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NOTE ON A PERTURBATION THEORY FOR INTERMOLECULAR INTERACTIONS IN THE WAVE OPERATOR FORMALISM

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Received 9 October 1967

It is proved that the wave function and energy and their perturbation expansions, given by a wave operator perturbation theory for intermolecular interactions [4], satisfy the conditions necessary to make this theory consistent.

That still a lively interest exists in perturbation theory for intermolecular interactions is shown by some recent papers [1-3], appearing almost simultaneously with this author's most recent publication [4]. It is also evident from the discussions on this subject held at Prof. Hirschfelder's group at the Theoretical Chemistry Institute of the University of Wisconsin this summer (see ref. [3]). On the wave operator theory, proposed by the author, some questions arose, that were not answered in ref. [4]. For this reason we will, in the present note, prove some more properties of this theory. The meaning of the symbols, their definitions and the numbering of equations are the same as those of ref. [4].

1) The wave function \( \psi \) and the energy \( E \), given by the equations

\[
\psi = \psi_0 + TH\psi_0 ;
\]

\[
E = \frac{\langle \psi_0 | H + HTH | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle},
\]  

(12) with \( T \) defined as

\[
T = P(\alpha (1-A) + \beta O + P(E-H)P)^{-1}P,
\]  

(8) or, alternatively, defined by the equations

\[
AT = TA = T ;
\]  

(9)

\[
OT = TO = 0 ;
\]  

(10)

\[
P(E-H)T = P ,
\]  

(11)

satisfy the Schrödinger equation \( H\psi = E\psi \).

This is shown as follows:

\[
(E-H)\psi = (E-H)A\psi - A(E-H)\psi = O(E-H)\psi + P(E-H)\psi .
\]

Treat the two parts separately.

In the first term, substitute \( \psi \), use (5) and (10) of ref. [4] and substitute the definition of \( O \):

\[
O(E-H)\psi = O(E-H)\psi_0 + O(E-H)TH\psi_0 =
\]

\[
= E\psi_0 - O\psi_0 - OHTH\psi_0 =
\]

\[
= \psi_0 \left[ E - \frac{\langle \psi_0 | H + HTH | \psi_0 \rangle}{\langle \psi_0 | \psi_0 \rangle} \right].
\]

The expression for \( E \) causes this term to vanish identically. In the second part, (5) and (11) are used:

\[
P(E-H)\psi = P(E-H)\psi_0 + P(E-H)TH\psi_0 =
\]

\[
= - PH\psi_0 + PH\psi_0 =
\]

\[
= 0
\]

This completes the proof.

2) The operator \( T \), given by its expansion

\[
T = \sum_{n=0}^{\infty} (PR_0U)^nPR_0P ,
\]

(19) satisfies (9), (10) and (11).

For (9) and (10) this follows immediately from (5). To prove (11) we substitute the equality

\[
(PR_0U)^nPR_0P = PR_0P(U^\dagger R_0P)^n ,
\]

(a) which is proved in the Appendix of ref. [4] directly from the definitions of \( P, R_0 \) and \( U \). Consequently, \( T \) can be written as

\[
T = \sum_{n=0}^{\infty} PR_0P(U^\dagger R_0P)^n .
\]

(19a)

Operating with \( P(E-H) \) on \( PR_0P \) yields, using \( HA = AH \) and \( PA = P \):
\[ P(E-H)PR_0P = \]
\[ = P(E-H)AR_0P - P(E-H)A|\phi_0\rangle A|\phi_0\rangle R_0P = \]
\[ = P(E-H)R_0P - P(E-H)|\phi_0\rangle R_0P. \]

Substitute \( E-H = E_0-H_0-V \) and use \( (E_0-H_0)\phi_0 = 0 \) to obtain:
\[ P(E-H)PR_0P = \]
\[ = P(E_0-H_0)R_0P - PV_0R_0P + P V_0|\phi_0\rangle R_0P. \]

As \( P(E_0-H_0)R_0P = P \) and the other two terms on the right-hand side just contain \( U \), this becomes:
\[ P(E-H)PR_0P = P - PU^\dagger R_0P. \] (b)

To prove (11) starting from (19a), one uses the equality (b):
\[ P(E-H)T = \sum_{n=0}^{\infty} P(E-H)PR_0P(U^\dagger R_0P)^n = \]
\[ = \sum_{n=0}^{\infty} P(U^\dagger R_0P)^n - \sum_{n=0}^{\infty} P(U^\dagger R_0P)^{n+1} = \]
\[ = P. \]

