General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

THEORETICAL CHEMISTRY INSTITUTE

THE UNIVERSITY OF WISCONSIN

NEW PARTITIONING PERTURBATION THEORY:

I. GENERAL FORMALISM

by

Phillip R. Certain and Joseph O. Hirschfelder

WIS-TCI-365   20 November 1969

MADISON, WISCONSIN

ERRATA WIS-TCI-365

page   correction

17   Middle of page, change "(24) with" to "(14) with N=1 and"

18   Third paragraph, change "(20)" to "(17)".

19   Eq. (29) should read, E^2_1 .

     Change "(20)" to "(17)" in two places.

21   Sixth line, change "(34)" to "(30)".

23   Line below Eq. (38), change "(5)" to "(11)".

27   Ref. 4 refers to ref. 12, not 52

NEW PARTITIONING PERTURBATION THEORY:

I. GENERAL FORMALISM[*]

by

Phillip R. Certain[+] and Joseph O. Hirschfelder

University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin 53706

ABSTRACT

By the use of partitioning techniques, a general formalism is
developed for considering degenerate, almost degenerate, and electron
exchange perturbation problems. In effect, we generalize the Van Vleck-
Kirtman approach to arbitrary orders and arbitrary normalization and
obtain three types of approximations: In the Modified Kirtman treatment
the functions through the N-th order are fully normalized and the
energy is obtained as the roots of the secular equation. The DE-FOP-VIM
approximation is the same except that the normalization of the functions
is energy optimized. The Kirtman approximation uses the same functions
as the Modified Kirtman but the energy is obtained as the roots of a
much simpler secular equation which results from a factorization of
the original secular equation (except for terms of order 2N+2). The
Kirtman energies are not upper bounds. Löwdin's formalism is equivalent
to the Modified Kirtman with the exception that Löwdin uses intermediate
normalization. Electron exchange problems are considered more explicitly
in a companion paper with the use of symmetry considerations.

- - - - - - - -

By the use of partitioning techniques, a general formalism is developed for considering degenerate, almost degenerate, and electron exchange perturbation problems. Our formalism is related to the methods of Van Vleck[1], Kato[2], Bloch[3], Hirschfelder[4], Kirtman[5], and Löwdin[6,7]. In all of these partitioning treatments, the energy is given as the roots of a secular equation. The matrix elements of the secular equation are assumed to be analytic in the perturbation parameter, but neither the energy nor the wave functions need to be analytic in this parameter. Thus, a partitioning formalism can have a greater range of validity than the Rayleigh-Schrödinger procedure.

Although our approach is quite different, we obtain a generalization of Kirtman's treatment[5] to arbitrary order and to arbitrary normalization. Although the choice of normalization is immaterial for infinite order calculations, it does play a role in low-order treatments and becomes increasingly important as the deviations from Rayleigh-Schrödinger behaviour becomes large. Thus, the choice of normalization is likely to be very important in using a low-order perturbation formalism to consider an electron exchange problem. We obtain three types of approximations:

1). The Modified Kirtman (MK) Approximation. The energy is determined by a secular equation in which the basis functions are accurate through the N-th order and fully normalized. Löwdin's partitioning formalism is equivalent to the MK with the exception that Löwdin uses intermediate normalization.

2). The DE-FOP-VIM Approximation. The DE-FOP-VIM is the same as the MK except that the normalization of the functions is optimized with respect to the particular state under consideration. This leads to secular equations having much larger dimensionality.

3). The Kirtman (K) Approximation. The Kirtman approximation is obtained by factorization of the MK secular equation (ignoring terms of order 2N+2) so that the Kirtman energy is given as the roots of a much simpler secular equation. The Kirtman energies are not upper bounds. However, this procedure has the advantage that the energies for all of a set of degenerate states are determined by solving a single secular equation regardless of the orders in which the degeneracies of the various states are resolved. This is to be contrasted with the "Löwdin"[6,7] and Choi[8] partitioning techniques which require the solution of different secular equations for degenerate states belonging to different classes (We have not yet seen a preprint of the unpublished results of Goscinski and Löwdin[9]).

In Section V of this paper, our partitioning formalism is modified so as to apply to electron exchange problems. This treatment is quite general and should be applicable to examples where atomic degeneracies and/or multiconfigurational interactions are involved. However, in any particular case, symmetry considerations can be used to greatly simplify the formalism. This is done in a companion paper[22] (Paper III). However, our present treatment is more general than Paper III in the sense that our basis set is not restricted to having no more than one function of each symmetry class.

In another companion paper[21] (Paper II), an example of an almost-degenerate perturbation is used to illustrate each of the different methods of solution which are given in Section IV.

I. General Formulation.

Consider the solution of the Schrödinger equation

$$(H(\lambda) - E_k(\lambda))\ \Psi_k(\lambda) = 0, \qquad (1)$$

(handwritten annotations: cap H, cap E, cap psi, i.e. lambda)

where the hamiltonian is the sum of two terms,

$$H(\lambda) = H^{(0)} + \lambda H^{(1)}.$$

(handwritten annotation: zero)

The $H^{(0)}$ is the hamiltonian for the unperturbed system, and the $H^{(1)}$ is a perturbation. The parameter λ in some cases has physical significance (e.g. field strength), but otherwise is a formal ordering parameter with a numerical value of unity. The unperturbed hamiltonian is assumed to possess a complete set of eigensolutions,

$$(H^{(0)} - \epsilon_k^{(0)})\ \phi_k^{(0)} = 0. \qquad (2)$$

(handwritten annotations: epsilon, i.e. phi)

Consider the linear manifold $\mathcal{S}$ which is spanned by S eigenfunctions $\overline{\Psi}_k$, $1 \le k \le S$, of the total Schrödinger equation (1). $\mathcal{S}$ is defined to have the property that if state k in $\mathcal{S}$ has the zeroth order energy $\epsilon_k^{(0)}$, then all states k' which have zeroth

order energies $\epsilon_{k'}^{(o)}$ that are <u>degenerate</u> or <u>almost degenerate</u> with $\epsilon_k^{(o)}$, are in $\mathcal{S}$. The sequential labelling of the states by k is for convenience and does not imply that they are the $\mathcal{S}$ lowest energy states of H.

The Ψ_k constitute an orthonormal basis for manifold $\mathcal{S}$. Any other basis in $\mathcal{S}$ may be defined by

— cap C

$$\Phi_k = \sum_{\ell=1}^{S} \Psi_\ell \, C_{\ell k} , \tag{3a}$$

where the numbers $C_{\ell k}$ are elements of a non-singular transformation. Thus, if $\mathbb{C}^{-1}$ is the inverse of the matrix $\mathbb{C}$,

$$\Psi_\ell = \sum_{j=1}^{S} \Phi_j \, C_{j\ell}^{-1} \tag{3b}$$

— cap phi

The basis functions Φ_k satisfy the <u>coupled equations</u>

$$H\Phi_k = \sum_{\ell=1}^{S} E_\ell \Psi_\ell \, C_{\ell k} = \sum_{j=1}^{S} \Phi_j \, \epsilon_{jk} , \tag{4}$$

where

$$\epsilon_{jk} = \sum_{\ell=1}^{S} C_{j\ell}^{-1} E_\ell \, C_{\ell k} ,$$

and

$$\delta_{jk} = \sum_{\ell=1}^{S} C_{j\ell}^{-1} \, C_{\ell k} . \tag{5}$$

Given the basis functions Φ_k, the eigensolutions (E_k, Ψ_k) are recovered by solving the secular equation

$$|\langle \Phi_k | H - E | \Phi_\ell \rangle| = 0 . \tag{6}$$

Thus, Eq. (4) and (6) are equivalent to the S uncoupled Schrödinger equations for (E_k, Ψ_k). Although Φ_k and $\epsilon_{k\ell}$ will later be expanded in powers of λ, it is not assumed that the roots of Eq. (6) are analytic in λ. That is, it is assumed that the matrix elements of H are analytic, but not necessarily the energy eigenvalues. An example where such an assumption is valid occurs for the interaction of two $2s$ or $2p$ hydrogen atoms, as discussed by Kim and Hirschfelder.[10] See also the example in Section IV.

At this point it is convenient to introduce a more compact matrix notation; e.g.,

Bold Face epsilon ——— $\mathbb{E} = (\epsilon_{k\ell})$,

Bold Face Cap phi ——— $\mathbf{\Phi} = (\Phi_k) = (\Phi_1, \Phi_2, \ldots \Phi_S)$.

