Perturbation Theory for Intermolecular Interactions in the Wave-Operator Formalism

Ad van der Avoird

Battelle Institute, Advanced Studies Center, Geneva, Switzerland

(Received 6 July 1967)

A Schrödinger-type perturbation theory for intermolecular or interatomic interactions is developed in the wave-operator formalism. To include all exchange effects, wavefunctions are used whose symmetry with respect to permutations of both electronic and nuclear coordinates can be prescribed arbitrarily. This necessitates a modification of the usual perturbation theory. The interaction energy is obtained as a series in ascending powers of the interaction operator. It is proved that every term in this series is real and that the terms of even order are negative definite for perturbation of the ground state. It is verified that up to and including third order the results of this theory, if they are restricted to electron exchange only, agree exactly with those of the Eisenschitz–London theory.

INTRODUCTION

When interactions between molecules or atoms are calculated by perturbation theory for distances where exchange is important, some complications are added to the usual perturbation-theory procedure. The unperturbed Hamiltonian $H_0$ describing the system of non-interacting molecules or atoms is a sum of molecular or atomic operators; its eigenfunctions are ordered products of molecular or atomic wavefunctions. A wavefunction describing the interacting system must be antisymmetric with respect to permutations of the electronic coordinates. It must also be antisymmetric or symmetric with respect to permutations of identical nuclei. Moreover, it may have additional symmetry properties in the spin and space coordinates (e.g., be an eigenfunction of $S^2$ and $S_z$ and have a certain symmetry in configuration space). A perturbation theory that takes into account all exchange effects should operate with functions of the proper symmetry. The usual procedure of expanding the corrections to the unperturbed function in eigenfunctions of $H_0$ cannot be applied directly, since these functions do not have the desired symmetry. A possible remedy is first to project the set of eigenfunctions of $H_0$ into the space of functions with the proper symmetry. Although each function belonging to this space can be expanded as a linear combination of projected eigenfunctions, one encounters the difficulty that these projected eigenfunctions are not eigenfunctions of $H_0$, that they are not orthogonal, and are even linearly dependent.

The first to find a solution to these problems were Eisenschitz and London in 1930. Their theory has been formulated more compactly and generally by the present author. Amos and Musher claim to obtain a combination of projected eigenfunctions, one encounters functions belonging to this space can be expanded as a linear combination of projected eigenfunctions. A perturbation theory that takes into account all exchange effects should operate with functions of the proper symmetry. The usual procedure of expanding the corrections to the unperturbed function in eigenfunctions of $H_0$ cannot be applied directly, since these functions do not have the desired symmetry. A possible remedy is first to project the set of eigenfunctions of $H_0$ into the space of functions with the proper symmetry. Although each function belonging to this space can be expanded as a linear combination of projected eigenfunctions, one encounters the difficulty that these projected eigenfunctions are not eigenfunctions of $H_0$, that they are not orthogonal, and are even linearly dependent.

The first to find a solution to these problems were Eisenschitz and London in 1930. Their theory has been formulated more compactly and generally by the present author. Amos and Musher claim to obtain a combination of projected eigenfunctions, one encounters the linear dependence of the symmetry-projected eigenfunctions of $H_0$ are not considered. With the Feenberg procedure, which avoids some of the difficulties encountered in perturbation theory, very complicated expressions are obtained that cannot be separated into independent contributions. In Ref. 6 the interaction energy is expanded in powers of the perturbation operator and of the overlap, terms higher than second order in both being neglected. One of the authors has remarked in a subsequent paper that the development in powers of the overlap is not rigorous. The perturbation theories described in Refs. 4 and 7 are developed in the wave-operator formalism. Although both assume that the total correction to the symmetrized unperturbed function has the proper symmetry, not all the perturbed functions are symmetric. Therefore, it is possible that in finite orders of perturbation not all exchange contributions to the interaction energy are obtained.

In the present paper a Schrödinger-type perturbation theory is developed in the wave-operator formalism with wavefunctions of arbitrary symmetry. All terms are retained, the perturbed functions have the proper symmetry, and the interaction energy is obtained as a sum of contributions of ascending order in the perturbation. We have found that the energy expressions up to and including third order agree exactly with the results of the Eisenschitz–London perturbation theory, if we restrict our results to electron exchange only.

5W. J. Carr, Phys. Rev. 131, 1947 (1963); and (private communication).