3) In a similar way it is shown that the different-order perturbation equations, i.e. the equations satisfied by \( \psi^{(n)} \) and \( \epsilon^{(n)} \) given by (20), add up to the Schrödinger equation:
\[ (E-H)\psi^{(n)} = (E-H)A\psi^{(n)} - A(E-H)\psi^{(n)} = \]
\[ = O(E-H)\psi^{(n)} + P(E-H)\psi^{(n)}. \]

The two terms are treated separately. The first term gives, for \( n = 1 \):
\[ O(E-H)\psi^{(1)} = O(E-H)(PR_0U)^{n-1}PR_0PV_0\phi_0 = \]
\[ = -OH(PR_0U)^{n-1}PR_0PV_0\phi_0, \]

since \( OP = 0 \). Substitute the definition of \( O \), use \( AH = HA \), write \( H = H_0 + V \) and remark that the term with \( H_0 \) vanishes:
\[ O(E-H)\psi^{(n)} = -A|\phi_0\rangle A|\phi_0\rangle (PR_0U)^{n-1}PR_0PV_0\phi_0 = \]
\[ = -A\phi_0 V(PR_0U)^{n-1}PR_0PV|\phi_0\rangle \]
\[ = -\epsilon^{(n+1)}A\phi_0. \]

For \( n = 0 \):
\[ O(E-H)\psi_0 = [E - E_0 - \epsilon^{(1)}]A\phi_0. \]

Adding the equations for \( n = 0, \ldots, \infty \) yields:
\[ O(E-H)\psi = [E - E_0 - \epsilon^{(1)} - \epsilon^{(2)} - \ldots]A\phi_0 = 0. \]

The second term gives, for \( n \neq 1 \),
\[ P(E-H)\psi^{(n)} = P(E-H)(PR_0U)^{n-1}PR_0PV_0\phi_0, \]
which becomes, upon using (a) and (b):
\[ P(E-H)\psi^{(n)} = P(E-H)PR_0P(U^\dagger R_0P)^n - V_0\phi_0 = \]
\[ = P(U^\dagger R_0P)^n - V_0\phi_0 - P(U^\dagger R_0P)^nV_0\phi_0. \]

For \( n = 0 \),
\[ P(E-H)\psi_0 = -PV_0\phi_0. \]

Adding the equations for \( n = 0, \ldots, \infty \) yields:
\[ P(E-H)\psi = PV_0\phi_0 - PV_0\phi_0 = 0. \]

If these results are added again, the Schrödinger equation is obtained:
\[ 0 = O(E-H)\psi + P(E-H)\psi = A(E-H)\psi = \]
\[ = (E-H)A\psi = (E-H)\psi. \]

With the completion of these proofs the theory becomes entirely consistent; the wave function and energy resulting from it do indeed satisfy the Schrödinger equation; their expansions satisfy perturbation equations that add up to the Schrödinger equation.

ACKNOWLEDGEMENT

The author likes to express his gratitude to Professor L. Jansen for many valuable discussions and to Professor S. T. Epstein for a very stimulating correspondence.

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COMMENT ON VAN DER AVOIRD’S WAVE OPERATOR FORMALISM

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Received 23 October 1967

In regard to the papers on the perturbation theory of forces by Van der Avoird [1,2], it is worthwhile to point out that if the matrix $PR_0P$, defined \* by eqs. 5 and 14, does not have an inverse in the space $P$, then the proposed solution will not satisfy the original Schrödinger equation. This follows since the set of equations

$$PR_0P(E-H)PT = PR_0P$$

will not have a unique solution, and the inverse of $PR_0P(E-H)P$, expressed as an expansion in eq. 19, will not exist.

For the case when $E_0$ is the ground state of $H_0$, the $R_0$ is negative definite so that $PR_0P$ has an inverse and there is no difficulty \**. For excited states $R_0$ is no longer a definite operator so that the inverse of $PR_0P$ might not exist. Although a slight change in the definition of $H_0$ would correct for this, convergence problems due to this difficulty may occur in the application of the theory to excited states.

REFERENCES


\* Here the equation numbers and notation are those of ref. [1].

\** Preliminary calculations on the ground states of some simple potentials have shown that the theory gives reasonable results.