset{\approx}{\varepsilon}^{(2n)}_{[2n-1]q}$ is determined by Eq. (133),

$$\underset{\approx}{\varepsilon}^{(2n)}_{[2n-1]q} = \langle \underset{\sim}{\phi}^{(0)}_{[2n-1]q} | H^{(n)} | \underset{\sim}{\phi}^{(0)}_{[2n-1]q} \rangle$$

$$+ \sum_{t=0}^{n}{}' \sum_{p=0}^{n-1}{}' \langle \underset{\sim}{\phi}^{(p)}_{[2n-1]q} | \bar{H}^{(2n-t-p)} | \underset{\sim}{\phi}^{(t)}_{[2n-1]q} \rangle \; . \tag{133}$$

Here the prime on the summations indicates that the term $t=0=p$ is omitted.

5) The $\varepsilon^{(2n)}_{[2n]\ell}$ is determined by the same equation (87) as occurs in step (2) of the basic cycle, except that now $n$ is replaced by $2n$ .

6) The $\underset{\sim}{\phi}^{(0)}_{[2n]\ell}$ is determined by the same equation (89) as occurs in step (3) of the basic cycle, except that now $n$ is replaced by $2n$ .

7) The $\underset{\sim}{\phi}^{(m)}_{[2n]\ell}$ for $1 \leq m \leq n$ are determined from the same equations (91), (93), (135) and (138) as occur in step (2), where now $j=n$ .

8) The $\underset{\approx}{\varepsilon}^{(2n+1)}_{[2n]q}$ is determined by Eq. (134),

$$\underset{\approx}{\varepsilon}^{(2n+1)}_{[2n]q} = \langle \underset{\sim}{\phi}^{(0)}_{[2n]q} | H^{(2n+1)} | \underset{\sim}{\phi}^{(0)}_{[2n]q} \rangle$$

$$+ \sum_{t=0}^{n}{}' \sum_{p=0}^{n}{}' \langle \underset{\sim}{\phi}^{(p)}_{[2n]q} | \bar{H}^{(2n+1-t-p)} | \underset{\sim}{\phi}^{(t)}_{[2n]q} \rangle \; . \tag{134}$$

Here the prime on the summations indicates that the term $t=0=p$ is omitted.

9) The $\varepsilon^{(2n+1)}_{[2n+1]\ell}$ is determined by the same equation (87) as occurs in step (2) of the basic cycle, except that now $n$ is replaced by $(2n+1)$ .

10) Finally, the $\underset{\sim}{\phi}^{(0)}_{[2n+1]\ell}$ is determined by the same equation (89) as occurs in step (3) of the basic cycle, except that now $n$ is replaced by $(2n+1)$ .

# VII. RESOLVED DEGENERACES AND SPECIAL CASES.

As the calculation outlined in Section VI proceeds to higher order, the original block of degenerate states is split into smaller blocks and eventually becomes non-degenerate (or reaches the degree of degeneracy which remains in infinite order). All of the equations and procedures in Section VI remain valid when this occurs (and, in fact, are correct even when the degeneracy is resolved in zeroth order, i.e. in the non-degenerate case). The character of the equations changes somewhat, however, and the procedures become simpler.

The major new feature which emerges when the degeneracy is resolved is that the wavefunctions $\psi_q^{(n)}$ begin to be completely determined. When the degeneracy of the state q of interest is <u>resolved in r-th order</u>, the original block of unperturbed states is resolved into $(r+1)$ subspaces: $\phi^{(0)}_{[r]q}$, $\underset{\sim}{\phi}^{(0)}_{[1]k}$, $\underset{\sim}{\phi}^{(0)}_{[2]k}$, ... $\underset{\sim}{\phi}^{(0)}_{[r]k}$. The subsets $\underset{\sim}{\phi}^{(0)}_{[r+1]k}$, $\underset{\sim}{\phi}^{(0)}_{[r+2]k}$, ... are empty. Then the magic formula (91) gives

$$\phi^{(n)}_{[r+n]q} = \phi^{(n)}_{[r+n+s]q}\ , \quad n\geqslant 0 \quad s\geqslant 1\ , \tag{139}$$

so that Eq. (82) gives

$$\psi_q^{(n)} = \phi^{(n)}_{[r+n]q} \qquad n\geqslant 0\ . \tag{140}$$

In order to discuss the simplifications which result in the procedures of Section VI, let us first consider the special cases when the degeneracy is resolved in first or second order and then discuss the general case.

(A) Degeneracy Resolved in First Order.

In this case Eqs. (140) and (91) give

$$\psi_q^{(n)} = \underset{\sim}{\phi}_{[n+1]q}^{(n)}$$

$$= \underset{\sim}{\phi}_{[n]q}^{(n)} + \sum_k \underset{\sim}{\phi}_{[1]k}^{(0)} \mathcal{E}_k^{(-1)} \underset{\approx}{A}_{[1]k}^{(n+1)} , \qquad (141)$$

where, according to Eqs. (140) and (94),

$$\underset{\sim}{\phi}_{[n]q}^{(n)} = R^{(0)} \sum_{t=1}^{n} \bar{H}^{(t)} \psi_q^{(n-t)} , \qquad (142)$$

and, according to Eqs. (140) and (92),

$$\underset{\approx}{A}_{[1]k}^{(n+1)} = \langle \underset{\sim}{\phi}_{[1]k}^{(0)} | \bar{H}^{(1)} | \underset{\sim}{\phi}_{[n]q}^{(n)} \rangle + \sum_{t=2}^{n+1} \langle \underset{\sim}{\phi}_{[1]k}^{(0)} | \bar{H}^{(t)} | \psi_q^{(n+1-t)} \rangle . \qquad (143)$$

The computational procedure involves solving Eq. (142) for $\underset{\sim}{\phi}_{[n]q}^{(n)}$ which allows $\psi_q^{(n)}$ to be calculated. Then the (2n)-th and (2n+1)-st order energies are calculated by Eqs. (9) and (10).

(B) Degeneracy Resolved in Second Order.

In this case Eqs. (140) and (91) give

$$\psi_q^{(1)} = \underset{\sim}{\phi}_{[3]q}^{(1)} = \underset{\sim}{\phi}_{[2]q}^{(1)} + \sum_k \underset{\sim}{\phi}_{[2]k}^{(0)} \mathcal{E}_k^{(-2)} \underset{\approx}{A}_{[2]k}^{(3)} , \qquad (144)$$

and

$$\underset{\sim}{\phi}_{[2]\ell}^{(1)} = \left[ \underset{\sim}{\phi}_{[1]q}^{(1)} + \sum_k \underset{\sim}{\phi}_{[1]k}^{(0)} \mathcal{E}_k^{(-1)} \underset{\approx}{A}_{[1]k}^{(2)} \right] \langle \underset{\sim}{\phi}_{[1]q}^{(0)} | \underset{\sim}{\phi}_{[2]\ell}^{(0)} \rangle . \qquad (145)$$

Then the higher order wavefunctions are given by

$$\psi_q^{(n)} = \underset{\sim}{\phi}_{[n+2]q}^{(n)} = \underset{\sim}{\phi}_{[n+1]q}^{(n)} + \sum_k \underset{\sim}{\phi}_{[2]k}^{(0)} \mathcal{E}_k^{(-2)} \underset{\approx}{A}_{[2]k}^{(n+2)} , \tag{146}$$

and

$$\underset{\sim}{\phi}_{[n+1]q}^{(n)} = \underset{\sim}{\phi}_{[n]q}^{(n)} + \sum_k \underset{\sim}{\phi}_{[1]k}^{(0)} \mathcal{E}_k^{(-1)} \underset{\approx}{A}_{[1]k}^{(n+1)} + \sum_k \underset{\sim}{\phi}_{[2]k}^{(1)} \mathcal{E}_k^{(-2)} \underset{\approx}{A}_{[2]k}^{(n+1)} , \tag{147}$$

where the coefficients in Eqs. (144), (145), (146) and (147) are

$$\underset{\approx}{A}_{[1]k}^{(n+1)} = \langle \underset{\sim}{\phi}_{[1]k}^{(0)} | \sum_{t=0}^{n-2} \bar{H}^{(n+1-t)} \psi_q^{(t)} + \bar{H}^{(2)} \underset{\sim}{\phi}_{[n]q}^{(n-1)} + \bar{H}^{(1)} \phi_{[n]q}^{(n)} \rangle ,$$

$$\underset{\approx}{A}_{[2]k}^{(n+1)} = \sum_{p=0}^{1} \langle \underset{\sim}{\phi}_{[2]k}^{(p)} | \sum_{t=0}^{n-2} \bar{H}^{(n+1-t-p)} \psi_q^{(t)} + \bar{H}^{(2-p)} \underset{\sim}{\phi}_{[n]q}^{(n-1)} \rangle , \tag{148}$$

$$\underset{\approx}{A}_{[2]k}^{(n+2)} = \sum_{p=0}^{1} \langle \underset{\sim}{\phi}_{[2]k}^{(p)} | \sum_{t=0}^{n-1} \bar{H}^{(n+2-t-p)} \psi_q^{(t)} + \bar{H}^{(2-p)} \underset{\sim}{\phi}_{[n+1]q}^{(n)} \rangle .$$

The energies are determined by Eqs. (9) and (10).

