Partitioning Method and Van Vleck's Perturbation Theory

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(Received October 29, 1974)

Energy expressions to fourth order are given for a degenerate zeroth order state by the use of a partitioning process in relation to Van Vleck's transformation. Double perturbation is discussed as a natural extension of this treatment. The mathematical essence of Dalgarno's interchange theorem is reinterpreted. By using this interpretation, it is demonstrated that there are more than one accessible correlation expressions of the interchange theorem for degenerate zeroth order states. It is also discussed whether or not the difficulty in obtaining the interchange theorem for a degenerate case remains.

§ 1. Introduction

In parallel with the Schrödinger and Heisenberg representations in quantum mechanics, there are two different approaches to perturbation theory. One is the direct Rayleigh-Schrödinger approach, the other is the use of canonical transformation. The latter often called the method of contact transformation by spectroscopists, has been conveniently utilized for treating vibration and rotation Hamiltonians. This method has been reviewed by Primas in operator form and extensively used by Robinson. Unfortunately, it is often difficult to find a proper transformation for the entire spectrum of a given Hamiltonian $H$. In connection with perturbation theory, however, the Van Vleck transformation allows us to concentrate on a particular zeroth order energy and enables us to avoid unnecessary complexity.

The first object of this article is to provide a resolvent form of the operator treatment of Van Vleck's perturbation theory, which gives a simple and compact form of the entire approach in a highly transparent way. The simple and lucid feature of this operator approach is particularly outstanding in the degenerate perturbation theory. The crux of this approach to Van Vleck's perturbation theory lies in the discovery of the recursion formula which allows us to generate wave functions and energies corresponding to any required order of perturbation. Löwdin has given the relations between various approaches to perturbation and his partitioning technique in a series of papers on perturbation theory. His treatment of perturbation has been primarily for nondegenerate cases. The author has treated degeneracies in the Schrödinger perturbation
theory by the use of partitioning technique. This treatment, however, reduces eventually to a one dimensional reference space and is not a convenient basis upon which to establish theorems such as the interchange theorem. The second object of this article is to give a simple mathematical form of the interchange theorem and to show the power of this operator approach in explaining the useful interchange theorem by the use of a simple property of Hermitian operators. This simple mathematical form leads us to prove that there are more than one accessible correlation expressions of the interchange theorem for degenerate zeroth order states.

§ 2. Eigenvalue condition under partitioning of space

Given an Hermitian operation $H$, our problem is to find $\epsilon$ and $\phi$ such that

$$(H - \epsilon)\phi = 0.$$  \hfill (2.1)

We consider a linear space spanned by eigenfunctions of $H$ and partition this into two subspaces $S(O)$ of dimension $g$ and its orthogonal complement $S(P)$, associated with the Hermitian projection operators $O$ and $P$, respectively. $O$ and $P$ have the following properties:

$$\mathbf{1} = O + P, \quad OP = PO = 0,$$

$$O^2 = O = O^+, \quad P^2 = P = P^+,$$  \hfill (2.2)

where $\mathbf{1}$ is the identity operator of the space concerned, and

$$\text{Tr}(O) = g. \quad (g: \text{nonzero integer})$$  \hfill (2.3)

If we are interested in a particular symmetry with respect to $H$, then we need only concentrate on the subspace associated with this symmetry, so that $S(O)$ and $S(P)$ together form this particular subspace.

Denoting, for an operator $A$

$$A_{oo} = OAO, \quad A_{op} = OAP,$$

$$A_{po} = PAO, \quad A_{pp} = PAP,$$  \hfill (2.4)

we apply a unitary transformation $U$ on $H$ so that

$$U^*HU = E = \begin{pmatrix} E_{oo} & 0 \\ 0 & E_{pp} \end{pmatrix}. $$  \hfill (2.5)

Because of the block diagonal form of $E$, (2.1) reduces to

$$(E_{oo} - \epsilon)\phi_o = 0, \quad \phi_o = O\phi$$  \hfill (2.6)

and
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\[(E_{PP} - \epsilon)\phi_{P} = 0, \quad \phi_{P} = P\phi, \quad (2.7)\]

where

\[\phi = U^{+}\phi. \quad (2.8)\]