In this nota-

tion, Eq. (4) and (6) become

$$H\mathbf{\Phi} = \mathbf{\Phi}\,\mathbb{E} \tag{4}$$

and

$$|\langle \mathbf{\Phi} | H - E | \mathbf{\Phi} \rangle| = 0 . \tag{6}$$

Perturbation Expansion. However, viewed as equations for the $\overline{\Phi}_k$ and $\epsilon_{k\ell}$, Eqs. (4) and (6) are not well-defined, since all reference to the particular linear manifold $\mathcal{S}$ has been lost. That is, Eq. (4) has solutions in any S-dimensional linear manifold defined by the exact eigenfunctions of H. Furthermore, within any particular linear manifold, there is an infinite number of solutions of Eq. (4) corresponding to different choices for the coefficients $C_{\ell k}$.

The lack of uniqueness in Eq. (4) is obviated by a _perturbation approach_ to its solution. The following expansions are assumed:

$$H = H^{(0)} + \lambda H^{(1)},$$

$$\Phi = \sum_{n=0}^{\infty} \lambda^n \phi^{(n)}, \tag{7}$$

$$\mathbb{E} = \sum_{n=0}^{\infty} \lambda^n \mathbb{E}^{(n)}.$$

It is convenient to define the sequence of partial sums,

$$\Phi(N) \equiv \sum_{m=0}^{N} \lambda^m \phi^{(m)} \tag{8}$$

$$\mathbb{E}(N) \equiv \sum_{m=0}^{N} \lambda^m \mathbb{E}^{(m)}$$

The linear manifold $\mathcal{S}$ is uniquely determined by specifying the zeroth order energies

$$\mathbb{E}_{k\ell}^{(0)} = \mathbb{E}_{k}^{(0)} \, \delta_{k\ell} . \tag{9}$$

Eq. (9) corresponds to the $\phi_k^{(0)}$ being eigenfunctions of $H^{(0)}$ with the energy $\mathbb{E}_k^{(0)}$. Furthermore, we assume that the $\phi_k^{(0)}$ are orthonormal,

$$\langle \phi^{(0)} | \phi^{(0)} \rangle = \mathbb{1} \tag{10}$$

where $\mathbb{1}$ is the unit matrix. If the eigenvalue $\mathbb{E}_k^{(0)}$ is degenerate, then it is assumed that all of the corresponding eigenfunctions are included in $\phi^{(0)}$. The set $\phi^{(0)}$ is a basis of unperturbed functions for the approximate calculation of S eigenstates $(E_k(\lambda), \Psi_k(\lambda))$ of the total Hamiltonian $H(\lambda)$ where $E_k(\lambda=0) = \mathbb{E}_k^{(0)}$ for $k = 1, \ldots, S$.

Substituting the expansions (7) into (4) and setting the co-efficient of each power of λ equal to zero yields the infinite set of perturbation equations

$$H^{(0)} \phi^{(0)} = \phi^{(0)} \mathcal{E}^{(0)}$$

$$H^{(1)} \phi^{(0)} + H^{(0)} \phi^{(1)} = \phi^{(1)} \mathcal{E}^{(0)} + \phi^{(0)} \mathcal{E}^{(1)}$$

$$\cdots$$

$$H^{(1)} \phi^{(N-1)} + H^{(0)} \phi^{(N)} = \sum_{\ell=0}^{N} \phi^{(\ell)} \mathcal{E}^{(N-\ell)}$$

$$\cdots$$

(11)

The first order perturbation equation(11) is equivalent to the first order equation of Van Vleck degenerate perturbation theory[1] and of the treatments of Kato[2] and Block.[3] Thus the present formalism represents an extension of these methods to arbitrary order.

Multiplying the N-th order perturbation equation by $\phi^{(0)+}$ and integrating gives an expression for $\mathcal{E}^{(N)}$. Making use of the hermitean property of $H^{(0)}$ together with the zeroth order perturbation equation,

$$\mathcal{E}^{(N)} = \langle \phi^{(0)} | H^{(1)} | \phi^{(N-1)} \rangle - \sum_{k=1}^{N-1} \langle \phi^{(0)} | \phi^{(k)} \rangle \mathcal{E}^{(N-k)}$$
$$+ \mathcal{E}^{(0)+} \langle \phi^{(0)} | \phi^{(N)} \rangle - \langle \phi^{(0)} | \phi^{(N)} \rangle \mathcal{E}^{(0)}$$

(12)

The energy E is then obtained in the following manner. Adding the perturbation equations through the N-th order and rearranging the terms,

$$H \Phi(N) = \Phi(N) \mathcal{E}(N) + \lambda^{N+1} \left\{ H^{(1)} \phi^{(N)} - \sum_{k=0}^{N-1} \lambda^k \sum_{\ell=0}^{N-k-1} \phi^{(k+\ell+1)} \mathcal{E}^{(N-\ell)} \right\}_0$$

Hence, after collecting terms according to order in λ

$$\langle \Phi(N) | H - E | \Phi(N) \rangle = \langle \Phi(N) | \Phi(N) \rangle \left(\mathcal{E}(N) - E \right)$$

(13)

$$+ \lambda^{N+1} \sum_{n=0}^{N-1} \lambda^n \left\{ \langle \phi^{(n)} | H^{(1)} | \phi^{(N)} \rangle \right.$$

$$\left. - \sum_{p=0}^{n} \sum_{q=0}^{N-n+p-1} \langle \phi^{(p)} | \phi^{(n+1-p+q)} \rangle \mathcal{E}^{(N-q)} \right\}$$

$$+ \lambda^{2N+1} \sum_{n=0}^{N-1} \lambda^n \left\{ \langle \phi^{(N)} | H^{(1)} | \phi^{(N)} \rangle \delta_{n0} \right.$$

$$\left. - \sum_{p=0}^{N-n-1} \sum_{q=0}^{p} \langle \phi^{(p+n+1)} | \phi^{(N-p+q)} \rangle \mathcal{E}^{(N-q)} \right\}.$$

Given the solution to the perturbation equation (11) through order
N , the eigenvalues and eigenvectors of the secular equations

$$\left| \left\langle \Phi(N) \left| H-E \right| \Phi(N) \right\rangle \right| = 0 \qquad (14)$$

provide a sequence of eigensolutions which, assuming convergence, approach
the exact solutions (E_k, Ψ_k) as N becomes successively larger.

Eq. (14) can be thought of as arising from the use of the
variational method with the linear variational function

$$\tilde{\Psi} = \sum_{k=1}^{s} \Phi_k(N)\, \tilde{a}_k, \qquad l.c.\ A$$

where the $\tilde{a}_k$ are variational parameters. In this connection, the
Hylleraas-Undheim theorem [11] is relevant: if the roots of Eq. (14)
are arranged in ascending order, they provide successive upper bounds
to the corresponding exact energy eigenvalues of H of the same
symmetry. Thus, in case that the states in δ are the lowest states
of H corresponding to particular symmetries, the roots of Eq. (14)
are upper bounds to the energies which they approximate.

In case the Rayleigh-Schrödinger expansion is possible, the $\Phi(N)$ forms
a basis for determining the Ψ_k accurately through terms of $O(\lambda^N)$.
Thus, by the Wigner theorem, regardless of the choice of $\mathbb{C}$, the roots
of the secular equation (13) are the energies E_k accurate through terms
of $O(\lambda^{2N+1})$. Thus a unique asymptotic expansion of (E_k, Ψ_k) is
obtained from the eigenvalues and eigenvectors of (14) by taking successively
larger values of N .

An alternative way to obtain the energies, which however are not
necessarily upper bounds to the exact values, is to solve the secular equation

$$\left| \mathbb{C}(2N+1) - E\mathbb{1} \right| = 0 \qquad (15)$$

Here the $\mathbb{G}(2N+1)$ is the $\mathbb{G}(N)$ of (9) with the N replaced by 2N+1 . According to Eq. (12),

$$\langle \bar{\Phi}(2N+1) \mid H - E \mid \Phi(2N+1) \rangle$$

$$= \langle \bar{\Phi}(2N+1) \mid \Phi(2N+1) \rangle \left[\mathbb{G}(2N+1) - E \right]$$

$$+ O(\lambda^{2N+2})$$

Thus, substituting this into (13), with the terms of $O(\lambda^{2N+2})$ omitted, and factoring the $\langle \bar{\Phi}(2N+1) \mid \bar{\Phi}(2N+1) \rangle$ from the determinant leads to Eq. (15). In those cases where the Rayleigh-Schrödinger expansion is possible, the roots of Eq. (15) are the exact energies E_k (with $1 \leq k \leq S$) accurate through $O(\lambda^{2N+1})$ regardless of the choice of $\mathbb{C}$. The analog of the secular equation (15) in the usual Rayleigh-Schrödinger theory is the partial sum of the perturbation energies. The secular equation (14) corresponds to the expectation value of $H \leftarrow$ *can H (not hold/acc)* with the wavefunction accurate through $O(\lambda^N)$. Even in the Rayleigh-Schrödinger theory, it is difficult to say which way of computing the energy is more accurate.[13] In any case, the roots of Eq. (14) differ from those of Eq. (15) by $O(\lambda^{2N+2})$.