(C) Degeneracy Resolved in r-th Order.

In the basic cycle, if the degeneracy is resolved in r-th order we immediately obtain $\psi_q^{(0)}$ by Eq. (140). Then in each succeeding cycle, we obtain one additional perturbed wavefunction. The only modification of the procedure is the omission of step (3). Of course, steps (1) and (2) are much simpler because $\underset{\approx}{\varepsilon}_{[n-1]q}^{(n)}$ is a number, not a matrix. In step (4), it is necessary to consider only $n-r \leq m \leq n-1$ and the upper limit in the sum over $p$ in Eq. (91) becomes $m-(n-r)$.

In the (2n+1) cycle, if the degeneracy is resolved in r-th order, again we immediately learn $\psi_q^{(0)}$. In the next cycle we obtain $\psi_q^{(1)}$

and $\psi_q^{(2)}$ ; and in each subsequent cycle, two additional $\psi_q^{(n)}$ until n=r . Thereafter, each additional cycle yields one additional $\psi_q^{(n)}$ . The modifications in the procedure are that steps (6) and (10) are omitted, while in steps (3) and (7), it is necessary to consider only those perturbed functions which are not complete according to Eq. (140). Thus after $\psi_q^{(r)}$ is obtained, steps (3) and (7) are omitted entirely. When the perturbed wavefunctions are known completely, Eqs. (133) and (134) reduce to Eqs. (9) and (10).

The computational procedure for the case when the degeneracy is resolved in fourth order is illustrated in Figure 1.

Figure 1. Computational Procedure. This figure illustrates the quantitites obtained in each computational cycle. The basic cycle is indicated by the dotted lines, while the (2n + 1) cycle is indicated by solid lines. See Section VI of the text. The illustration is for the case when the degeneracy is resolved in fourth order.

| Basic Cycle ↓ | (2n+1) Cycle → 1 | | | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $\underset{\approx}{\varepsilon}^{(1)}_{[0]q}$ | $\varepsilon^{(1)}_{[1]\ell}$ | $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$ | $\underset{\sim}{\phi}^{(1)}_{[1]\ell}$ | | | | | | | | | |
| 2 | $\underset{\approx}{\varepsilon}^{(2)}_{[1]q}$ | $\varepsilon^{(2)}_{[2]\ell}$ | $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$ | $\underset{\sim}{\phi}^{(1)}_{[2]\ell}$ | $\underset{\sim}{\phi}^{(2)}_{[2]\ell}$ | | | | | | | | |
| 3 | $\underset{\approx}{\varepsilon}^{(3)}_{[2]q}$ | $\varepsilon^{(3)}_{[3]\ell}$ | $\underset{\sim}{\phi}^{(0)}_{[3]\ell}$ | $\underset{\sim}{\phi}^{(1)}_{[3]\ell}$ | $\underset{\sim}{\phi}^{(2)}_{[3]\ell}$ | $\underset{\sim}{\phi}^{(3)}_{[3]\ell}$ | | | | | | | |
| 4 | $\underset{\approx}{\varepsilon}^{(4)}_{[3]q}$ | $\varepsilon^{(4)}_{[4]\ell}$ | $\underset{\sim}{\phi}^{(0)}_{[4]\ell}$ | $\underset{\sim}{\phi}^{(1)}_{[4]\ell}$ | $\underset{\sim}{\phi}^{(2)}_{[4]\ell}$ | $\underset{\sim}{\phi}^{(3)}_{[4]\ell}$ | $\underset{\sim}{\phi}^{(4)}_{[4]\ell}$ | | | | | | |
| 5 | $\underset{\approx}{\varepsilon}^{(5)}_{[4]q} = \varepsilon^{(5)}_{q}$ | | | $\psi^{(1)}_{q}$ | $\phi^{(2)}_{[5]q}$ | $\phi^{(3)}_{[5]q}$ | $\phi^{(4)}_{[5]q}$ | $\phi^{(5)}_{[5]q}$ | | | | | |
| 6 | $\underset{\approx}{\varepsilon}^{(6)}_{[5]q} = \varepsilon^{(6)}_{q}$ | | | | $\psi^{(2)}_{q}$ | $\phi^{(3)}_{[6]q}$ | $\phi^{(4)}_{[6]q}$ | $\phi^{(5)}_{[6]q}$ | $\phi^{(6)}_{[6]q}$ | | | | |
| 7 | $\underset{\approx}{\varepsilon}^{(7)}_{[6]q} = \varepsilon^{(7)}_{q}$ | | | | | $\psi^{(3)}_{q}$ | $\phi^{(4)}_{[7]q}$ | $\phi^{(5)}_{[7]q}$ | $\phi^{(6)}_{[7]q}$ | $\phi^{(7)}_{[7]q}$ | | | |
| 8 | $\underset{\approx}{\varepsilon}^{(8)}_{[7]q} = \varepsilon^{(8)}_{q}$ | | | | | | $\psi^{(4)}_{q}$ | $\phi^{(5)}_{[8]q}$ | $\phi^{(6)}_{[8]q}$ | $\phi^{(7)}_{[8]q}$ | $\phi^{(8)}_{[8]q}$ | | |
| 9 | $\underset{\approx}{\varepsilon}^{(9)}_{[8]q} = \varepsilon^{(9)}_{q}$ | | | | | | | $\psi^{(5)}_{q}$ | $\phi^{(6)}_{[9]q}$ | $\phi^{(7)}_{[9]q}$ | $\phi^{(8)}_{[9]q}$ | $\phi^{(9)}_{[9]q}$ | |
| 10 | $\underset{\approx}{\varepsilon}^{(10)}_{[9]q} = \varepsilon^{(10)}_{q}$ | | | | | | | | $\psi^{(6)}_{q}$ | $\phi^{(7)}_{[10]q}$ | $\phi^{(8)}_{[10]q}$ | $\phi^{(9)}_{[10]q}$ | $\phi^{(10)}_{[10]q}$ |
| 11 | $\underset{\approx}{\varepsilon}^{(11)}_{[10]q} = \varepsilon^{(11)}_{q}$ | | | | | | | | | $\psi^{(7)}_{q}$ | $\phi^{(8)}_{[11]q}$ | $\phi^{(9)}_{[11]q}$ | $\phi^{(10)}_{[11]q}$ |

# VIII. VARIATIONAL METHODS FOR APPROXIMATING THE $\underset{\sim}{\phi}^{(n)}_{[n]q}$.

As mentioned in Section V, the most intractable aspect of degenerate perturbation problems is the solution of the partial differential equation (83) with the Eq. (85) constraint (or equivalently, the solution of Eq. (94)) for the function $\underset{\sim}{\phi}^{(n)}_{[n]q}$. The problems involved are similar to those of determining the n-th order wavefunction in a non-degenerate example. In this section, we consider variational methods of approximation which can be used when Eq. (83) cannot be solved exactly. In this section, tildes are used to indicate approximate functions or energies.

The basis of the variational method is the usual variational principle: Define the functional $J$ as

$$J = \langle\tilde{\psi}_q|H(\lambda) - \tilde{E}_q(\lambda)|\tilde{\psi}_q\rangle . \qquad (149)$$

Holding $\tilde{E}_q$ fixed, vary $\tilde{\psi}_q$ so as to make $\delta J = 0$. Repeat this process for different values of $\tilde{E}_q$ until simultaneously

$$J = 0 \quad \text{and} \quad \delta J = 0 , \qquad (150)$$

The application of variational methods to degenerate problems has been considered previously by Epstein.[12]

## (A) Linear basis set.[28]

A generally applicable method is to express $\tilde{\psi}_q$ as a linear combination of the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ and a fixed set of basis functions $f_k$. It is convenient to express the set of $f_k$ in vector form as $\underset{\sim}{f}$. Without loss of generality we can require that the $\underset{\sim}{f}$ be ortho-normal, orthogonal to the $\underset{\sim}{\phi}^{(0)}_{[0]q}$, and diagonalize $H^{(0)}$,

$$<\underset{\sim}{f}|\underset{\sim}{f}> = \underset{\approx}{1}\,, \quad <\underset{\sim}{f}|\underset{\sim}{\phi}^{(0)}_{[0]q}> = 0 \tag{151}$$

and

$$<f_k|H^{(0)}|f_j> = \tilde{\varepsilon}_k^{(0)}\delta_{k,j} \,. \tag{152}$$

The effect of the linear basis approximation is to reduce the infinite dimensional Hilbert space to the sum of the two finite subspaces, $\underset{\sim}{f}$ and $\underset{\sim}{\phi}^{(0)}_{[0]q}$. The projector onto this reduced subspace is

$$P = |\underset{\sim}{f}><\underset{\sim}{f}| + |\underset{\sim}{\phi}^{(0)}_{[0]q}><\underset{\sim}{\phi}^{(0)}_{[0]q}| \,. \tag{153}$$