Thus eigenvalues of \(E_{00}\) and \(E_{PP}\) are those of \(H\), and eigenvectors of \(E\) are completely localized in either \(S(O)\) or \(S(P)\). Thus we have

\[\phi = U\phi_{0} \quad (2.9)\]

or

\[\phi = U\phi_{P}. \quad (2.10)\]

Without losing generality, in the following, we assume that we are interested in eigenvalues associated with \(E_{00}\). In this case \(\phi_{0}\) can be viewed as a reference vector in \(S(O)\) to generate \(\phi\).

Concentrating on \(S(O)\) and using the notation in (2.4) we obtain from (2.5)

\[H_{00}U_{00} + H_{OP}U_{P0} = U_{00}E_{00}, \quad (2.11)\]

\[H_{P0}U_{00} + H_{PP}U_{P0} = U_{P0}E_{00}. \quad (2.12)\]

In the following context of our treatment we assume that \(U_{00}\) is not singular:

\[\det\{U_{00}\} = |U_{00}| \neq 0. \quad (2.13)\]

Multiplying \(U_{00}^{-1} = (U_{00})^{-1}\) from the left-hand side to (2.11), we obtain

\[E_{00} = U_{00}^{-1}H_{00}U_{00} + U_{00}^{-1}H_{OP}U_{P0}. \quad (2.14)\]

Given \(H\) and \(U_{00}, U_{P0}\) can be estimated from (2.12) as a function of \(E_{00}\), then we can utilize (2.14) for estimating \(E_{00}\).

\[\S 3. \quad \text{Perturbational approach}\]

Let us consider a system whose Hamiltonian

\[H = H^{(0)} + V \quad (3.1)\]

is only slightly different from the Hamiltonian \(H^{(0)}\) of some problem which has already been solved. In connection with a perturbational approach to our problem we consider a particular eigenvalue \(E^{(0)}\) of \(H^{(0)}\) and identify \(S(O)\) with the subspace spanned by all the eigenfunctions of \(H^{(0)}\) with eigenvalue \(E^{(0)}_{i}\):

\[O = \sum_{i}^{i_{r}} |\phi_{i}^{(0)}\rangle \langle \phi_{i}^{(0)}| \quad (3.2)\]

with

\[H^{(0)}\phi_{i}^{(0)} = E_{i}^{(0)}\phi_{i}^{(0)}, \quad 1 \leq j \leq i_{r}, \quad (3.3)\]

where \(i_{r}\) is the multiplicity of \(E_{i}^{(0)}\). Then using the relations (2.2) and (3.3)
it follows that
\[ H^{(0)}_0 = 0, \quad H^{(0)}_{P0} = V_{P0}. \] (3.4)

We assume a perturbational expansion and write
\[ E_{oo} = O E_{t}^{(0)} + \sum_{l=1}^{\infty} E_{l}^{(0)}, \] (3.5)
\[ U_{oo} = O + \sum_{l=1}^{\infty} U_{l}^{(0)}, \] (3.6)
\[ U_{P0} = \sum_{l=1}^{\infty} U_{P0}^{(l)}, \] (3.7)

where \( l \) denotes order of perturbation with respect to \( V \) and \( E_{t}^{(0)} \) is a constant in \( S(O) \).

Introducing (3.1) \~ (3.7) into (2.12) and collecting terms according to order of perturbation, we obtain
\[ U_{P0}^{(0)} = R^{(0)} V_{P0}, \] (3.8)

where
\[ R^{(0)} = P [\alpha O + P (E_{t}^{(0)} - H^{(0)}) P]^{-1} P \] (3.9)
with \( \alpha \neq 0 \). We also obtain, for \( n \geq 2 \), the recursion relation
\[ U_{P0}^{(n)} = R^{(0)} [V U_{oo}^{(n-1)} + V U_{P0}^{(n-1)} - \sum_{l=1}^{n-1} U_{P0}^{(l)} E_{l}^{(n-1)}], \] (3.10)

which is essential for the estimation of wavefunction and energy corrections. From the definition (3.9) one can immediately see that \( R^{(0)} \) is Hermitian.