In Appendix A, Eq. (14) and the perturbation equations (11) are derived on the basis of Kirtman's treatment[5] of Van Vleck's degenerate perturbation theory.[1] This is quite a different approach and helps to clarify the significance of the partitioning technique.

Normalization conditions and the choice of the transformation $\mathbb{C}$ must be given to fully specify $\Phi^{(n)}$ and $\mathbb{G}^{(n)}$. Clearly any choice of $\mathbb{C}$ consistent with the normalization of the Φ_k and the Ψ_k is permissable. In cases where the Rayleigh-Schrödinger expansion of (E_k, Ψ_k) is possible, different choices of $\mathbb{C}$ have very little effect on the accuracy of the calculated energy or wavefunction, and $\mathbb{C}$ is frequently chosen on the basis of mathematical convenience, as we shall see in the next two sections. In cases where the Rayleigh-Schrödinger expansion does not converge, the choice of $\mathbb{C}$ is more critical.

For degenerate and almost-degenerate perturbations, full normalization of the Φ is most convenient since it results in $\mathcal{E}^{(n)}$ being hermitean. The <u>Kirtman</u> method[5] corresponds to using the full normalization and determining the energies from the secular equation (15). What we call the <u>Modified Kirtman</u> method corresponds to using the full normalization and determining the energies from the secular equation (14). Instead of using the full normalization, the DE-FOP-VIM procedure[4] corresponds to leaving the integrals $\langle \phi_j^{(o)} | \phi_\ell^{(o)} \rangle$ as undetermined parameters in Φ (N) to be fixed by minimizing the roots E_k of the secular equation (14). This procedure is developed in more detail in Section IV in connection with the almost degenerate case and is particularly useful for exchange perturbations (considered in a companion paper).

In the <u>usual</u> presentation of the Rayleigh-Schrödinger formalism, $\mathcal{E}$ is taken to be $\mathcal{E}^{(o)}$ and the normalization is restricted (usually taken to be <u>intermediate</u>). The $\mathcal{E}^{(o)}$ is determined by successively diagonalizing the matrix for different orders of the perturbation until the degeneracy is resolved. In the Modified Kirtman treatment, $\mathcal{E}$ is varied so as to give the best energy but the normalization is still restricted (to <u>full</u>). In the DE-FOP-VIM, both $\mathcal{E}$ and the normalization are variationally determined. Thus, if the wave functions are truncated after the N-th order, the DE-FOP-VIM energies should be more accurate than the Modified Kirtman, which in turn should be more accurate than the <u>usual</u> Rayleigh-Schrödinger. Of the three methods as applied to a degenerate perturbation, the Modified Kirtman is the simplest and the DE-FOP-VIM requires the most work. The Kirtman (not Modified Kirtman) energies are not upper bounds to the exact energies and therefore may be better or worse than the energies determined by the other three methods.

II. Full Normalization of the $\overline{\Phi}$

By <u>full normalization</u> we mean that $\langle\overline{\Phi}|\overline{\Phi}\rangle = \mathbb{1}$ and the phases of the $\overline{\Phi}$ are specified. With full normalization it is easy to show that $\mathbb{E}$ is a hermitean matrix. From Eq. (4),

$$\langle\overline{\Phi}|H|\overline{\Phi}\rangle = \langle\overline{\Phi}|\overline{\Phi}\rangle\,\mathbb{E} = \mathbb{E} \tag{16}$$

Since $\langle\overline{\Phi}|H|\overline{\Phi}\rangle$ is hermitean, $\mathbb{E}$ is hermitean. Further-more expanding $\mathbb{E}$ in powers of λ, it follows that each of the $\mathbb{E}^{(n)}$ are also hermitean. If instead, we had used <u>intermediate</u> <u>normalization</u>, $\langle\phi^{(0)}|\overline{\Phi}\rangle = \mathbb{1}$, the resulting matrix $\mathbb{E}$ would be non-hermitean.

Expanding $\langle\overline{\Phi}|\overline{\Phi}\rangle = \mathbb{1}$ in powers of λ,

$$\langle\phi^{(0)}|\phi^{(m)}\rangle + \langle\phi^{(m)}|\phi^{(0)}\rangle = -\sum_{k=1}^{m-1}\langle\phi^{(k)}|\phi^{(m-k)}\rangle$$

Thus, the full normalization condition only determines the <u>real</u> part of $\langle\phi^{(0)}|\phi^{(m)}\rangle$. The imaginary part is left arbitrary. This is associated with the fact that $\overline{\Phi}$ could be multiplied by an arbitrary phase factor $\exp(i\,A(\lambda))$.

In the present section we use <u>full normalization</u> and fix the imaginary part of $\langle\phi^{(0)}|\phi^{(m)}\rangle$ by the conditions

$$\langle\phi^{(0)}|\phi^{(2n+1)}\rangle = -\sum_{k=1}^{m}\langle\phi^{(k)}|\phi^{(2n+1-k)}\rangle$$

$$\langle\phi^{(0)}|\phi^{(2n)}\rangle = -\frac{1}{2}\langle\phi^{(m)}|\phi^{(m)}\rangle$$
$$-\sum_{k=1}^{m-1}\langle\phi^{(k)}|\phi^{(2m-k)}\rangle \tag{17}$$

In Appendix B, expressions for $\mathbb{E}^{(2n+1)}$ and $\mathbb{E}^{(2n)}$ are derived in terms of $\overline{\Phi}$ accurate through $O(\lambda^n)$. The expressions are considerably simplified by adopting the convention for the

$$E^{(2n+1)} = \langle \phi^{(n)} | H^{(1)} | \phi^{(n)} \rangle$$

$$- \frac{1}{2} \sum_{k=1}^{n} \sum_{\ell=0}^{k-1} \left\{ E^{(k)} \langle \phi^{(n+\ell+1-k)} | \phi^{(n-\ell)} \rangle + \langle \phi^{(n-\ell)} | \phi^{(n+\ell+1-k)} \rangle E^{(k)} \right\}$$

$$- \frac{1}{2} \sum_{k=2}^{n} \sum_{\ell=0}^{\{\frac{k}{2}\}} E^{(k)} \left\{ \langle \phi^{(n+\ell+1-k)} | \phi^{(n-\ell)} \rangle - \langle \phi^{(n-\ell)} | \phi^{(n+\ell+1-k)} \rangle \right\}$$

$$+ \frac{1}{2} \sum_{k=2}^{n} \sum_{\ell=0}^{\{\frac{k}{2}\}} \left\{ \langle \phi^{(n+\ell+1-k)} | \phi^{(n-\ell)} \rangle - \langle \phi^{(n-\ell)} | \phi^{(n+\ell+1-k)} \rangle \right\} E^{(k)}$$

$$\tag{18}$$

where $\left\{ \dfrac{k}{2} \right\} = \begin{cases} \dfrac{k-2}{2} & , \; k \text{ even} \\[2mm] \dfrac{k-3}{2} & , \; k \text{ odd;} \end{cases}$

$$E^{(2n)} = \frac{1}{2} \left\{ \langle \phi^{(n-1)} | H^{(1)} | \phi^{(n)} \rangle + \langle \phi^{(n)} | H^{(1)} | \phi^{(n-1)} \rangle \right\}$$

$$- \frac{1}{2} \sum_{k=1}^{n} \sum_{\ell=0}^{k-1} \left\{ E^{(k)} \langle \phi^{(n-\ell)} | \phi^{(n-k+\ell)} \rangle + \langle \phi^{(n-k+\ell)} | \phi^{(n-\ell)} \rangle E^{(k)} \right\}$$

$$- \frac{1}{2} \sum_{k=1}^{n-1} \sum_{\ell=0}^{[\frac{k}{2}]} E^{(k)} \left\{ \langle \phi^{(n-\ell)} | \phi^{(n-k+\ell)} \rangle - \langle \phi^{(n-k+\ell)} | \phi^{(n-\ell)} \rangle \right\}$$

$$+ \frac{1}{2} \sum_{k=1}^{n-1} \sum_{\ell=0}^{[\frac{k}{2}]} \left\{ \langle \phi^{(n-\ell)} | \phi^{(n-k+\ell)} \rangle - \langle \phi^{(n-k+\ell)} | \phi^{(n-\ell)} \rangle \right\} E^{(k)}$$

$$\tag{19}$$

where $\left[\dfrac{k}{2} \right] = \begin{cases} \dfrac{k-2}{2} & , \; k \text{ even} \\[2mm] \dfrac{k-1}{2} & , \; k \text{ odd.} \end{cases}$