In this notation,

$$\tilde{\psi}_q = P\tilde{\psi}_q = \underset{\sim}{f}<\underset{\sim}{f}|\tilde{\psi}_q> + \underset{\sim}{\phi}^{(0)}_{[0]q}<\underset{\sim}{\phi}^{(0)}_{[0]q}|\tilde{\psi}_q> \,. \tag{154}$$

Here the expansion coefficients $<\underset{\sim}{f}|\tilde{\psi}_q>$ and $<\underset{\sim}{\phi}^{(0)}_{[0]q}|\tilde{\psi}_q>$ are variational parameters. Substituting Eq. (154) into Eq. (149) and satisfying the variational condition Eq. (150), we obtain the familiar eigenvalue-eigenvector equation

$$[\tilde{H}(\lambda) - \tilde{E}_q]\tilde{\psi}_q = 0 \,, \tag{155}$$

where

$$\tilde{H}(\lambda) = PH(\lambda)P \quad \text{and} \quad \tilde{H}^{(n)} = PH^{(n)}P \,. \tag{156}$$

From Eqs. (151) and (152), the zeroth order equation becomes

$$[\tilde{H}^{(0)} - \tilde{\varepsilon}_k^{(0)}]f_k = 0 \quad \text{and} \quad [\tilde{H}^{(0)} - \varepsilon_q^{(0)}]\underset{\sim}{\phi}^{(0)}_{[0]q} = 0. \tag{157}$$

The resolvent corresponding to $\tilde{H}^{(0)}$ is then

$$\tilde{R}^{(0)} = \sum_k [\varepsilon_q^{(0)} - \tilde{\varepsilon}_k^{(0)}]^{-1} |f_k\rangle\langle f_k| \; . \tag{158}$$

Thus, if PF is an arbitrary function in the reduced space then

$$-(\tilde{H}^{(0)} - \varepsilon_q^{(0)})\tilde{R}^{(0)}PF = PF - \underset{\sim}{\phi}_{[0]q}^{(0)} \langle \underset{\sim}{\phi}_{[0]q}^{(0)} | PF\rangle \; . \tag{159}$$

The resolvent $\tilde{R}^{(0)}$ then plays the same role in the reduced space as the resolvent $R^{(0)}$ plays in the full Hilbert space.

Thus, we may apply the formalism of Sections II-VII to solve Eq. (155) exactly to any desired order by using the tilde matrices in place of the corresponding operators and by using PF in place of all functions F . Thus, the solution of the degenerate perturbation equations is reduced to the solution of a set of matrix equations.

(B) Variational principle for $\underset{\approx}{\varepsilon}_{[1]q}^{(2)}$ .

The general application of variational methods to degenerate problems leads to considerable ambiguity. Here we restrict our consideration to the determination of the energy through second order.

Let us consider a trial wavefunction of the form

$$\tilde{\psi}_q = \tilde{\psi}_q^{(0)} + \lambda\tilde{\psi}_q^{(1)} \; , \tag{160}$$

where, as suggested by Eq. (28),

$$\tilde{\psi}_q^{(0)} = \underset{\sim}{\phi}_{[1]q}^{(0)} \langle \underset{\sim}{\phi}_{[1]q}^{(0)} | \tilde{\psi}_q^{(0)}\rangle \tag{161}$$

and

$$\tilde{\psi}_q^{(1)} = \tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)} \langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | \tilde{\psi}_q^{(0)} \rangle + \underset{\sim}{\phi}{}_{[0]q}^{(0)} \langle \underset{\sim}{\phi}{}_{[0]q}^{(0)} | \tilde{\psi}_q^{(1)} \rangle . \qquad (162)$$

The notation implies that we know the sets $\underset{\sim}{\phi}{}_{[0]q}^{(0)}$ and $\underset{\sim}{\phi}{}_{[1]q}^{(0)}$ exactly, and the quantities with tildes are to be obtained from the variational principle. Substituting Eq. (162) into $J$ and expanding in powers of $\lambda$ gives as the leading term

$$J^{(2)} = \langle \tilde{\psi}_q^{(0)} | \underset{\sim}{\phi}{}_{[1]q}^{(0)} \rangle [\tilde{\underset{\approx}{\varepsilon}}{}_{[1]q}^{(2)} - \tilde{\varepsilon}_q^{(2)}] \langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | \tilde{\psi}_q^{(0)} \rangle ,$$

where

$$\tilde{\underset{\approx}{\varepsilon}}{}_{[1]q}^{(2)} = \langle \tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)} | \bar{H}^{(0)} | \tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)} \rangle + \langle \tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)} | \bar{H}^{(1)} | \underset{\sim}{\phi}{}_{[1]q}^{(0)} \rangle$$

$$+ \langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | \bar{H}^{(1)} | \tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)} \rangle + \langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | H^{(2)} | \underset{\sim}{\phi}{}_{[1]q}^{(0)} \rangle . \qquad (163)$$

Note that when $\tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)}$ is exact, $\tilde{\underset{\approx}{\varepsilon}}{}_{[1]q}^{(2)}$ becomes $\underset{\approx}{\varepsilon}{}_{[1]q}^{(2)}$ exactly. Also, the $J^{(2)}$ does not involve the coefficients $\langle \underset{\sim}{\phi}{}_{[0]q}^{(0)} | \tilde{\psi}_q^{(1)} \rangle$ at all.

The variational equation for one of the members of the set $\tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)}$, say $\tilde{\phi}_{[1]q\alpha}^{(1)}$, is obtained by putting $\delta J^{(2)}=0$ for variations $\delta\tilde{\phi}_{[1]q\alpha}^{(1)}$. This gives

$$\delta J^{(2)} = \left[ \langle \delta\tilde{\phi}_{[1]q\alpha}^{(1)} | \bar{H}^{(0)} | \tilde{\underset{\sim}{\phi}}{}_{[1]q}^{(1)} \rangle + \langle \delta\tilde{\phi}_{[1]q\alpha}^{(1)} | \bar{H}^{(1)} | \underset{\sim}{\phi}{}_{[1]q}^{(0)} \rangle \right] \langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | \tilde{\psi}_q^{(0)} \rangle$$

$$+ \text{complex conjugate} = 0 . \qquad (164)$$

The variational equation for the $\langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | \tilde{\psi}_q^{(0)} \rangle$ is then obtained by variations $\delta \langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | \tilde{\psi}_q^{(0)} \rangle$, which give

$$[\tilde{\underset{\approx}{\varepsilon}}{}_{[1]q}^{(2)} - \tilde{\varepsilon}_q^{(2)}] \langle \underset{\sim}{\phi}{}_{[1]q}^{(0)} | \psi_q^{(0)} \rangle = 0 , \qquad (165)$$

Thus, as discussed by Epstein, the equations for the $\tilde{\phi}^{(1)}_{\sim[1]q}$ and the $\langle\phi^{(0)}_{\sim[1]q}|\tilde{\psi}^{(0)}_{q}\rangle$ are coupled together and presumably must be solved by an iterative procedure.

(c) Quasi-variational procedure.

It is easy to write down a set of functionals whose stationary points are the exact solutions $\phi^{(n)}_{\sim[n]q}$. If $\phi^{(n)}_{[n]q\alpha}$ is a member of the set, then

$$J^{(2n)}_{q\alpha} = \langle\tilde{\phi}^{(n)}_{[n]q\alpha}|\bar{H}^{(0)}|\tilde{\phi}^{(n)}_{[n]q\alpha}\rangle + \sum_{t=1}^{n} \{\langle\tilde{\phi}^{(n)}_{[n]q\alpha}|\bar{H}^{(t)}|\phi^{(n-t)}_{[n]q\alpha}\rangle + \text{c.c.}\} \quad (166)$$

is such a functional, where we assume that the lower order functions are known exactly. The most straightforward procedure is to use $\delta J^{(2n)}_{q\alpha}=0$ to determine $\tilde{\phi}^{(n)}_{[n]q\alpha}$, and then to use this set in the computational procedure outlined in Sections VI and VII, treating it as though it were exact. It should be emphasized, however, that this is not a truly variational procedure in the sense of making the total energy stationary.

## IX. THE OPERATOR TREATMENT.[29]

In the present section, we wish to develop the operator approach independently of the direct treatment and then show how the two are related.