A. Orthonormal condition

The unitary condition of \( U \) is identical with
\[ U_{oo}^{\dagger} U_{oo} + U_{ab}^{\dagger} U_{ab} = O, \] (3.11)
\[ U_{oo}^{\dagger} U_{op} + U_{op}^{\dagger} U_{Pp} = 0, \] (3.12)
\[ U_{Po}^{\dagger} U_{op} + U_{Pp}^{\dagger} U_{Pp} = P, \] (3.13)

where the notation \( U_{ab}^{\dagger} = (U^{\dagger})_{ab} \) is used. Let us assume that the relation (3.11) is satisfied. Then, noting that \( U_{oo} \) is not singular, by a proper adjustment of \( U_{op} \) and \( U_{Pp} \) one can satisfy (3.12) and (3.13). Since eigenvalues of \( H \) associated with \( E_{oo} \) do not depend on \( U_{op} \) and \( U_{Pp} \), as evidenced by (2.11), (2.12) and (2.14), we are allowed to proceed only with (3.11). Only the product \( U_{oo}^{\dagger} U_{oo} \) appears in (3.11), thus, without losing generality, we may ask
\[ U_{oo}^{\dagger} U_{oo} = U_{oo}, \] (3.14)

\( ^{(*)} \alpha O \) in (3.9) is introduced to overcome the singular property of \( (E_{t}^{(0)} - H^{(0)})^{-1} \) noting that \( O(E_{t}^{(0)} - H^{(0)}) = (E_{t}^{(0)} - H^{(0)}) O = 0. \)
Introducing the expansion (3·6) and (3·7) into (3·11), we obtain
\[ U_{00}^{(2)} = 0, \]
\[ U_{00}^{(0)} + U_{00}^{(0)} = 0, \]
\[ \sum_{n=1}^{n} U_{00}^{(n)} U_{00}^{(n-1)} + \sum_{n=1}^{n} U_{00}^{(n)} U_{00}^{(n-1)} = 0, \quad n > 2. \]

The combination of (3·14) and (3·16) yields
\[ U_{00}^{(0)} = 0. \]

B. Estimation of \( E_{00} \)

Starting from (3·15), (3·18) and (3·8), we will get the expansions (3·6) and (3·7) by a repetitive simultaneous use of (3·10) and (3·17). The first few sequences are:

\[ U_{00}^{(2)} = 0, \]
\[ U_{00}^{(0)} = 0, \]
\[ U_{00}^{(2)} = R^{(0)} V O, \]
\[ U_{00}^{(0)} = R^{(0)} [V U_{00}^{(0)} - U_{00}^{(0)} E_{00}^{(0)}], \]
\[ U_{00}^{(0)} = -\frac{1}{2} U_{00}^{(0)} U_{00}^{(0)}, \]
\[ U_{00}^{(0)} = R^{(0)} [V U_{00}^{(0)} + V U_{00}^{(0)} - U_{00}^{(0)} E_{00}^{(0)} - U_{00}^{(0)} E_{00}^{(0)}]. \]

The expansion of \( U_{00}^{(1)} \) is obtained from (3·6). It reads
\[ U_{00}^{(1)} = O - U_{00}^{(0)} - U_{00}^{(0)} - U_{00}^{(0)} U_{00}^{(0)} + \ldots. \]