These formulas are derived in Appendix B by algebraic manipulations of Eqs. (11), (12), and (17) in a manner completely analogous to nondegenerate theory.[12]

It is at first sight surprising that Eq. (18) and (19) depend on a particular choice of normalization, in view of the proof that $\Phi(N)$ is sufficient to compute the energies E_k, accurate through $O(\lambda^{2N+1})$, regardless of the normalization. There is no conflict in the two results, however, since, for example, the off-diagonal elements of $\mathbb{C}^{(2N+1)}$ do not contribute to the roots of Eq. (14) through $O(\lambda^{2N+1})$.

Solution of the Perturbation Equations. The n-th order perturbation equation (11) may be solved exactly in terms of the eigenfunctions of the unperturbed hamiltonian $H^{(0)}$. This is facilitated by the introduction of the reduced resolvent,

$$R^{(0)} = \sum_k{}' \frac{|\phi_k^{(0)}\rangle\langle\phi_k^{(0)}|}{\epsilon^{(0)} - \epsilon_k^{(0)}} \tag{20}$$

where the prime on the summation means that all the members in $\phi^{(0)}$ are to be excluded from the sum. Otherwise, the sum is over a complete set of eigenstates of $H^{(0)}$. It may be readily shown that

$$R^{(0)}\phi^{(0)} = 0, \tag{21}$$

$$(H^{(0)} - \epsilon^{(0)})R^{(0)} = |\phi^{(0)}\rangle\langle\phi^{(0)}| - 1.$$

In terms of $R^{(0)}$ the solutions of the perturbation equations which satisfy the normalization conditions (17) may be written

$$\phi^{(n)} = R^{(0)}\left\{H^{(1)}\phi^{(n-1)} - \sum_{k=1}^{n-1}\phi^{(n-k)}\mathbb{C}^{(k)}\right\} + \phi^{(0)}N^{(n)}, \tag{22}$$

where the matrix $N^{(n)}$ is determined by requiring that $\phi^{(n)}$ satisfy the normalization conditions Eq. (17). The explicit formula for $N^{(n)}$ is, in terms of lower order functions,

$$N^{(2n+1)} = -\sum_{k=1}^{n} \langle \phi^{(k)} | \phi^{(2n+1-k)} \rangle,$$

and

$$N^{(2n)} = -\frac{1}{2}\langle \phi^{(n)} | \phi^{(n)} \rangle - \sum_{k=1}^{n-1} \langle \phi^{(k)} | \phi^{(2n-k)} \rangle.$$

(23)

That $\phi^{(n)}$ defined by Eq. (22) actually solves the perturbation equation (11) with $\epsilon^{(n)}$ given by (12).

Except for simple examples, the expressions given above are of formal interest only, since the summations over excited states cannot be evaluated. In general, however, it is possible to obtain variational approximations to $\phi^{(n)}$. For example, the first-order functions may be determined by finding the stationary points of the functionals

$$J_k[\tilde{\phi}_k^{(1)}] = \langle \tilde{\phi}_k^{(1)} | H^{(0)} - \epsilon^{(0)} | \tilde{\phi}_k^{(1)} \rangle + \langle \tilde{\phi}_k^{(1)} | H^{(1)} | \phi_k^{(0)} \rangle$$

$$+ \langle \phi_k^{(0)} | H^{(1)} | \tilde{\phi}_k^{(1)} \rangle - \sum_{\ell=1}^{S} \left\{ \langle \tilde{\phi}_k^{(1)} | \phi_\ell^{(0)} \rangle + \langle \phi_\ell^{(0)} | \tilde{\phi}_k^{(1)} \rangle \right\} \epsilon_{\ell k}^{(1)}$$

(24)

where $\tilde{\phi}_k^{(1)}$ is a trial function corresponding to the exact function $\phi_k^{(1)}$ which belongs to $\phi^{(1)}$. It is evident that if δJ_k vanishes for arbitrary variations $\delta\tilde{\phi}_k^{(1)}$ in $\tilde{\phi}_k^{(1)}$, then $\tilde{\phi}_k^{(1)}$ satisfies Eq. (11) for $n=1$. This is analogous to the Hylleraas variational method in non-degenerate Rayleigh-Schrödinger perturbation theory.[12,14]

III. Degenerate Perturbation Theory.

The formalism developed in Section I is particularly useful for considering the perturbation of degenerate states. The $\mathcal{E}^{(n)}$ and the $\phi^{(n)}$ are determined without requiring knowledge of the "correct zeroth order" wavefunctions. Thus the eigenvalues of either the secular equation (14) or (15) gives the energy of all of the degenerate states accurate through a given order of perturbation. The eigenvectors of (14) give the wavefunctions.

If either the secular equation (14) or (15) is solved by expansion in powers of λ, the usual Rayleigh-Schrödinger perturbation theory for the states in $\mathcal{S}$ is obtained. One must then determine the correct zeroth order wavefunctions, which depend on the order in which the degeneracy is lifted. Hirschfelder[15] has given a very thorough discussion of the complicated equations which result. The present formalism is much simpler because it does not contemplate the expansion of the secular equation, which may be solved by other procedures.[16]

For a degenerate perturbation problem, the special set of states $\phi^{(0)}$ is defined to be any linearly independent set which spans precisely the same space as the S eigenfunctions of the S-fold degenerate level of the unperturbed hamiltonian

$$\left(H^{(0)} - \mathcal{E}^{(0)} \right) \phi_k^{(0)} = 0, \qquad 1 \leqslant k \leqslant S. \qquad (25)$$

It is convenient to choose the $\phi^{(0)}$ to be orthonormal, (10), but it is not necessary to assume any other special properties.

Clearly we are using a partitioning technique. The basic notion of partitioning goes back to Van Vleck,[1] Lennard-Jones,[17] Brillouin,[18] and others in the early days of quantum mechanics. Löwdin and his co-workers[6] have developed the partitioning techniques into very elegant and powerful approaches to perturbation theory. Our equations appear to be quite different from Löwdin's although the results must be similar. Thus it is interesting to compare the two treatments. In place of the secular equation (13), Löwdin solves the secular equation

$$\left| \langle \phi^{(0)} | \tilde{H} - E | \phi'^{(0)} \rangle \right| = 0. \tag{26}$$

where

$$\tilde{H} = H + H T(E) H,$$

and

$$T(E) = R^{(0)} \sum_{m=0}^{2N-1} \left[(V - E + \epsilon_0) R^{(0)} \right]^m + O(\lambda^{2N}) \tag{27}$$

Since $\tilde{H}$ is a function of E, Eq. (26) is not an ordinary secular equation. Nevertheless, it can be solved in an iterative fashion. In contrast, the matrix elements of (14) or (15) are linear in the energy E. Nevertheless, in Appendix C it is shown that the Löwdin secular equation factors into the product of a non-vanishing determinant times a secular equation equivalent to (14). Thus the equivalence of the two treatments is established.

IV. Almost-Degenerate Perturbation Theory.

In many ways, almost-degenerate states are more difficult to treat than degenerate states. This is the case where two or more states interact sufficiently that the Rayleigh-Schrödinger expansions do not apply. One of the standard techniques is to manipulate the zeroth order hamiltonian in order to make the set of almost-degenerate levels appear degenerate. Clearly this is a type of problem where partitioning techniques should be applied. And, as we shall see, our formalism is particularly useful.