### A. Definitions and basic strategy.

Before proceeding with the derivations, let us introduce some of the new Hermitean operators which we require: First of all, there is a family of resolvents

$$R^{(-s)} = \sum_{k} \mathcal{E}^{(-s)}_{k} |\phi^{(0)}_{\sim[s]k}\rangle\langle\phi^{(0)}_{\sim[s]k}| . \quad (167)$$

Then, letting $V = H - H^{(0)}$ ,

$$Q_0 = \sum_{t=0}^{\infty} [(V - E_q + \varepsilon_q^{(0)})R^{(0)}]^t (V - E_q + \varepsilon_q^{(0)}) = \sum_{n=1}^{\infty} \lambda^n Q_0^{(n)} . \quad (168)$$

Here the n-th order of $Q_0$ is given by the recursion relation

$$Q_0^{(n)} = \bar{H}^{(n)} + \sum_{t=1}^{n-1} \bar{H}^{(n-t)} R^{(0)} Q_0^{(t)} . \quad (169)$$

And, finally, there is the set of operators

$$Q_p = K_p + \sum_{t=0}^{\infty} [(Q_{p-1} - K_p)R^{(-p)}]^t (Q_{p-1} - K_p) = \sum_{n=1}^{\infty} \lambda^n Q_p^{(n)} , \quad (170)$$

where

$$K_1 \equiv Q_0^{(1)} \quad \text{and} \quad K_p = Q_0^{(1)} + \sum_{m=2}^{p} Q_{m-2}^{(m)} . \quad (171)$$

One of the most important properties of the $Q_0$ and $Q_p$ is that

$$Q_0 = [V - E_q + \varepsilon_q^{(0)}][1 + R^{(0)} Q_0] \quad (172)$$

and

$$Q_p = Q_{p-1} + (Q_{p-1} - K_p)R^{(-p)}(Q_p - K_p) . \quad (173)$$

Using Eq. (173), it is easy to show by induction that the $Q_p^{(n)}$ are given by the recursion relations,

$$\begin{aligned} Q_p^{(n)} &= Q_{p-1}^{(n)} = \ldots = Q_{n-2}^{(n)} , && n<p+2 \\ Q_{n-2}^{(n)} &= Q_{n-3}^{(n)} + Q_{n-3}^{(n-1)} R^{(-n+2)} Q_{n-3}^{(n-1)} , && n=p+2 \quad (174) \\ Q_p^{(n)} &= Q_{p-1}^{(n)} + \sum_{s=p+1}^{n-1} Q_{p-1}^{(s)} R^{(-p)} Q_p^{(n+p-s)} , && n>p+2 \end{aligned}$$

In order to explain the significance of these operators, let us briefly sketch the strategy of the operator development which is given in subsection B. Our attention is focused on the wavefunction $\psi_q$, which we relate by means of infinite order operators to the unperturbed functions $\underset{\sim}{\phi}^{(0)}_{[0]q}$. The most general form for $\psi_q$ is

$$\psi_q = (1 + R^{(0)}Q_0)\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle , \qquad (175)$$

where $Q_0$ is an operator to be determined so that $\psi_q$ satisfies the Schrödinger equation. Here $\psi_q$ might be any of the functions $\psi_{[0]q}$. Since $R^{(0)}$ annihilates all of the functions $\underset{\sim}{\phi}^{(0)}_{[0]q}$, we complete the definition of $Q_0$ by

$$\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|Q_0|\underset{\sim}{\phi}^{(0)}_{[0]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = 0 . \qquad (176)$$

Thus $Q_0$ becomes an effective Hamiltonian operator in the space $\underset{\sim}{\phi}^{(0)}_{[0]q}$. This is not a true secular equation, however, since $Q_0$ is not linear in $E_q$. However if we consider the leading term in Eq. (176), we obtain the standard eigenvalue equation

$$\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|Q_0^{(1)}|\underset{\sim}{\phi}^{(0)}_{[0]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q^{(0)}\rangle = 0 , \qquad (177)$$

where

$$Q_0^{(1)} = H^{(1)} - \varepsilon_q^{(1)} . \qquad (178)$$

This is identical to Eq. (37) of the direct treatment and defines the resolution of $\underset{\sim}{\phi}^{(0)}_{[0]q}$ onto the subspaces $\underset{\sim}{\phi}^{(0)}_{[1]q}$ and $\underset{\sim}{\phi}^{(0)}_{[1]k}$. Then we resolve $\psi_q$ in the more specific manner,

$$\psi_q = (1 + R^{(0)}Q_0)(1 + R^{(-1)}Q_1)\underset{\sim}{\phi}^{(0)}_{[1]q}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q\rangle \qquad (179)$$

where $Q_1$ is an operator to be determined so that $\psi_q$ satisfies Eq. (176). Here $\psi_q$ might be any of the functions $\psi_{[1]q}$. In this way we proceed progressively to resolve the degeneracy in exactly the same manner as in the direct treatment so that $\psi_{[n]\ell}$ and the $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ have the same significance in the two formulations. If the degeneracy is resolved in the r-th order, the final expression for $\psi_q$ is

$$\psi_q = \prod_{p=0}^{r} (1 + R^{(-p)}Q_p)\psi_q^{(0)} \, , \qquad (180)$$

where the $Q_p$ is an effective Hamiltonian in the subspace $\underset{\sim}{\phi}^{(0)}_{[p]q}$,

$$\langle\underset{\sim}{\phi}^{(0)}_{[p]q}|Q_p|\underset{\sim}{\phi}^{(0)}_{[p]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[p]q}|\psi_q\rangle = 0 \, . \qquad (181)$$

A key step in the development is to show that $Q_p$ is given by Eq. (170) or (173) and that, as a result, the expression for $\psi_q$ can be rewritten in the more useful form of Eq. (231) below.

From this analysis it becomes evident that

$$\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} = \langle\underset{\sim}{\phi}^{(0)}_{[n-1]q}|Q^{(n)}_{n-2} + \varepsilon^{(n)}_q|\underset{\sim}{\phi}^{(0)}_{[n-1]q}\rangle \qquad (182)$$

so that $\varepsilon^{(n)}_{[n]\ell}$ and $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ are determined in exactly the same manner in the operator and in the direct approaches. The operator equivalent of $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ is obtained in subsection C.

We turn now to the detailed derivation of the operator treatment.

B. <u>Infinite Order Perturbation Theory</u>.

We start with the unperturbed Schrodinger equation

$$(H^{(0)} - \varepsilon^{(0)}_q)\underset{\sim}{\phi}^{(0)}_{[0]q} = 0 \, . \qquad (183)$$

At each stage of the development, we seek the energy $E_q$ and the wavefunction $\psi_q$ corresponding to the perturbed Schrödinger equation

$$(H - E_q)\psi_q = 0 . \tag{184}$$

The most general functional form for the wavefunction is

$$\psi_q = [R^{(0)}J_0 + 1]\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle , \tag{185}$$

where $J_0$ is an operator which we wish to determine. Since $R^{(0)}$ is orthogonal to the space of the $\underset{\sim}{\phi}^{(0)}_{[0]q}$, without loss of generality we can require that

$$\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|J_0|\underset{\sim}{\phi}^{(0)}_{[0]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = 0 . \tag{186}$$

Since $\underset{\sim}{\phi}^{(0)}_{[0]q}$ can be resolved into the spaces of $\underset{\sim}{\phi}^{(0)}_{[n]q}$ and $\sum_{s=1}^{n-1}\underset{\sim}{\phi}^{(0)}_{[s]k}$, Eq. (186) is equivalent to the set of equations

$$\langle\underset{\sim}{\phi}^{(0)}_{[n]q}|J_0|\underset{\sim}{\phi}^{(0)}_{[0]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = 0 \tag{187}$$

and

$$R^{(-s)}J_0\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = 0 \qquad 1\leq s\leq n . \tag{188}$$

Applying the operator $\bar{H}^{(0)}$ onto $\psi_q$ as given by Eq. (185)

$$\bar{H}^{(0)}\psi_q = \bar{H}^{(0)}R^{(0)}J_0\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = -J_0\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle . \tag{189}$$

But rewriting the perturbed Schrodinger equation,

$$\bar{H}^{(0)}\psi_q = -[V - E_q + \varepsilon^{(0)}_q]\psi_q =$$

$$- [V - E_q + \varepsilon^{(0)}_q][R^{(0)}J_0 + 1]\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle . \tag{190}$$

Then, comparing Eqs. (189) and (190),

$$J_0 \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi^{(0)}_q \rangle = [V - E_q + \varepsilon^{(0)}_q][1 + R^{(0)} J_0] \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi_q \rangle \ . \quad (191)$$

Applying the operator $R^{(0)}$ on both sides of Eq.(191), we get a Lippmann-Schwinger type of equation[30],

$$a = b(c + a) = b[c + b(c + a)] = b[c + b\{c + b(c + a)\}] =$$

$$\ldots = \sum_{t=1}^{\infty} (b)^t c \ . \quad (192)$$

Thus, we obtain

$$R^{(0)} J_0 \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]} | \psi_q \rangle = R^{(0)} Q_0 \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi_q \rangle \ , \quad (193)$$

where $Q_0$ is the infinite order Hermitean operator given by Eq. (168). Substituting Eq. (193) into Eq. (191) and making use of Eq. (172),

$$J_0 \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}_{[0]q} | \psi_q \rangle = Q_0 \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi_q \rangle \ . \quad (194)$$

The wavefunction (185) can then be written in the form

$$\psi_q = [R^{(0)} Q_0 + 1] \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi_q \rangle \ . \quad (195)$$

Also, the condition on $J_0$ becomes

$$\langle \underset{\sim}{\phi}^{(0)}_{[0]q} | Q_0 | \underset{\sim}{\phi}^{(0)}_{[0]q} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi_q \rangle = 0 \ . \quad (196)$$

The energy $E_q$ is one of the roots of the "generalized secular equation"

$$\left\| \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | Q_0 | \underset{\sim}{\phi}^{(0)}_{[0]q} \rangle \right\| = 0 \ . \quad (197)$$

Eq. (197) is not a true secular equation since $Q_0$ is not linear in $E_q$. Except for notation, Eqs. (195)-(197) have been derived and rederived many times in connection with "infinite order perturbation theory". If $\varepsilon_q^{(0)}$ were non-degenerate, then $\psi_q = \underset{\sim}{\phi}_{[0]q}^{(0)}$ ; $\psi_{(q)}^{(m)} = R^{(0)} Q_0^{(m)} \psi_q^{(0)}$ ; and $\varepsilon_q^{(n)} = \langle\psi_q^{(0)}|Q_0^{(n)} + \varepsilon_q^{(n)}|\psi_q^{(0)}\rangle$. For degenerate states, it is not necessary, but it is convenient, to successively resolve the set of degenerate states.