Substituting the relations (3·19) and (3·20) into (2·14) we obtain the expressions for \( E_{00}^{(0)} \):

\[ E_{00}^{(0)} = O E_{00}^{(0)}, \]
\[ E_{00}^{(0)} = O V O, \]
\[ E_{00}^{(0)} = V_{00} U_{00}^{(0)} = O V R^{(0)} V O, \]
\[ E_{00}^{(0)} = \frac{1}{2} \{ E_{00}^{(0)} + E_{00}^{(0)} \}, \]
\[ E_{00}^{(0)} = \frac{1}{2} \{ E_{00}^{(0)} + E_{00}^{(0)} \}, \]
\[ \ldots. \]

where
\[ E_{00}^{(0)} = U_{00}^{(0)} V U_{00}^{(0)} - U_{00}^{(0)} U_{00}^{(0)} E_{00}^{(0)}, \]
\[ E_{00}^{(0)} = U_{00}^{(0)} V U_{00}^{(0)} - U_{00}^{(0)} U_{00}^{(0)} E_{00}^{(0)} - U_{00}^{(0)} U_{00}^{(0)} E_{00}^{(0)}. \]

For simplicity let us introduce the notation \( \mathcal{H}^{(0)} \):
\[ \mathcal{H}^{(0)} = \sum_{l=0}^{n} E_{l0}^{(0)}, \]
then $\mathcal{H}^{(n)}$ is an approximate operator* of $E_{oo}$ correct to $n$th order.  

C. Eigenfunctions and eigenvalues  

Since $\mathcal{H}^{(n)}$ is Hermitian and its domain, as well as its range, is $S(O)$, we can diagonalize $\mathcal{H}^{(n)}$ by a unitary transformation $G$ in $S(O)$:

$$G = \sum_{k,l} |\psi_{kl}^{(0)}\rangle G_{kl} \langle \phi_{kl}^{(0)}|,$$

$$G + G^* = GG^* = O,$$  

(3.24)  

$$G + \mathcal{H}^{(n)} G = e^{(n)}$$  

(3.25)  

where $e^{(n)}$ is diagonal and gives us $i_{\phi}$ eigenvalues of $H$ associated with the degenerate state $E_{l}^{(0)}$ correct to $n$th order.  

Let $e_{j}^{(n)}$ be the $j$th eigenvalue of the diagonal operator $e^{(n)}$, then we obtain

$$G + \mathcal{H}^{(n)} G \psi_{jl}^{(n)} = e_{j}^{(n)} \psi_{jl}^{(n)}.$$  

(3.26)  

Denoting

$$\phi_{j} = G \psi_{jl}^{(n)} = \sum_{l} G_{jl} \psi_{kl}^{(0)},$$  

(3.27)  

and using (3.24), one can reduce (3.26) to

$$\mathcal{H}^{(n)} \phi_{j} = e_{j}^{(n)} \phi_{j}.$$  

(3.28)  

By the use of the unitary property of $G$, it can be easily seen that $\phi_{j}, 1 \leq j \leq i_{\phi}$, form an orthonormal set spanning $S(O)$.  

In view of the relations (2.6) and (3.28), $\phi_{j}$ corresponds to $\phi_{0}$ of (2.6) for the approximate Hamiltonian $\mathcal{H}^{(n)}$ of $H$. Once $\phi_{j}$ is known, by using the relations (2.9), (3.6), (3.7), (3.21) and (3.28), eigenfunctions $\psi_{f}^{(l)}$ of $H$ correct to $l$th order are given by

$$\psi_{f}^{(l)} = [O + \sum_{k=1}^{l} (U_{j0}^{(k)} + U_{j0}^{(k)})] \phi_{j},$$  

(3.29)  

where

$$l = \frac{n}{2} \text{ if } n \text{ is even},$$

$$l = \frac{(n-1)}{2} \text{ if } n \text{ is odd}. $$  

(3.30)  

The relations (3.29) demonstrate the $(2l+1)$ rule* between an approximate eigenfunction and the approximate eigenvalue attainable from it.