For an almost-degenerate perturbation problem, the special set of states $\phi^{(o)}$ is defined to be S states $(\epsilon_k^{(o)}, \phi_k^{(o)})$ of the unperturbed hamiltonian,

which are almost degenerate in the sense that the ratios

$$\frac{\langle \phi_k^{(o)} | H^{(1)} | \phi_{k'}^{(o)} \rangle}{\epsilon_k^{(o)} - \epsilon_{k'}^{(o)}} \quad , \quad 1 \leqslant k, k' \leqslant S,$$

are large. For simplicity, it is assumed that each of the levels $\epsilon_k^{(o)}$ is itself non-degenerate and that $\langle \phi^{(o)} | \phi^{(o)} \rangle = 1$.

Again the general equations to be solved are Eqs. (11) and (14) or (15). These equations are similar to the degenerate case, except that now $\mathfrak{C}^{(o)}$ is diagonal but it is not a multiple of the unit matrix. Furthermore, the perturbation energies are not fixed by requirements of mathematical consistency.

Thus the off-diagonal elements of $\mathbb{C}$ are not fixed by the formalism. Each choice of these numbers results in a different expansion of $\hat{\Phi}$ and $\mathbb{C}$. Although the roots of the secular equation (14) obtained by different choices differ only by "higher-order terms", it is of interest to examine various ways of fixing the off-diagonal elements of $\mathbb{C}$.

The DE-FOP-VIM Formalism.[4] A general method of handling the indeterminancy in $\mathbb{C}$ is to solve for each $\hat{\phi}^{(n)}$ as an implicit function of the off-diagonal elements $\epsilon_{jk}^{(n)}$. Then these quantities can be determined by minimizing the roots of the secular equation (14) with respect to variations in the $\epsilon_{jk}^{(n)}$.

To gain insight into this procedure, consider the solution of the first order perturbation equation (11) with $\epsilon_{jk}^{(1)} \ (j \neq k)$ arbitrary. The general solution may be written

$$\hat{\phi}_k^{(1)} = \phi_k^{(1)} + \sum_{\substack{j \neq k}}^{S} \phi_j^{(0)} \left[\frac{\langle \phi_j^{(0)} | H^{(1)} | \phi_k^{(0)} \rangle - \epsilon_{jk}^{(1)}}{\epsilon_k^{(0)} - \epsilon_j^{(0)}} \right] + a_k^{(1)} \phi_k^{(0)},$$

where $\phi_k^{(1)}$ satisfies

$$\left(H^{(0)} - \epsilon_k^{(0)}\right)\phi_k^{(1)} + H^{(1)}\phi_k^{(0)} = \sum_{j=1}^{S} \phi_j^{(0)} \langle \phi_j^{(0)} | H^{(1)} | \phi_k^{(0)} \rangle,$$

$$\langle \phi_k^{(1)} | \phi_j^{(0)} \rangle = 0, \qquad 1 \leq j \leq S,$$

and $a_k^{(1)}$ is an arbitrary normalization constant. Then the S-dimensional variational basis set

$$\Phi_k(1) = \phi_k^{(0)} + \lambda \hat{\phi}_k^{(1)}, \qquad 1 \leq k \leq S,$$

which leads to the SxS secular equation (24) with $\phi^{(1)}$ replaced by $\hat{\phi}^{(1)}$, is clearly equivalent to the 2S-dimensional basis

$$\phi_k^{(0)} \quad \text{and} \quad \phi_k^{(1)}, \qquad 1 \leq k \leq S.$$

This leads to the 2Sx2S secular equation

$$0 = \begin{vmatrix} \langle \phi^{(0)} | H - E | \phi^{(0)} \rangle & \langle \phi^{(0)} | H - E | \phi^{(1)} \rangle \\ \langle \phi^{(1)} | H - E | \phi^{(0)} \rangle & \langle \phi^{(1)} | H - E | \phi^{(1)} \rangle \end{vmatrix} \qquad (28)$$

S roots of Eq. (28) are identical to the roots of Eq. (14) if in the latter equation $N = 1$ and the $\epsilon_{jk}^{(1)}$ and $a_k^{(1)}$ are varied freely and independently to a stationary point.

The Eq. (28) appears also in Hirschfelder's DE-VOP-VIM formalism[4] for degenerate and almost-degenerate perturbation problems. It is easily seen that the extension to N-th order of this method of choosing $\mathcal{C}$ leads to an $(N+1)S \times (N+1)S$ secular equation, S roots of which give the desired energies accurate through $O(\lambda^{2N+1})$.

The DE-FOP-VIM method is simplest to apply in case that the states k in $\mathcal{S}$ are the lowest energy states of H corresponding to particular symmetries. Then, by Hylleraas-Undheim theorem, the S smallest roots of the DE-FOP-VIM secular equation can be identified as the approximations to the corresponding exact energies. In case that there are lower energy states of H than the states in $\mathcal{S}$, the interpretation of the roots of the DE-FOP-VIM secular equation can become ambiguous. Clearly, the DE-FOP-VIM procedure cannot be applied to the secular equation (15) since this equation cannot be derived from the variational method.

The Kirtman Formalism.[5] Another method of choosing the off-diagonal elements of $\mathcal{C}$ is by analogy with the degenerate case. The full normalization conditions (20) uniquely fix all elements of $\mathcal{C}$, just as in the degenerate case. Furthermore, in the present case $\mathcal{C}$ is hermitean and the formulas (18) and (19) for $\mathcal{C}^{(n)}$ continue to hold if the wavefunction is required to satisfy Eq. (17).

This method of fixing $\mathcal{C}$ was first discussed by Kirtman[5] in his extension of Van Vleck degenerate perturbation theory to the almost degenerate case. Kirtman considered in detail the calculation of the energy through third order, which in his formalism is given as a root of the secular equation

$$\left| \mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)} + \lambda^2 \mathcal{E}^{(2)} + \lambda^3 \mathcal{E}^{(3)} - E \right| = 0, \qquad (29)$$

which is Eq. (15) for $N = 1$.

Hence the <u>Kirtman formalism</u> will denote the treatment of almost degenerate perturbation problems by the secular equation (15) with the full normalization conditions (20).

The <u>modified Kirtman formalism</u> will be used to label the treatment based on the secular equation (14) with the full normalization conditions (20).

The advantage of the Kirtman or modified Kirtman formalism is that the energy is obtained as a root of an S×S secular equation, rather than the $(N+1)S \times (N+1)S$ secular equation for the DE-FOP-VIM formalism. The roots of the DE-FOP-VIM secular equation are necessarily more accurate than the corresponding roots of the modified

Kirtman secular equation in case that the lowest energy states of H are being treated. In any case the corresponding roots of the three different equations differ by $O(\lambda^{2N+2})$. Thus, if the almost degenerate block of states is well separated from the remaining unperturbed states, the energies obtained by the three methods differ by terms which are, by hypothesis, negligible.

Transformation to an Exactly Degenerate Problem. The lack of uniqueness of the off-diagonal elements of $\mathcal{C}$ can be avoided by defining a new split of H into an unperturbed hamiltonian and a perturbation, such that the unperturbed limit is exactly degenerate. In some cases there is a natural choice for the new unperturbed hamiltonian and eigenfunctions. However, it is always possible to define

$$\bar{H}^{(0)} = H^{(0)} + |\phi^{(0)}\rangle \left[\bar{\mathcal{C}}^{(0)} - \mathcal{C}^{(0)} \right] \langle \phi^{(0)} |, \qquad (30)$$

and

$$\bar{H}^{(1)} = \lambda H^{(1)} + |\phi^{(0)}\rangle \left[\mathcal{C}^{(0)} - \bar{\mathcal{C}}^{(0)} \right] \langle \phi^{(0)} |, \qquad (31)$$

where

$$\bar{\mathcal{C}}^{(0)} = \bar{\epsilon}^{(0)} \mathbf{1}, \qquad (32)$$

and $\bar{\epsilon}^{(0)}$ may be taken to be an averaged unperturbed energy, i.e. esz

$$\bar{\epsilon}^{(0)} = S^{-1} \sum_{k=1}^{S} \epsilon_k^{(0)}. \qquad (33)$$

or $\bar{\epsilon}^{(0)}$ may be taken to be a variational parameter.