(1) First Resolution.

In the limit that $\lambda$ becomes small, $Q_0$ becomes $Q_0^{(1)} = \bar{H}^{(1)}$ and $\psi_q$ becomes $\psi_q^{(0)}$. In this limit, Eq. (196) becomes

$$\langle\underset{\sim}{\phi}_{[0]q}^{(0)}|Q_0^{(1)}|\underset{\sim}{\phi}_{[0]q}^{(0)}\rangle\langle\underset{\sim}{\phi}_{[0]q}^{(0)}|\psi_q^{(0)}\rangle = 0 \tag{198}$$

Of course we recognize that

$$\underset{\approx}{\varepsilon}_{[0]q}^{(1)} = \langle\underset{\sim}{\phi}_{[0]q}^{(0)}|Q_0^{(1)} + \varepsilon_q^{(1)}|\underset{\sim}{\phi}_{[0]q}^{(0)}\rangle \tag{199}$$

and Eq. (199) is exactly the same eigenvalue-eigenvector equation as the first order Eq. (99). Thus, in exactly the same manner as in the direct treatment, we determine the $\varepsilon_{[1]\ell}^{(1)}$ and the corresponding $\underset{\sim}{\phi}_{[1]\ell}^{(0)}$. The adjoint of the eigenvalue-eigenvector equation Eq. (102) is then

$$\underset{\approx}{A}_{[1]\ell}^{(1)} = \langle\underset{\sim}{\phi}_{[1]\ell}^{(0)}|Q_0^{(1)}|\underset{\sim}{\phi}_{[0]q}^{(0)}\rangle = (\varepsilon_{[1]\ell}^{(1)} - \varepsilon_q^{(1)})\langle\underset{\sim}{\phi}_{[1]\ell}^{(0)}|\underset{\sim}{\phi}_{[0]q}^{(0)}\rangle \tag{200}$$

However, when $s > t$

$$\underset{\sim}{\phi}_{[s]\ell}^{(0)} = \underset{\sim}{\phi}_{[t]q}^{(0)}\langle\underset{\sim}{\phi}_{[t]q}^{(0)}|\underset{\sim}{\phi}_{[t+1]q}^{(0)}\rangle\langle\underset{\sim}{\phi}_{[t+1]q}^{(0)}|\cdots|\underset{\sim}{\phi}_{[s-1]q}^{(0)}\rangle\langle\underset{\sim}{\phi}_{[s-1]q}^{(0)}|\underset{\sim}{\phi}_{[s]\ell}^{(0)}\rangle . \tag{201}$$

It follows that if we "back-load" Eq. (200) by using Eq. (201), when $s > 1$,

$$\underset{\approx}{A}^{(1)}_{[s]\ell} = \langle \underset{\sim}{\phi}^{(0)}_{[s]\ell} | Q_0^{(1)} | \underset{\sim}{\phi}^{(0)}_{[0]q} \rangle = (\varepsilon^{(1)}_{[1]\ell} - \varepsilon^{(1)}_q)\delta_{s,1} \langle \underset{\sim}{\phi}^{(0)}_{[1]\ell} | \underset{\sim}{\phi}^{(0)}_{[0]q} \rangle . \quad (202)$$

Then, if we "front-load" Eq. (202) by using Eq. (201) and Eq. (84),

$$\langle \underset{\sim}{\phi}^{(0)}_{[s]\ell} | Q_0^{(1)} | \underset{\sim}{\phi}^{(0)}_{[t]\ell'} \rangle = (\varepsilon^{(1)}_{[1]\ell} - \varepsilon^{(1)}_q)\delta_{s,1}\delta_{t,1}\delta_{\ell,\ell'}\underset{\approx}{1} , \quad \underline{s\geq 1,\ t\geq 1} . \quad (203)$$

Eq. (203) can then be stated compactly in the form of two relations

$$R^{(-s)}Q_0^{(1)}\underset{\sim}{\phi}^{(0)}_{[t]q} = 0 , \quad s\geq 1,\ t\geq 1 \quad (204)$$

and

$$R^{(-s)}Q_0^{(1)}R^{(-t)} = -R^{(-1)}\delta_{s,1}\delta_{t,1} , \quad s\geq 1,\ t\geq 1 . \quad (205)$$

Now let us return to the problem of completing the first resolution. If we define $R^{(-1)}J_1$ so that

$$\sum_k \underset{\sim}{\phi}^{(0)}_{[1]k} \langle \underset{\sim}{\phi}^{(0)}_{[1]k} | \psi_q \rangle = R^{(-1)}J_1 \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi_q \rangle \quad (206)$$

Then, resolving the $\underset{\sim}{\phi}^{(0)}_{[0]q}$ onto the space of the $\underset{\sim}{\phi}^{(0)}_{[1]\ell}$ , Eq. (194) becomes

$$J_0 \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi_q \rangle = Q_0[1 + R^{(-1)}J_1] \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi_q \rangle . \quad (207)$$

It follows from Eqs. (188) and (207) that

$$[R^{(-1)}(Q_0 - Q_0^{(1)}) + R^{(-1)}Q_0^{(1)}][1 + R^{(-1)}J_1] \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi_q \rangle = 0 . \quad (208)$$

Making use of Eqs. (204) and (205) and rearranging, Eq. (208) becomes

$$R^{(-1)}J_1 \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi_q \rangle = R^{(-1)}(Q_0 - Q_0^{(1)})[1 + R^{(-1)}J_1] \underset{\sim}{\phi}^{(0)}_{[1]q} \langle \underset{\sim}{\phi}^{(0)}_{[1]q} | \psi_q \rangle \quad (209)$$

Eq. (209) is another equation of the Lippmann-Schwinger type[30] which has as its solution

$$R^{(-1)}J_1\underset{\sim}{\phi}^{(0)}_{[1]q}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q\rangle = R^{(-1)}(Q_1 - Q_0^{(1)})\underset{\sim}{\phi}^{(0)}_{[1]q}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q\rangle$$

$$= R^{(-1)}Q_1\underset{\sim}{\phi}^{(0)}_{[1]q}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q\rangle . \qquad (210)$$

Making use of Eqs. (174) and (204), Eq. (207) becomes

$$J_0\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = (1 + Q_0^{(1)}R^{(-1)})Q_1\underset{\sim}{\phi}^{(0)}_{[1]q}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q\rangle . \qquad (211)$$

Thus, making use of Eqs. (206), (210), and (211), the wavefunction (185) becomes

$$\psi_q = [R^{(0)}(1 + Q_0^{(1)}R^{(-1)})Q_1 + 1 + R^{(-1)}Q_1]\underset{\sim}{\phi}^{(0)}_{[1]q}\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q\rangle \qquad (212)$$

Also, making use of Eq. (204), the condition (187) on $J_0$ gives the new eigenvalue-eigenvector equation for $E_q$ ,

$$\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|Q_1|\underset{\sim}{\phi}^{(0)}_{[1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q\rangle = 0 . \qquad (213)$$

(2) Second Resolution.

The subsequent resolutions follow rather closely to the pattern established by the first resolution so that it is not necessary to give as much detail.