§ 4. Double perturbation and interchange theorem

A. Double perturbation

By using $\mathcal{H}^{(n)}$ defined by (3.23), a double perturbation for a degenerate

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* It is interesting to compare (3.21) with Eq. (91) of Ref. 7) and Eq. (3.12) of Ref. 9).
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The double perturbation is characterized by \( V \) consisting of two physically different terms:

\[
V = V_1 + V_2. \tag{4.1}
\]

The substitution of (4.1) into (3.21) would yield the required result. We are, however, often interested in dealing with orders of perturbation with respect to \( V_1 \) and \( V_2 \) separately for either a physical or mathematical reason. In this case we have to collect terms according to multiplicative order of \( V_1 \) and \( V_2 \). Suppose we are interested in the accuracy of \( m \)th order in \( V_1 \) and \( n \)th order in \( V_2 \), then we have to consider \( \mathcal{H}^{(m+n)} \). For this we expand an operator \( A \)

\[
A = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} A^{(m,n)} \tag{4.2}
\]

so that \( A^{(m,n)} \) represents the terms of \( A \) which are of \( m \)th order in \( V_1 \) and of \( n \)th order in \( V_2 \). Let us define

\[
A^{(l)} = \sum_{n=0}^{l} A^{(l-n,n)}, \tag{4.3}
\]

where \( l \) denotes combined order with respect to \( V_1 \) and \( V_2 \). We shall illustrate the derivation of \( \mathcal{H}^{(m,n)} \) from \( \mathcal{H}^{(m+n)} \) by taking an example for the case \( m=1 \) and \( n=2 \). In order to collect terms to the order \( V_1^1 V_2^2 \) we eliminate the terms associated with \( V_1^2 \) and \( V_1^0 V_2^3 \) from \( \mathcal{H}^{(3)} \). Thus we obtain \( \mathcal{H}^{(1,2)} \) correct to first order in \( V_1 \) and second order in \( V_2 \):

\[
\mathcal{H}^{(1,2)} = \sum_{n=0}^{2} \sum_{n=0}^{2} E_{00}^{(m,n)}, \tag{4.4}
\]

where

\[
E_{00}^{(0,0)} = O E_1^{(0)},
\]
\[
E_{00}^{(0,1)} = O V_2 O,
\]
\[
E_{00}^{(1,0)} = O V_1 R^{(0)} V_2 O,
\]
\[
E_{00}^{(1,1)} = O V_1 R^{(0)} V_2 O + \text{Hermitian Conjugate},
\]
\[
E_{00}^{(1,2)} = O V_2 R^{(0)} V_1 R^{(0)} V_2 O + \{O V_1 R^{(0)} V_2 R^{(0)} V_2 O + \text{Hermitian Conjugate}\}
\]
\[
- \frac{1}{2} \{O V_1 R^{(0)} R^{(0)} V_2 E_{00}^{(0,1)} + O V_2 R^{(0)} R^{(0)} V_1 E_{00}^{(0,1)}
\]
\[
+ O V_2 R^{(0)} R^{(0)} V_1 E_{00}^{(0,1)} + \text{Hermitian Conjugate}\}. \tag{4.5}
\]

It is also apparent from the relations (3.19), (4.2) and (4.3) that

\[
U_{00}^{(0,0)} = O,
\]
\[
U_{00}^{(0,1)} = U_{00}^{(1,0)} = 0,
\]
\[
U_{20}^{(0,1)} = R^{(0)} V_2 O,
\]
\[
U_{20}^{(1,1)} = 0.
\]
The $\phi_j$ obtained through the diagonalization of $\mathcal{H}^{(1,2)}$ should give the corresponding approximate eigenfunction $\phi_j^{(0)}$

$$\phi_j^{(0)} = [O + U_{P_0}^{(0)}] \phi_j.$$  

Any multiple perturbation greater than double can be treated in a manner similar to that in which we have done for the double perturbation.

B. Interchange theorem

The interchange theorem established by Dalgarno has been conveniently used in perturbation theory. The mathematical essence of this theorem is the relation

$$A_{ij} = \langle A^+ F_i \mid F_j \rangle = \langle F_i \mid A \mid F_j \rangle = \langle F_i \mid A F_j \rangle,$$

where $A$ is an operator and $F_i$, $F_j$ are quadratically integrable functions in the domain $A$. As far as one is interested in $A_{ij}$ itself, one has a choice of evaluating either $AF_j$ or $A^+ F_i$.