Then all of the states $\phi^{(o)}$ are exactly degenerate with respect to $\bar{\bar{E}}^{(o)}$

$$\left(\overline{H}^{(o)} - \bar{\bar{E}}^{(o)} \right) \phi^{(o)} = 0,$$

so that the formalism of Sections II and IV can be applied. This method of handling almost-degeneracy is suggested in most textbooks.[20]

Let a bar denote perturbation terms in the expansion of $\bar{\Phi}$ and $\mathbb{C}$ based on Eq. (34):

$$\bar{\Phi} = \phi^{(o)} + \bar{\Phi}^{(1)} + \cdots,$$

and

$$\mathbb{C} = \bar{\bar{\mathbb{C}}}^{(o)} + \bar{\bar{\mathbb{C}}}^{(1)} + \bar{\bar{\mathbb{C}}}^{(2)} + \cdots.$$

Through first order, $\bar{\bar{E}}^{(o)}$ does not contribute to $\mathbb{C}$ since, by Eq. (18),

$$\bar{\bar{\mathbb{C}}}^{(1)} = \langle \phi^{(o)} | \overline{H}^{(1)} | \phi^{(o)} \rangle = \lambda \mathbb{C}^{(1)} + \mathbb{C}^{(o)} - \bar{\bar{\mathbb{C}}}^{(o)}$$

so that

$$\bar{\bar{\mathbb{C}}}^{(o)} + \bar{\bar{\mathbb{C}}}^{(1)} = \mathbb{C}^{(o)} + \lambda \mathbb{C}^{(1)}.$$

With the normalization (16), $\langle \phi^{(o)} | \bar{\Phi}^{(1)} \rangle = 0$, the first order equation (11) can be written

$$\left(H^{(o)} - \bar{\bar{E}}^{(o)} \right) \bar{\Phi}^{(1)} + H^{(1)} \phi^{(o)} = \phi^{(o)} \mathbb{C}^{(1)}.$$

(34)

Eq. (34) reveals that $\overline{\overline{\mathcal{E}}}^{(0)}$ enters into $\overline{\Phi}^{(1)}$, and hence $\overline{\overline{\mathcal{E}}}^{(2)}$, in a non-trivial way, so that the latter quantities are not simply related to $\Phi^{(1)}$ and $\mathcal{E}^{(2)}$. Thus, it is possible to energy optimize the $\overline{\overline{\mathcal{E}}}^{(0)}$.

The solution of the almost-degenerate perturbation problem is thus reduced to the solution of an equivalent degenerate perturbation and the techniques of Section III may be applied.

The relationship between the DE-FOP-VIM, Kirtman, and modified Kirtman formalisms as well as the reduction to a truly degenerate problem is best understood by considering the example given in the following companion paper.[20] $(Part\ II)$.

V. Electron Exchange Perturbation Problems.

In this section, the perturbation formalism given in Section I
is generalized so as to be suitable for a wide range of electron
exchange problems including those which involve configurational
interactions. The dimensionality of the secular equations which
we derive can be greatly reduced by making use of symmetry considerations.
This is done in the companion paper III[22].

In order to apply to electron exchange problems, the partitioning
formalism developed in Section I must be modified in the following ways:

1). The zeroth order functions $\phi_1^{(0)}, \ldots, \phi_s^{(0)}$ no
longer need to be eigenfunctions of the same zeroth
order Hamiltonian. Thus,

$$(H_k^{(0)} - \epsilon_k^{(0)}) \, \phi_k^{(0)} = 0 \tag{35}$$

2). In order to express the perturbed Hamiltonian in the
form

$$H = H_1^{(0)} + \lambda H_1^{(1)} = \ldots = H_s^{(0)} + \lambda H_s^{(1)} \tag{36}$$

the perturbation parameter λ can only have the value
of unity.

3). The zeroth order functions $\phi_1^{(0)}, \ldots, \phi_s^{(0)}$ are
normalized but not orthogonal. Thus,

$$\langle \phi_j^{(0)} | \phi_k^{(0)} \rangle = S_{jk} \tag{37}$$

Here $S_{kk} = 1$, but the overlap matrix S is not
unitary.

These modifications do not lead to any major changes in the treatment. As in Section I,

$$\epsilon_{k\ell}^{(0)} = \epsilon_k^{(0)} \delta_{k\ell} \tag{9}$$

The only difference in the perturbation equation in Section I and the equations here are the subscripts on $H^{(0)}$ and $H^{(1)}$. Thus, corresponding to Eq.(11), we now have

$$(H_k^{(0)} - \epsilon_k^{(0)}) \phi_k^{(n)} + H_k^{(1)} \phi_k^{(n-1)} = \sum_{\ell=0}^{n-1} \sum_{j=1}^{s} \phi_j^{(\ell)} \epsilon_{jk}^{(n-\ell)} \tag{38}$$

Note that Eq.(38) reduces to Eq.(5). Multiplying Eq.(38) by $\sum_{i=1}^{s} S_{ji}^{-1} \phi_i^{(0)*}$ and integrating, we obtain

$$\epsilon_{jk}^{(m)} = \sum_{i=1}^{s} S_{ji}^{-1} \left[\langle \phi_i^{(0)} | H_k^{(0)} | \phi_k^{(m)} \rangle + \langle \phi_i^{(0)} | H_k^{(1)} | \phi_k^{(m-1)} \rangle \right. $$
$$\left. - \sum_{\ell=1}^{m-1} \langle \phi_i^{(0)} | \phi_j^{(\ell)} \rangle \epsilon_{jk}^{(m-\ell)} \right] \tag{39}$$

corresponding to Eq.(12). Adding together the first N perturbation equations,

$$H \Phi_k(N) = H_k^{(1)} \phi_k^{(N)} + \sum_{\ell=0}^{N} \sum_{j=1}^{s} \Phi_j^{(N-\ell)} \epsilon_{jk}^{(\ell)}$$
$$= \sum_{j=1}^{s} \Phi_j(N) \epsilon_{jk}(N) + O(\lambda^{N+1}) \tag{40}$$

The energy is then determined accurately through terms of $O(\lambda^{2N+1})$ by solving the secular equation

$$\left| \langle \Phi(N) | H - E | \Phi(N) \rangle \right| = 0 \tag{14}$$

The presentation in the companion paper[22] is given from the Kirtman-Van Vleck approach considered in Appendix A. As noted in Appendix A, the two approaches lead to the same working equations.

Now let us consider the first order perturbation equation, Eq.(38) with n=1,

$$(H_k^{(0)} - \epsilon_k^{(0)}) \phi_k^{(1)} + H_k^{(1)} \phi_k^{(0)} = \sum_{\lambda=1}^{s} \phi_\lambda^{(0)} \epsilon_{jk}^{(1)} \quad (41)$$

The most general expression for $\phi_k^{(1)}$ is

$$\phi_k^{(1)} = \hat{\phi}_k^{(1)} + \sum_{j}^{(1)} \phi_j^{(0)} \alpha_{jk} - \sum_{\ell}^{(2)} \omega_{k\ell} \epsilon_{\ell k}^{(1)} \quad (42)$$

Here $\hat{\phi}_k^{(1)}$ is the first order __polarization__ function which is orthogonal to $\phi_k^{(0)}$ and satisfies the equation,

$$\left(H_k^{(0)} - \epsilon_k^{(0)}\right) \hat{\phi}_k^{(1)} + H_k^{(1)} \phi_k^{(0)} = \sum_{j=1}^{(1)} \phi_j^{(0)} \langle \phi_j^{(0)} | H_k^{(1)} | \phi_k^{(0)} \rangle \quad (43)$$

In both Eqs.(42) and (43), the $\sum_j^{(1)}$ mean that the summation is to be taken over all states j (including k) such that

$$(H_k^{(0)} - \epsilon_k^{(0)}) \phi_j^{(0)} = 0 \quad (44)$$

The $\sum_\ell^{(2)}$ is the summation over the remainder of the s basis functions. The functions $\omega_{k\ell}$ are the __exchange__ functions which are orthogonal to $\phi_k^{(0)}$ and satisfy the equation

$$\left(H_k^{(0)} - \epsilon_k^{(0)}\right) \omega_{k\ell} = \phi_\ell^{(0)} - \sum_{j}^{(1)} S_{j\ell} \phi_j^{(0)} \quad (45)$$

The constants α_{jk} and $\epsilon_{\ell k}^{(1)}$ are best determined by optimizing the energy E for the state under consideration. This corresponds to the DE-FOP-VIM procedure. Thus, different values of both the α_{jk} and $\epsilon_{\ell k}^{(1)}$ are obtained for each state. Substituting (42) into (41) and making use of Eqs.(43)-(45), it follows that for those states j in sub-set (1),

$$\epsilon_{jk}^{(1)} = \langle \phi_j^{(0)} | H_k^{(1)} | \phi_k^{(0)} \rangle - \sum_{\ell}^{(2)} S_{j\ell} \, \epsilon_{\ell k} \qquad (46)$$

References

1. J. H. Van Vleck, Phys. Rev. $\underline{33}$, 467 (1929); see also ref. 11, p. 394.

2. T. Kato, Prog. Theor. Phys. $\underline{4}$, 154 (1949); see also ref. 20, p. 712-20.

3. C. Bloch, Nucl. Phys. $\underline{6}$, 329 (1958); see also ref. 20, p. 719-20.

4. J. O. Hirschfelder, J. Chem. Phys. $\underline{39}$, 2009 (1963); see also ref. 52, p. 312.

5. B. Kirtman, J. Chem. Phys. $\underline{49}$, 3890 (1968); ibid., 3895 (1968).

6. P.-O. Löwdin in Perturbation Theory and in Quantum Mechanics. C. H. Wilcox, ed. (Wiley, New York, 1966) and references contained therein.