In the limit that $\lambda$ is small, Eq. (213) becomes

$$\lambda\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|Q_0^{(1)}|\underset{\sim}{\phi}^{(0)}_{[1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q^{(0)}\rangle + \lambda^2\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|Q_0^{(1)}|\underset{\sim}{\phi}^{(0)}_{[1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q^{(1)}\rangle$$

$$+ \lambda^2\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|Q_0^{(2)}|\underset{\sim}{\phi}^{(0)}_{[1]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q^{(0)}\rangle + 0(\lambda^3) = 0 . \qquad (214)$$

According to Eq. (203) the first two terms in Eq. (214) vanish so that in the limit that $\lambda$ is small,

$$<\underset{\sim}{\phi}^{(0)}_{[1]q}|Q_0^{(2)}|\underset{\sim}{\phi}^{(0)}_{[1]q}><\underset{\sim}{\phi}^{(0)}_{[1]q}|\psi_q^{(0)}> = 0 . \qquad (215)$$

Here $Q_0^{(2)} = \bar{H}^{(1)}R^{(0)}\bar{H}^{(1)} + \bar{H}^{(2)}$. Thus, we recognize that

$$\underset{\approx}{\varepsilon}^{(2)}_{[1]q} = <\underset{\sim}{\phi}^{(0)}_{[1]q}|Q_0^{(2)} + \varepsilon_q^{(2)}|\underset{\sim}{\phi}^{(0)}_{[1]q}> . \qquad (216)$$

and Eq. (215) is exactly the same as the second order eigenvalue-eigenvector Eq. (99). Thus, in exactly the same manner as the <u>direct</u> treatment, we determine the $\varepsilon^{(2)}_{[2]\ell}$ and the corresponding $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$. Also, in the same manner as Eqs. (200)-(205) we can prove that

$$R^{(-s)}Q_0^{(2)}\underset{\sim}{\phi}^{(0)}_{[t]q} = 0 , \quad s\geq 2,\ t\geq 2 \qquad (217)$$

and

$$R^{(-s)}Q_0^{(2)}R^{(-t)} = -R^{(-2)}\delta_{s,2}\delta_{t,2} , \quad s\geq 2,\ t\geq 2 . \qquad (218)$$

In order to complete the second resolution, let us define $R^{(-2)}J_2$ so that

$$\sum_k \underset{\sim}{\phi}^{(0)}_{[2]k}<\underset{\sim}{\phi}^{(0)}_{[2]k}|\psi_q> = R^{(-2)}J_2\underset{\sim}{\phi}^{(0)}_{[2]q}<\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q> . \qquad (219)$$

Then, resolving the space of the $\underset{\sim}{\phi}^{(0)}_{[1]q}$ onto the spaces of the $\underset{\sim}{\phi}^{(0)}_{[2]\ell}$, Eq. (211) becomes

$$J_0\underset{\sim}{\phi}^{(0)}_{[0]q}<\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q> = (1 + Q_0^{(1)}R^{(-1)})Q_1(1 + R^{(-2)}J_2)\underset{\sim}{\phi}^{(0)}_{[2]q}<\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q> \qquad (220)$$

Thus, using Eqs. (188), (205), and (218),

$$[R^{(-2)}(Q_1 - K_2)(1 + R^{(-2)}J_2) - R^{(-2)}J_2]\underset{\sim}{\phi}^{(0)}_{[2]q}\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q\rangle = 0 . \quad (221)$$

Eq. (221) is a Lippmann-Schwinger type equation[30] whose solution is

$$R^{(-2)}J_2\underset{\sim}{\phi}^{(0)}_{[2]q}\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q\rangle = R^{(-2)}(Q_2 - K_2)\underset{\sim}{\phi}^{(0)}_{[2]q}\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q\rangle$$

$$= R^{(-2)}Q_2\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q\rangle . \quad (222)$$

Then with the help of Eqs. (173), (204), and (217), Eq. (220) becomes

$$J_0\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = (1 + Q_0^{(1)}R^{(-1)})(1 + K_2R^{(-2)})Q_2\underset{\sim}{\phi}^{(0)}_{[2]q}\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q\rangle . \quad (223)$$

Making use of Eqs. (173) and (217), Eq. (212) becomes

$$\psi_q = \begin{bmatrix} R^{(0)}(1 + Q_0^{(1)}R^{(-1)})(1 + K_2R^{(-2)})Q_2 \\ + (1 + R^{(-1)}Q_1)(1 + R^{(-2)}Q_2) \end{bmatrix} \underset{\sim}{\phi}^{(0)}_{[2]q}\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q\rangle . \quad (224)$$

Also, making use of Eqs. (204) and (218), the condition (187) on $J_0$ gives the new eigenvalue-eigenvector equation for $E_q$ ,

$$\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|Q_2|\underset{\sim}{\phi}^{(0)}_{[2]q}\rangle\langle\underset{\sim}{\phi}^{(0)}_{[2]q}|\psi_q\rangle = 0 . \quad (225)$$

(3) The General (n+1)-st Resolution.

The general pattern for the resolutions seems to be well established in the first and second resolutions. We wish to prove by induction that it applies in general. The proof consists in demonstrating that if the pattern applies to the first n resolutions, it also applies to the (n+1)st . The pattern may be outlined as follows:

First, is the n-th order energy-eigenvector relation

$$<\underset{\sim}{\phi}^{(0)}_{[n-1]q}|Q^{(n)}_{n-2}|\underset{\sim}{\phi}^{(0)}_{[n-1]q}><\underset{\sim}{\phi}^{(0)}_{[n-1]q}|\psi_q> = 0 . \qquad (226)$$

Comparing Eq. (226) with Eq. (99), it appears that

$$\underset{\approx}{\varepsilon}^{(n)}_{[n-1]q} = <\underset{\sim}{\phi}^{(0)}_{[n-1]q}|Q^{(n)}_{n-2} + \varepsilon^{(n)}_q|\underset{\sim}{\phi}^{(0)}_{[n-1]q}> . \qquad (227)$$

The real proof of Eq. (227) for a general value of $n$ is made in the subsection C. Thus, in exactly the same manner as in the direct treatment, the $\varepsilon^{(n)}_{[n]\ell}$ and the corresponding $\underset{\sim}{\phi}^{(0)}_{[n]\ell}$ are determined. Also, in the same manner as Eqs. (200)-(205) it follows that

$$R^{(-s)}Q^{(n)}_{n-2}\underset{\sim}{\phi}^{(0)}_{[t]} = 0 , \quad s\geq n, \ t\geq n \qquad (228)$$

and

$$R^{(-s)}Q^{(n)}_{n-2}R^{(-t)} = -R^{(-n)}\delta_{s,n}\delta_{t,n} , \quad s\geq n, \ t\geq n . \qquad (229)$$

After the n-th resolution, we assert that

$$J_0\underset{\sim}{\phi}^{(0)}_{[0]q}<\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q> = [\prod_{p=1}^{n} (1 + K_pR^{(-p)})]Q_n\underset{\sim}{\phi}^{(0)}_{[n]q}<\underset{\sim}{\phi}^{(0)}_{[n]q}|\psi_q> , \qquad (230)$$

$$\psi_q = \begin{bmatrix} R^{(0)}\{\prod_{p=1}^{n} (1 + K_pR^{(-p)})\}Q_n \\ + \prod_{p=1}^{n} (1 + R^{(-p)}Q_p) \end{bmatrix}\underset{\sim}{\phi}^{(0)}_{[n]q}<\underset{\sim}{\phi}^{(0)}_{[n]q}|\psi_q> \qquad (231)$$

and

$$<\underset{\sim}{\phi}^{(0)}_{[n]q}|Q_n|\underset{\sim}{\phi}^{(0)}_{[n]q}><\underset{\sim}{\phi}^{(0)}_{[n]q}|\psi_q> = 0 . \qquad (232)$$

This completes the pattern.

Now we will start on the inductive proof. According to Eq. (174),

$$Q_n = \lambda Q_0^{(1)} + \sum_{p=2}^{n+2} \lambda^p Q_{p-2}^{(p)} + \sum_{p=n+3}^{\infty} \lambda^p Q_n^{(p)} . \quad (233)$$

Thus, Eq. (232) can be expanded in powers of $\lambda$ to obtain

$$\sum_{t=1}^{n+1} \lambda^t \sum_{s=0}^{t} \langle \underset{\sim}{\phi}^{(0)}_{[n]q} | Q^{(s)}_{s-2} | \underset{\sim}{\phi}^{(0)}_{[n]q} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[n]q} | \psi_q^{(t-s)} \rangle + O(\lambda^{n+2}) = 0 . \quad (234)$$

Here, for convenience, we have let $Q_{-1}^{(1)} = Q_0^{(1)}$ . Then, making use of Eqs. (201) and (226),

$$\langle \underset{\sim}{\phi}^{(0)}_{[n]q} | Q^{(s)}_{s-2} | \underset{\sim}{\phi}^{(0)}_{[n]q} \rangle = \ldots \langle \underset{\sim}{\phi}^{(0)}_{[s]q} | \underset{\sim}{\phi}^{(0)}_{[s-1]q} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[s-1]q} | Q^{(0)}_{s-2} | \underset{\sim}{\phi}^{(0)}_{[s-1]q} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[s-1]q} | \underset{\sim}{\phi}^{(0)}_{[s]q} \rangle \ldots = 0 , \quad s \geq n . \quad (235)$$

Thus, the only term in Eq. (234) which has not previously been shown to be zero corresponds to $t = n+1 = s$ . This means that in the limit of $\lambda$ becomes small, Eq. (232) becomes

$$\langle \underset{\sim}{\phi}^{(0)}_{[n]q} | Q^{(n+1)}_{n-1} | \underset{\sim}{\phi}^{(0)}_{[n]q} \rangle \langle \underset{\sim}{\phi}^{(0)}_{[n]q} | \psi_q^{(0)} \rangle = 0 . \quad (236)$$

From Eq. (236), the sequence of Eqs. (227)-(229) with $n$ replaced by $(n+1)$ follows easily.