Suppose $V_1$ is not a simple operator to handle in the sense that the estimation of $R^{(0)}V_1O$ in (4.5) is difficult, whereas $V_2$ is simple so that the estimation of $R^{(0)}V_2R^{(0)}V_2O$ and $R^{(0)}R^{(0)}V_2O$ can be accomplished without difficulty. Then using the relations (3·2) and (4·8) one can write typical matrix elements of $E_{P_0}^{(0)}$ and $E_{P_0}^{(2)}$ as

$$\langle \psi_{ij}^{(0)} \mid E_{P_0}^{(0)} \mid \psi_{kl}^{(0)} \rangle = \langle \psi_j^{(0)} \mid V_1^{(0)} R^{(0)} V_{P_0}^{(0)} \psi_{kl}^{(0)} \rangle + \text{Complex Conjugate},$$

$$\langle \psi_{ij}^{(0)} \mid E_{P_0}^{(2)} \mid \psi_{kl}^{(0)} \rangle = \langle R^{(0)} V_{P_0}^{(0)} \psi_{ij}^{(0)} \mid V_1^{(0)} R^{(0)} V_{P_0}^{(0)} \psi_{kl}^{(0)} \rangle$$

$$+ \{ \langle \psi_j^{(0)} \mid V_1^{(0)} R^{(0)} V_2^{(0)} V_{P_0}^{(0)} \psi_{kl}^{(0)} \rangle - \frac{1}{2} \langle \psi_j^{(0)} \mid V_1^{(0)} R^{(0)} V_2^{(0)} V_{P_0}^{(0)} \psi_{kl}^{(0)} \rangle \}$$

$$- \frac{1}{2} \langle R^{(0)} V_2^{(0)} V_{P_0}^{(0)} \mid V_1^{(0)} R^{(0)} V_2^{(0)} V_{P_0}^{(0)} \psi_{ij}^{(0)} \rangle$$

$$+ \text{Complex Conjugate}$$

which are accessible correlation expressions.

§ 5. Discussion

An operator formalism has the advantage of being compact in its notation
without referring to each function concerned. Unlike a previous work this treatment does not depend on the manner in which the degeneracy is resolved. The partitioning of a space into two, one called a reference space and the other a complementary space, is particularly convenient for a perturbation theory because the higher order corrections to energies as well as to wave functions are generated from the information about a reference space. It is a point worthy of emphasis that Dalgarno's interchange theorem even for a degenerate level of $H$ is exclusively due to the relation (4·8) and does not depend at all on the choice of $U_{00}$. Our expression (4·5) for $\mathcal{H}^{(1,1)}$ is identical with that of Kirtman's except for some terms associated with $E_{00}$ [16]. This difference is due to our different choice of $U_{00}$. $U_{00}$ is arbitrary as long as (3·11) is satisfied. By way of an example it is shown in the Appendix that if we choose $U_{00}$ the same, Kirtman's expression for $\mathcal{H}^{(1,1)}$ becomes the same as ours. The two different forms of $\mathcal{H}^{(1,1)}$, however, should yield eigenvalues which are the same at least up to first order in $V_1$ and second order in $V_2$ since they result from equivalent operators related by a unitary transformation.

Hirschfelder et al. remarked that there is a difficulty in establishing the interchange theorem in a degenerate system of $H$. In discussing this apparent contradiction one has to distinguish expectation values of two different types of operators:

(i) an operator which is a part of the total Hamiltonian,
(ii) an operator which is not a part of the total Hamiltonian.

For degenerate case one can apply the double perturbation theory to the first type of operator only. The energy corrections $E^{(3,1)}_{00}$ in (4·5) and Kirtman's $(E^*)_{a\theta}$ are of the first type and require only the knowledge of $\psi^{(0,1)}_0$ in (4·7) in accordance with the $(2I+1)$ rule between an eigenfunction and its corresponding energy. Thus the difficulty met by Hirschfelder et al. is not encountered by the first type of operator.