7. P.-O. Löwdin, J. Math. Phys. $\underline{6}$, 1341 (1965).

8. J. H. Choi, J. Math. Phys. (to be published); see also Univ. of Fla. Quantum Theory Project Preprint No. 89, 1966 (unpublished).

9. S. O. Goscinski and P.-O. Löwdin, Univ. Uppsala Quant. Chem. Reports No. 205 and 206, 1969, (unpublished).

10. H. Kim and J. O. Hirschfelder, J. Chem. Phys. $\underline{46}$, 4553 (1967).

11. E. C. Kemble, Quantum Mechanics (Dover, New York, 1958), p. 415.

12. J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Adv. in Quant. Chem. 1, P.-O. Löwdin, Ed. (Academic Press, New York, 1964).

13. Ref. 12, p. 359 and p. 267.

14. E. A. Hylleraas, Z. Physik $\underline{48}$, 469 (1928) and $\underline{65}$, 209 (1930); also, "The Variational Principle in Quantum Mechanics", Rept. No. 1, Inst. Theoret. Phys., University of Oslo (1961).

15. J. O. Hirschfelder, Int. J. Quant. Chem. $\underline{3}$, 731 (1969).

16. J. H. Wilkenson, <u>The Algebraic Eigenvalue Problem</u> (Clarendon
     Press, Oxford, 1965).

17. J. E. Lennard-Jones, Proc. Roy. Soc. (London) <u>129</u>, 604 (1930).

18. L. Brillouin, J. Phys. radium (7) <u>3</u>, 373 (1932).

19. P.-O. Löwdin, J. Math. Phys. <u>3</u>, 939 (1962).

20. Ref. 12, p. 297.

21. P. R. Certain, D. R. Dion, and J. O. Hirschfelder, J. Chem. Phys.
     (companion paper, Paper I).

22. P. R. Certain and J. O. Hirschfelder, J. Chem. Phys., (companion
     paper; Paper III).

APPENDIX A. Derivation of Secular Equation and Perturbation Equations Using Kirtman-Van Vleck Approach.

Consider a complete set of functions, which is split into two classes, $\phi^{(0)}$ and $\chi^{(0)}$, and which spans the Hilbert space of the hamiltonian $H(\lambda) = H^{(0)} + \lambda H^{(1)}$. We have already discussed the $\phi^{(0)}$. The remaining functions (in general, infinite in number) which complete the set are denoted by

$$\boldsymbol{\chi}^{(0)} = (\chi_1^{(0)}, \chi_2^{(0)}, \ldots).$$

Bold Face
l.c. chi

Without loss of generality, it is assumed that

$$\langle \chi^{(0)} | \chi^{(0)} \rangle = 1 \qquad\qquad (A.1)$$

and

$$\langle \chi^{(0)} | \phi^{(0)} \rangle = \mathbb{O}, \qquad\qquad (A.2)$$

where $\mathbb{O}$ is the null matrix. No other assumptions are made regarding $\chi^{(0)}$; in particular, the $\chi_k^{(0)}$ is not necessarily an eigenfunction of $H^{(0)}$.

In general, to compute the (E_k, Ψ_k) exactly, it is necessary to consider both $\phi^{(0)}$ and $\chi^{(0)}$ since the interaction elements $\langle \phi^{(0)} | H | \chi^{(0)} \rangle$ are non-vanishing. Then the E_k are roots of the infinite-dimensional secular equation

$$\begin{vmatrix} \langle \phi^{(0)} | H-E | \phi^{(0)} \rangle & \langle \phi^{(0)} | H-E | \chi^{(0)} \rangle \\ \\ \langle \chi^{(0)} | H-E | \phi^{(0)} \rangle & \langle \chi^{(0)} | H-E | \chi^{(0)} \rangle \end{vmatrix} = 0. \qquad (A.3)$$

Following Van Vleck[1] and Kirtman,[5] the solution of Eq. (A.3) is obtained by transforming the initial basis into the new set

$$\Phi(N) \quad \text{and}$$

$$\chi(N) = \chi^{(0)} + \lambda \chi^{(1)} + \cdots + \lambda^N \chi^{(N)}. \quad \text{(A.4)}$$

The functions $\phi^{(k)}$, $\chi^{(k)}$ are chosen so as to make the <u>overlap</u> and <u>hamiltonian</u> matrix elements connecting $\Phi(N)$ and $\chi(N)$ vanish through terms $O(\lambda^N)$:

$$\langle \Phi(N) \mid H - E \mid \chi(N) \rangle = O(\lambda^{N+1}). \quad \text{(A.5)}$$

Then the leading contribution of the functions $\chi(N)$ to the energies E_k, $1 \leqslant k \leqslant S$, is proportional to

$$|\langle \Phi(N) \mid H \mid \chi(N) \rangle|^2 = O(\lambda^{2N+2}). \quad \text{(A.6)}$$

Hence the roots of the $S \times S$ secular equation,

$$|\langle \Phi(N) \mid H - E \mid \Phi(N) \rangle| = 0, \quad \text{(A.8)}$$

are accurate through $O(\lambda^{2N+2})$.

To obtain equations for $\phi^{(k)}$, $\chi^{(k)}$, it is convenient to introduce the projector onto the set $\Phi(N)$:

$$\mathcal{O} = \mathcal{O}^\dagger = \mathcal{O}^2 ; \quad \text{(A.7)}$$

$$\mathcal{O} \Phi(N) = \Phi(N).$$

script
cap oh

The perturbation terms of $\chi(N)$ are given by

$$\chi(N) = (1 - \mathcal{O})\,\chi(N) \qquad\qquad (A.8)$$

which assures orthgonality between $\Phi(N)$ and $\chi(N)$ through $O(\lambda^N)$.
The perturbation terms of $\Phi(N)$ are determined by

$$|\langle \Phi(N) | H | \chi(N) \rangle| = O(\lambda^{N+1}). \qquad (A.9)$$

The $\chi(N)$ is a complete set of functions in the space orthogonal to
$\Phi(N)$. If overlap of $H\Phi(N)$ with all of $\chi(N)$ vanishes, then
$H\Phi(N)$ must be expressible as a linear combination of the $\Phi(N)$.
Thus, Eq. (A.9) is equivalent to

$$H\Phi(N) = \Phi(N)\,\mathcal{E}(N) + O(\lambda^{N+1}), \qquad (A.10)$$

where the elements of $\mathcal{E}(N)$ are numbers to be determined. In the
limit $N \to \infty$, Eq. (A.10) clearly becomes Eq. (4) .

APPENDIX B. Proof of Eqs. (18) and (19) for Expressing

$\mathcal{E}^{(2N)}$ and $\mathcal{E}^{(2N+1)}$.

Eqs. (18) and (19) are very important in the application of our formalism. When this formalism is extended to the calculation of physical properties other than energy it will be necessary to make use of additional expressions for these energy matrices. These are derived in this Appendix.