In order to complete our $(n+1)$st resolution, let us define $R^{(-n-1)}J_{n+1}$ so that

$$\sum_k \underset{\sim}{\phi}^{(0)}_{[n+1]k} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]k} | \psi_q \rangle = R^{(-n-1)} J_{n+1} \underset{\sim}{\phi}^{(0)}_{[n+1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]q} | \psi_q \rangle . \quad (237)$$

Then, resolving the space of the $\underset{\sim}{\phi}^{(0)}_{[n]q}$ onto the subspaces of the $\underset{\sim}{\phi}^{(0)}_{[n+1]\ell}$ , Eq. (230) becomes

$$J_0 \underset{\sim}{\phi}^{(0)}_{[0]q} \langle \underset{\sim}{\phi}^{(0)}_{[0]q} | \psi_q \rangle =$$

$$\left[ \prod_{p=1}^{n} (1 + K_p R^{(-p)}) \right] Q_n (1 + R^{(-n-1)} J_{n+1}) \underset{\sim}{\phi}^{(0)}_{[n+1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]q} | \psi_q \rangle \ . \quad (238)$$

But according to Eq. (188), if $R^{(-n-1)}$ is applied to Eq. (238), both sides of the resulting equation vanish. Making use of Eq. (229), the resulting equation is

$$R^{(-n-1)} Q_n (1 + R^{(-n-1)} J_{n+1}) \underset{\sim}{\phi}^{(0)}_{[n+1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]q} | \psi_q \rangle = 0 \ . \quad (239)$$

First, we replace the $Q_n$ by $(Q_n - Q^{(n+1)}_{n-1}) + Q^{(n+1)}_{n-1}$ . Then remembering that by the Eq. (229) with n replaced by (n+1) [which we have just shown], $R^{(-n-1)} Q^{(n+1)}_{n-1} R^{(-n-1)} = -R^{(-n-1)}$ , Eq. (239) becomes

$$[R^{(-n-1)} (Q_n - K_{n+1})(1 + R^{(-n-1)} J_{n+1}) - R^{(-n-1)} J_{n+1}] \underset{\sim}{\phi}^{(0)}_{[n+1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]q} | \psi_q \rangle = 0 \ . \quad (240)$$

Actually, in Eq. (240) we have done one more thing. We have replaced $Q^{(n+1)}_{n-1}$ in the first term by $K_{n+1}$ . Our justification is that the extra terms, $K_{n+1} - Q^{(n+1)}_{n-1} = K_n$ , do not contribute to Eq.(240) because of Eqs. (228) and (229). The Eq. (240) is of the Lippmann-Schwinger type[30] and has as its solution

$$R^{(-n-1)} J_{n+1} \underset{\sim}{\phi}^{(0)}_{[n+1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]q} | \psi_q \rangle = R^{(-n-1)} (Q_{n+1} - K_{n+1}) \underset{\sim}{\phi}^{(0)}_{[n+1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]q} | \psi_q \rangle$$

$$= R^{(-n-1)} Q_{n+1} \underset{\sim}{\phi}^{(0)}_{[n+1]q} \langle \underset{\sim}{\phi}^{(0)}_{[n+1]q} | \psi_q \rangle \ . \quad (241)$$

Next, let us note that as a result of Eqs. (173) and (228)

$$Q_n[1 + R^{(-n-1)}(Q_{n+1} - K_{n+1})]\underset{\sim}{\phi}^{(0)}_{[n+1]q}$$

$$= [(1 + K_{n+1}R^{(-n-1)})Q_{n+1} - K_{n+1}R^{(-n-1)}K_{n+1}]\underset{\sim}{\phi}^{(0)}_{[n+1]q}$$

$$= (1 + K_{n+1}R^{(-n-1)})Q_{n+1}\underset{\sim}{\phi}^{(0)}_{[n+1]q} \quad (242)$$

Thus, substituting (the first form of) Eq. (241) into Eq. (238), we obtain Eq. (230) with $n$ replaced by $(n+1)$ .

Then, comparing Eq. (185) with Eq.(231) and using the second form of Eq. (241),

$$\underset{\sim}{\phi}^{(0)}_{[0]q}\langle\underset{\sim}{\phi}^{(0)}_{[0]q}|\psi_q\rangle = \prod_{p=1}^{n}(1 + R^{(-p)}Q_p)\underset{\sim}{\phi}^{(0)}_{[n]q}\langle\underset{\sim}{\phi}^{(0)}_{[n]q}|\psi_q\rangle$$

$$= \prod_{p=1}^{n}(1 + R^{(-p)}Q_p)(1 + R^{(-n-1)}J_{n+1})\underset{\sim}{\phi}^{(0)}_{[n+1]q}\langle\underset{\sim}{\phi}^{(0)}_{[n+1]q}|\psi_q\rangle$$

$$= \prod_{p=1}^{n+1}(1 + R^{(-p)}Q_p)\underset{\sim}{\phi}^{(0)}_{[n+1]q}\langle\underset{\sim}{\phi}^{(0)}_{[n+1]q}|\psi_q\rangle \quad (243)$$

Thus, substituting Eq. (230) with $n$ replaced by $(n+1)$ together with Eq. (243) into Eq. (185), we obtain Eq. (231) with $n$ replaced by $(n+1)$ .

And finally, using Eqs. (228) and (230) with $n$ replaced by $(n+1)$ , Eq. (187) with $n$ replaced by $(n+1)$ becomes Eq.(232) with $n$ replaced by $(n+1)$ . This completes our proof!

We have shown that if Eqs. (226)-(232) are valid for the first $n$ resolutions, they are also valid for the $(n+1)$-st resolution. And since these equations apply to the first and second resolutions, it follows that they are valid for all values of $n$ .

C. The Operator Expressions for the $\underset{\sim}{\phi}^{(m)}_{[n]\ell}$ and the Operators $Q^{(n)}_{n-2}$ .

Having completed our formal development of the infinite order perturbations, let us make a closer examination of the operators which occur in that treatment. First of all, we can write $Q_0^{(n)}$ in the form

$$Q_0^{(n)} = \sum \bar{H}^{(a)} R^{(0)} \bar{H}^{(b)} \ldots R^{(0)} \bar{H}^{(c)} , \quad n \geq 1 , \tag{244}$$

where the summation is taken over all possible terms such that

$$a + b + \ldots + c = n$$

and

$$1 \leq a, b, \ldots, c \leq n . \tag{245}$$

Also, $Q_p^{(n)}$ can be expressed in the compact form

$$Q_p^{(n)} = \sum Q_{p-1}^{(a)} R^{(-p)} Q_{p-1}^{(b)} \ldots R^{(-p)} Q_{p-1}^{(c)} , \quad n \geq p+2 . \tag{246}$$

Here the summation is taken over all possible terms such that

$$a + (b - p) + \ldots + (c - p) = n$$

and

$$p + 1 \leq a, b, \ldots, c \leq n . \tag{247}$$

Another useful expression for $Q_n$ is

$$Q_n = \bar{H}^{(1)}[1 + R^{(0)}Q_0 \prod_{s=1}^{n} \{1 + R^{(-s)}(Q_s - K_s)\}]$$

$$+ \sum_{t=2}^{\infty} \bar{H}^{(t)}[1 + R^{(0)}Q_0] \prod_{s=1}^{n} \{1 + R^{(-s)}(Q_s - K_s)\}$$

$$+ \sum_{t=2}^{n} Q_{t-2}^{(t)}[1 - \prod_{s=t}^{n} \{1 + R^{(-s)}(Q_s - K_s)\}] \ . \qquad (248)$$

Eq. (248) can be proved by induction in the following manner: first, expand $(V - E_q + \varepsilon_q)$ in Eq. (172). Then use Eq.(173) together with the new Eq. (172) to express $Q_1$ in the form of Eq. (248). Next, express $Q_p$ by Eq. (173) in which $Q_{p-1}$ is given by Eq. (248). Finally, rearrange the terms so that $Q_p$ is given by Eq. (248).