For the second type of operator one has to know $O_0^{(3,1)}$ with which Hirschfelder et al. found a difficulty in their Eq. (IV·52). Even in our scheme one cannot estimate the correction corresponding to $O_0^{(3,1)}$ without considering $E_{00}^{(3,1)}$. This is an intrinsic property of the perturbation theory and does not depend upon the formalism we choose. In this sense their claim remains true. For a nondegenerate case it can be easily seen that it is not necessary to distinguish between these two types of operator as far as the first order correction is concerned.

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* Note that this is contrary to the statement made by Kirtman in Ref. 12) that there should be a unique choice of $U_{00}$ which leads to the interchange theorem.

** Note that in our formalism $O_0^{(3,1)}$ and $O_0^{(3,2)}$ are zero according to the second relation of (4·6). These corrections, however, are absorbed in $\psi$ of (4·7) when we diagonalize $\mathcal{H}^{(1,1)}$. 
**Acknowledgement**

The author wishes to thank Professor Walter R. Thorson for encouragement and support of this work through a Research Grant from the National Research Council of Canada. He also would like to thank Professor Fraser W. Birss, Dr. S. Katsuki and Mr. S. Barton for many helpful comments and discussions.

**Appendix**

In Kirtman's notation our choice of \(U_{10}^{(2)}\), characterized by \((3·14)\) and \((4·6)\), becomes

\[
\langle X_{1a}^0 | \phi_\beta^0 \rangle = \langle \phi_\alpha^0 | X_{1\beta}^0 \rangle = - \frac{1}{2} \{ \langle X_{1a}^0 | X_{1\beta}^0 \rangle + \langle X_{0a}^0 | X_{1\beta}^0 \rangle \}. \tag{A·1}
\]

If \((A·1)\) is used in place of his choice\(^{22}\)

\[
\langle X_{1a}^0 | \phi_\beta^0 \rangle = - \langle X_{0a}^0 | X_{1\beta}^0 \rangle, \tag{A·2}
\]

his equation \((22)\) becomes

\[
(E_2)^a_b = \langle \phi_\alpha^0 | V_0 | X_{0b}^0 \rangle + \langle X_{0a}^0 | V_1^0 | \phi_\beta^0 \rangle + \langle X_{1a}^0 | V_0^0 | X_{1b}^0 \rangle + \frac{1}{2} \sum_r \langle X_{1a}^0 | X_{1r}^0 \rangle \langle \phi_\alpha^0 | V_1^0 | \phi_\beta^0 \rangle - \frac{1}{2} \sum_r \langle X_{1a}^0 | X_{1r}^0 \rangle \langle \phi_\alpha^0 | V_1^0 | \phi_\beta^0 \rangle + \frac{1}{2} \sum_r \langle \phi_\alpha^0 | V_1^0 | \phi_\beta^0 \rangle \langle X_{1r}^0 | X_{1b}^0 \rangle - \frac{1}{2} \sum_r \langle \phi_\alpha^0 | V_1^0 | \phi_\beta^0 \rangle \langle X_{1r}^0 | X_{1b}^0 \rangle. \tag{A·3}
\]

In terms of our notations \((4·1)\) and \((4·6)\), \((A·3)\) is equivalent to

\[
O(E_2)^a_b = [(O V_1 (U_{10}^{(0)} + U_{10}^{(1)}) + \frac{1}{2}(U_{00}^{(2),0} U_{00}^{(0),0})
- U_{00}^{(0),0} V_0 O) + \text{Hermitian Conjugate}]

+ U_{00}^{(0),0} V_0 U_{00}^{(0),0}. \tag{A·4}
\]

In view of the relations \((4·6)\), \(O(E_2)^a_b\) in \((A·4)\) is identical with \(E_{10}^{(2)}\) in \((4·5)\).

**References**

1) E. Schrödinger, Ann. der Phys. (4), 80 (1928), 437.
   (pp. 284–296).