First, however, it is convenient to establish some intermediate results. By taking the adjoint of Eq. (17) and adding it to the original equation, one obtains

$$\sum_{k=0}^{m} \langle \phi^{(k)} | \phi^{(m-k)} \rangle = 0 \quad , \quad m > 0 \tag{B.1}$$

The following relation will be needed later:

$$\langle \phi^{(\ell-1)} | H^{(1)} | \phi^{(n-\ell)} \rangle = \langle \phi^{(\ell)} | H^{(1)} | \phi^{(n-\ell-1)} \rangle$$

$$(B.2)$$

$$- \sum_{k=0}^{n-\ell} \langle \phi^{(\ell)} | \phi^{(n-\ell-k)} \rangle \epsilon^{(k)} + \sum_{k=0}^{\ell} \epsilon^{(k)\dagger} \langle \phi^{(\ell-k)} | \phi^{(n-\ell)} \rangle$$

This is proved by multiplying the ℓ-th order perturbation equation (11) from the left by $\phi^{(n-\ell)\dagger}$ and integrating.

$$\langle \phi^{(n-\ell)} | H^{(0)} | \phi^{(\ell)} \rangle + \langle \phi^{(n-\ell)} | H^{(1)} | \phi^{(\ell-1)} \rangle$$

$$(B.3)$$

$$= \sum_{k=0}^{\ell} \langle \phi^{(n-\ell)} | \phi^{(\ell-k)} \rangle \epsilon^{(k)} ,$$

and multiplying the $(n-\ell)$-th order equation from the left by $\phi^{(\ell)\dagger}$ and integrating,

$$\langle \phi^{(\ell)} | H^{(0)} | \phi^{(n-\ell)} \rangle + \langle \phi^{(\ell)} | H^{(1)} | \phi^{(n-\ell-1)} \rangle$$

(B.4)

$$= \sum_{k=0}^{n-\ell} \langle \phi^{(\ell)} | \phi^{(n-\ell-k)} \rangle \mathcal{E}^{(k)}.$$

Taking the adjoint of Eq. (B.3) and subtracting Eq. (B.4) from it yields Eq. (B.2).

Application of Eq. (B.2) q $(\leqslant p-1)$ times to Eq. (12) yields

$$\mathcal{E}^{(p)} = \langle \phi^{(q)} | H^{(1)} | \phi^{(p-q-1)} \rangle + \sum_{\ell=0}^{q} \sum_{k=0}^{\ell} \mathcal{E}^{(k)\dagger} \langle \phi^{(\ell-k)} | \phi^{(p-\ell)} \rangle$$

$$- \sum_{\ell=1}^{q} \sum_{k=0}^{p-1} \langle \phi^{(\ell)} | \phi^{(p-\ell-k)} \rangle \mathcal{E}^{(k)} - \sum_{k=0}^{p-1} \langle \phi^{(0)} | \phi^{(p-k)} \rangle \mathcal{E}^{(k)}.$$

Interchanging the order of summation gives

$$\mathcal{E}^{(p)} = \langle \phi^{(q)} | H^{(1)} | \phi^{(p-q-1)} \rangle + \sum_{k=0}^{q} \mathcal{E}^{(k)\dagger} \sum_{l=0}^{q-k} \langle \phi^{(l)} | \phi^{(p-k-l)} \rangle$$

$$- \sum_{k=0}^{p-q-1} \sum_{l=0}^{q}{}' \langle \phi^{(l)} | \phi^{(p-l-k)} \rangle \mathcal{E}^{(k)} - \sum_{k=p-q}^{p-1} \sum_{l=0}^{p-k}{}' \langle \phi^{(l)} | \phi^{(p-l-k)} \rangle \mathcal{E}^{(k)} .$$

The final term vanishes by the normalization condition Eq. (B.1).

Furthermore, $\mathcal{E}^{(n)} = \mathcal{E}^{(n)\dagger}$. Hence,

$$\mathcal{E}^{(p)} = \langle \phi^{(q)} | H^{(1)} | \phi^{(p-q-1)} \rangle + \sum_{k=0}^{q}{}' \mathcal{E}^{(k)} \sum_{l=0}^{q-k} \langle \phi^{(l)} | \phi^{(p-k-l)} \rangle$$

(B.5)

$$- \sum_{k=0}^{p-q-1} \sum_{l=0}^{q} \langle \phi^{(l)} | \phi^{(p-l-k)} \rangle \mathcal{E}^{(k)} .$$

Eq. (18) then follows from Eq. (B.5) by setting $p = 2n + 1$, $q = n$ and making use of Eq. (17). Similarly Eq. (19) follows from Eq. (B.5) by setting $p = 2n$, $q = n - 1$ and making use of Eq. (17).

In order to compare our treatment with Löwdin's it is necessary that we switch from full to intermediate normalization. To avoid confusion with the results using full normalization, <u>subscripts rather than superscripts will be used to denote order in intermediate normalization</u>. It is also convenient to absorb λ into the definitions of the perturbation terms and to define

$$V = \lambda H^{(1)},$$

$$V' = V - (E - \mathcal{E}_0),$$

$$\mathcal{E}_k' = \begin{cases} \mathcal{E}_0 + \mathcal{E}_1 - E, & k = 1 \\ \\ \mathcal{E}_k, & k \neq 1 \end{cases}.$$

For intermediate normalization

$$\langle \phi_0 | \phi_n \rangle = 0, \quad n \geq 1. \tag{C.1}$$

Multiplying Eq. (11) from the left by $\phi^\dagger$ and integrating gives

$$\mathcal{E}_n = \langle \phi_0 | V | \phi_{n-1} \rangle. \tag{C.2}$$

Eq. (C.1) allows $N^{(m)}$ to be omitted from Eq. (22) so that the perturbation wavefunctions are

$$\phi_{n+1} = R_0 V' \phi_n - \sum_{k=1}^{n} R_0 \phi_{n+1-k} \mathcal{E}_k'.$$

Iterating this equation, it follows that

$$\phi_{n+1} = (R_0 V')^{n+1} \phi_0 - \sum_{\ell=0}^{n-1} \sum_{k=1}^{n-\ell} (R_0 V') R_0 \phi_{n+1-\ell-k} \mathcal{E}_k'. \tag{C.3}$$

From Eqs. (29) and (C.3) (using the fact that $R^{(0)} \phi^{(0)} = 0$),

$$T(E) V \phi_0 = \sum_{n=0}^{2N-1} \phi_{n+1} +$$

$$+ \sum_{n=1}^{2N-1} \sum_{l=0}^{n-1} \sum_{k=1}^{n-l} (R^{(0)} V')^l R^{(0)} \phi_{n+1-l-k} \, \mathcal{E}'_k$$

$$+ O(\lambda^{2N}) .$$

Substitution of this result into Eq. (26) and using Eq. (C.2), and
rearranging the terms gives

$$0 = \begin{vmatrix} \sum_{n=0}^{2N+1} \mathcal{E}_n - E \qquad + \qquad O(\lambda^{2N+2}) \\[2em] + \sum_{n=1}^{2N-1} \sum_{l=1}^{n} \langle \phi_l | \phi_{n+1-l} \rangle \sum_{k=1}^{2N-n} \mathcal{E}'_k \\[2em] + \sum_{n=1}^{2N-2} \mathcal{E}'_n \sum_{p=0}^{2N-n-2} \sum_{t=0}^{p} \sum_{v=0}^{p-t} \langle \phi_{v+1} | R_0 (V' R_0)^t | \phi_{p-t+1-v} \rangle \sum_{k=1}^{2N-n-p-1} \mathcal{E}'_k \end{vmatrix}$$

It is now clear that, in the summations over k, the upper limit may be replaced by $2N+1$ if terms $O(\lambda^{2N+2})$ are neglected. Hence,

$$0 = \left| \begin{array}{c} 1 + \sum_{n=1}^{2N-1} \sum_{\ell=1}^{n} \langle \phi_\ell | \phi_{n+1-\ell} \rangle \\ + \sum_{h=1}^{2N-2} \mathfrak{C}_n'^{\,t} \sum_{p=0}^{2N-h-2} \sum_{t=0}^{p} \sum_{v=0}^{t-t} \langle \phi_{v+1} | R_0 (V'R_0)^t | \phi_{p-t+1-v} \rangle \end{array} \right|$$

$$\times \left| \sum_{n=0}^{2N+1} \mathfrak{C}_n - E \qquad + \qquad O(\lambda^{2N+2}) \right|.$$

Assuming that the first determinant is nonvanishing yields

$$0 = \left| \sum_{n=0}^{2N+1} \mathfrak{C}_n - E \quad + \quad O(\lambda^{2N+2}) \right|. \qquad (C.4)$$

Hence, the energies determined by Eq. (26) are identical with the energies determined by Eq. (C.4) through $O(\lambda^{2N+1})$. Furthermore, it was shown in Chapter Two that the change from intermediate to full normalization also affects the roots of Eq. (15) by $O(\lambda^{2N+2})$ terms. Hence, it follows that the roots of secular equations (26) and (15) differ by $O(\lambda^{2N+2})$ terms.