Of all of these operators, the special family of $Q_{n-2}^{(n)}$ is especially important. And, of all the expansions of $Q_{n-2}^{(n)}$ the most useful one is

$$Q_{n-2}^{(n)} = \sum_{t=0}^{n-1} \bar{H}^{(n-t)} G_n^{(t)} = \sum_{t=0}^{n-1} G_n^{(t)\dagger} \bar{H}^{(n-t)} \ . \qquad (249)$$

Although the $\bar{H}^{(n)}$, the $Q_n$, and the resolvents are all Hermitean, the operator $G_n^{(t)}$ is not Hermitean. However, its adjoint $G_n^{(t)\dagger}$ is easily obtained by reversing the order of the Hermitean operators which form $G_n^{(t)}$. The operator expressions for $G_n^{(t)}$ can be obtained by expanding Eq. (248). The expressions for $G_n^{(t)}$ through $n=5$ are given in Table 1. For all values of $n$,

$$G_n^{(0)} = 1 \ . \qquad (250)$$

For values of $n > 2$, we found two equivalent recursion relations for determing the $G_n^{(t)}$ :

Table 1. The Operators $G_n^{(t)}$ through $n = 5$ .

$$G_n^{(0)} = 1 \qquad \text{for all values of } n$$

---

$$G_2^{(1)} = R^{(0)}Q_0^{(1)}$$

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$$G_3^{(1)} = R^{(0)}Q_0^{(1)} + R^{(-1)}Q_0^{(2)}$$

$$G_3^{(2)} = R^{(0)}[1 + Q_0^{(1)}R^{(-1)}]Q_0^{(2)}$$

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$$G_4^{(1)} = R^{(0)}Q_0^{(1)} + R^{(-1)}Q_0^{(2)} + R^{(-2)}Q_1^{(3)}$$

$$G_4^{(2)} = R^{(0)}[(1 + Q_0^{(1)}R^{(-1)}Q_0^{(2)} + Q_0^{(1)}R^{(-2)}Q_1^{(3)}] + R^{(-1)}[1 + Q_0^{(2)}R^{(-2)}]Q_1^{(3)}$$

$$G_4^{(3)} = R^{(0)}[1 + Q_0^{(1)}R^{(-1)}][1 + Q_0^{(2)}R^{(-2)}]Q_1^{(3)}$$

---

$$G_5^{(1)} = R^{(0)}Q_0^{(1)} + R^{(-1)}Q_0^{(2)} + R^{(-2)}Q_1^{(3)} + R^{(-3)}Q_2^{(4)}$$

$$G_5^{(2)} = R^{(0)}[Q_0^{(2)} + Q_0^{(1)}(R^{(-1)}Q_0^{(2)} + R^{(-2)}Q_1^{(3)} + R^{(-3)}Q_2^{(4)})] + R^{(-1)}[(1 + Q_0^{(2)}R^{(-2)})Q_1^{(3)} + Q_0^{(2)}R^{(-3)}Q_2^{(4)}] + R^{(-2)}[1 + Q_1^{(3)}R^{(-3)}]Q_2^{(4)}$$

$$G_5^{(3)} = R^{(0)}\left[(1 + Q_0^{(1)}R^{(-1)})[(1 + Q_0^{(2)}R^{(-2)})Q_1^{(3)} + Q_0^{(2)}R^{(-3)}Q_2^{(4)}] + Q_0^{(1)}R^{(-2)}[1 + Q_1^{(3)}R^{(-3)}]Q_2^{(4)}\right] + R^{(-1)}[1 + Q_0^{(2)}R^{(-2)}][1 + Q_1^{(3)}R^{(-3)}]Q_2^{(4)}$$

$$G_5^{(4)} = R^{(0)}[1 + Q_0^{(1)}R^{(-1)}][1 + Q_0^{(2)}R^{(-2)}][1 + Q_1^{(3)}R^{(-3)}]Q_2^{(4)}$$

(1) The first set of relations is obtained directly by using Eq. (248) to successively expand $Q_0^{(2)}, Q_1^{(3)}, \ldots$ . In using Eq. (248) to express $Q_{n-2}^{(n)}$ , only the previously expanded $Q_{t-2}^{(t)}$ are needed for the right-hand side of Eq. (248). Thus we obtain

$$G_n^{(1)} = R^{(0)}Q_0^{(1)} + \sum_{s=1}^{n-2} R^{(-s)}Q_{s-1}^{(s+1)} , \tag{251}$$

$$G_n^{(t)} = G_{n-1}^{(t)} + \left[ G_{n-2}^{(t-1)}R^{(-n+2)} + \sum_{s=2}^{t} G_{(n-1-s)}^{(t-s)}R^{(-n+1+s)} \prod_{p=n-s}^{n-2} \left(1 + Q_{p-2}^{(p)}R^{(-p)}\right) \right] Q_{n-3}^{(n-1)} ,$$

$$2 \leq t \leq n-2 \tag{252}$$

and

$$G_n^{(n-1)} = R^{(0)} \prod_{p=1}^{n-2} \left(1 + Q_{p-2}^{(p)}R^{(-p)}\right)Q_{n-3}^{(n-1)} . \tag{253}$$

(2) The second set of relations is the operator equivalent of the magic formula

$$G_n^{(n-1)} = \left[R^{(0)} + \sum_{p=1}^{n-2} G_{p+1}^{(p)}R^{(-p)}\right]Q_{n-3}^{(n-1)} \tag{254}$$

and

$$G_n^{(t)} = G_{n-1}^{(t)} + \sum_{p=1}^{t} G_{n-p}^{(t-p)}R^{(-n+1+p)}Q_{n-3}^{(n-1)} , \quad 0 < t < n-1 . \tag{255}$$

Eqs. (254) and (255) can be proved by starting with Eqs. (251)-(253), making use of the identity

$$\prod_{p=n-s}^{n-2} (1 + Q^{(p)}_{p-2} R^{(-p)}) = 1 + Q^{(n-s)}_{n-s-2} R^{(-n+s)}$$

$$+ \sum_{u=0}^{s-3} \prod_{\nu=n-s}^{n-u-3} (1 + Q^{(\nu)}_{\nu-2} R^{(-\nu)}) Q^{(n-2-u)} R^{(-n+2+u)} , \qquad (256)$$

interchanging the order of the summations over $s$ and $u$, and then making use of Eqs. (251) to (253) to identify the terms which go together to form $G$'s on the right-hand side of the resulting equation.

The point of the greatest interest is that

$$\underset{\sim}{\phi}^{(m)}_{[n]\ell} = G^{(m)}_{n+1} \underset{\sim}{\phi}^{(0)}_{[n]\ell} . \qquad (257)$$

Eqs. (250), (254), and (255) provide the operator equivalent of the magic formula. On account of Eq. (256), Eq. (249) gives

$$\sum_{t=1}^{n} \bar{H}^{(t)} \underset{\sim}{\phi}^{(n-t)}_{[n-1]q} = Q^{(n)}_{n-2} \underset{\sim}{\phi}^{(0)}_{[n-1]q} . \qquad (258)$$

Thus,

$$\underset{\approx}{A}^{(n)}_{[s]\ell} = \langle \underset{\sim}{\phi}^{(0)}_{[s]\ell} | Q^{(n)}_{n-2} | \underset{\sim}{\phi}^{(0)}_{[n-1]q} \rangle , \qquad (259)$$

and our whole <u>direct</u> formulation can be transcribed into the formal operator language. The "unwinding" of the $\underset{\approx}{A}^{(n)}_{[s]\ell}$ as given by Eq. (90) corresponds to the unlikely-looking identity

$$Q^{(n)}_{n-2} = \sum_{p=0}^{u} \sum_{t=0}^{n-1-u} G^{(p)}_{s+1} \bar{H}^{(n-p-t)} G^{(t)}_{n} , \qquad (260)$$

<u>where $u \le s+1 \le n$</u>. If $s > u$, then the expressions for $Q^{(n)}_{n-2}$ are more complicated than the ones obtained with $s = u$. However, the additional terms cancel each other because of Eq. (205).

In the order-by-order development of the energies and the wave-functions, it is the functions $G_{n+1}^{(t)}\underset{\sim}{\phi}_{[n]\ell}^{(0)} = \underset{\sim}{\phi}_{[n]\ell}^{(t)}$ which are determined and these functions, in turn, determine the $Q_{n-1}^{(n+1)}\underset{\sim}{\phi}_{[n]\ell}^{(0)}$ . The determination of the $G_{n+1}^{(t)}\underset{\sim}{\phi}_{[n]\ell}^{(0)}$ and the order-by-order development of the operator formalism proceeds in exactly the same manner as for the <u>direct</u> formalism given in Sections III-VII. If $r$ is the order in which the degeneracy is resolved, then $Q_n = Q_r$ if $n > r$ . Thus, the relationships between our present work and the previous formal operator treatments becomes apparent. The one approach can be completely transcribed into the other.

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24. Throughout this paper, we use the convention that whenever the upper bound of a summation is less than the lower bound, the sum is equal to zero.

25. If the Hilbert space is finite so that $R^{(0)}$ is a known matrix, $R^{(0)}F$ can be obtained simply by matrix multiplication [see Section VIII].

26. For example if $\chi_q(\lambda)$ is fully normalized so that $\sum_{s=0}^{n} \langle\chi_q^{(s)}|\chi_q^{(n-s)}\rangle = \delta_{n,0}$ then:

$$c_q^{(0)} = 1 ;$$

$$c_q^{(1)} = i\, a_1 ;$$

$$c_q^{(2)} = -\frac{1}{2}\langle\psi_q^{(1)}|\psi_q^{(1)}\rangle - \frac{1}{2} a_1^2 + i\, a_2 ;$$

$$c_q^{(3)} = -\frac{1}{2}\langle\psi_q^{(1)}|\psi_q^{(2)}\rangle - \frac{1}{2}\langle\psi_q^{(2)}|\psi_q^{(1)}\rangle - a_1 a_2 + i\, a_3 ;$$

etc. Here the $a_k$ are constants which must be determined by some additional condition. Usually they are taken to be zero.

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29. Many of the concepts and much of the notation in Section IX is given in Ref. (1).

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