3649
PERTURBATION THEORY

We use the framework of the perturbation theory described by Brueckner and Löwdin. Define a projection operator $A$ that projects the total $N$-particle function space $\{\phi\}$ onto the subspace of functions with all desired symmetry properties $\{\psi = A\phi\}$. $A$ is idempotent, $A^2 = A$, and self-adjoint $A^* = A$. Since the Hamiltonian describing a system is invariant under operations of the symmetry group of the system, $H$ commutes with $A : AH = HA$. If $H$ is separated into the intramolecular interactions and the intermolecular interactions, $H = H_0 + V$, both parts correspond to a certain ordering of electrons and nuclei in molecules and do not, therefore, commute with $A$. Let us consider the influence of the perturbation $V$ on a certain unperturbed state described by $\phi_0$, an eigenfunction of $H_0$ with eigenvalue $E_0$. The symmetry projection of $\phi_0$ is denoted by $\psi_0 = A\phi_0$. Note that $\psi_0$ is not an eigenfunction of $H_0$. Except for exchange degeneracy, the unperturbed level is nondegenerate.

The wave operator $W$ is defined by writing the solution of the Schrödinger equation, $H\psi = E\psi$, as

$$\psi = W\psi_0.$$  

(1)

Assume that $W$ satisfies the conditions

$$WA = AW$$  

(2)

(in order to secure that $\psi$ has the proper symmetry: $\psi = W\psi_0 = WA\phi_0 = AW\phi_0$)

and

$$\langle \psi_0 | \psi \rangle = \langle \psi_0 | W\psi_0 \rangle = \langle \psi_0 | \psi_0 \rangle.$$  

(3)

This implies that $\psi - \psi_0$ is orthogonal to $\psi_0$. (If $\phi_0$ is normalized to unity and $A$ is idempotent, then $\psi_0$ is not normalized.)

The energy $E$ is obtained as

$$E = \langle \psi_0 | H\psi \rangle / \langle \psi_0 | \psi_0 \rangle = \langle \psi_0 | HW\psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle.$$  

(4)

To derive the expression for $W$ we define another projection operator

$$O = |\psi_0\rangle\langle \psi_0 | \psi_0 \rangle = A |\phi_0\rangle\langle \phi_0 | \phi_0 \rangle A / |\phi_0\rangle\langle \phi_0 | A \phi_0 \rangle$$

and its complement in $|\psi\rangle$

$$P = A - O.$$  

These operators have the properties

$$O^2 = O, \quad O^* = O, \quad AO = OA = O, \quad O\psi_0 = \psi_0;$$

$$P^2 = P, \quad P^* = P, \quad AP = PA = P, \quad P\psi_0 = 0;$$

$$OP = PO = 0.$$  

(5)

Because of the normalization condition (3) the projections of $\psi$ are

$$O\psi = \psi_0,$$

$$P\psi = A\psi - O\psi = \psi - \psi_0.$$  

(6)

A third condition for $W$ can be derived since $\psi$ is a solution to the Schrödinger equation $H\psi = E\psi$. It follows that

$$P(E-H)\psi = 0,$$

and substituting $\psi = A\psi = (O + P)\psi$ into this equation and using $PO = 0$,

$$P(E-H)P\psi = PH0\psi,$$

$$P(E-H)PW\psi_0 = PH\psi_0.$$  

(7)

It is shown easily that all the imposed conditions for $W$ [Eqs. (2), (3), and (7)], are satisfied by

$$W = A + TH,$$

with

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

(8)

Besides $\beta O$, we have to add $\alpha(1-A)$ ($\alpha$ and $\beta$ are nonzero real scalars) to the operator $P(E-H)P$ in order to define the inverse of this operator, not only in $|\psi\rangle$, but in the total function space $|\phi\rangle$. (Recall that $O + P = A$ and not $O + P = 1$ as usual.)

$T$ does not depend on $\alpha$ and $\beta$: $\partial T / \partial \alpha = 0$, $\partial T / \partial \beta = 0$ and has the following properties:

$$(1-A) T = T (1-A) = 0$$

or written differently

$$AT = TA = T.$$  

(9)

Further,

$$OT = TO = 0,$$

and

$$P(E-H)T = P.$$  

(11)

Introducing the result for $W$ into the equations (1) and (4) yields

$$\psi = \psi_0 + TH\psi_0,$$

$$E = \langle \psi_0 | H + HTH | \psi_0 \rangle / \langle \psi_0 | \psi_0 \rangle,$$

or after substituting successively $\psi_0 = A\phi_0$, $HA = AH$, $H = H_0 + V$, and $H\phi_0 = E\phi_0$, and using (5),

$$\psi = A\phi_0 + TV\phi_0,$$

$$E = E_0 + \langle A\phi_0 | AV\phi_0 \rangle / \langle A\phi_0 | A\phi_0 \rangle + \langle AV\phi_0 | T | AV\phi_0 \rangle / \langle A\phi_0 | A\phi_0 \rangle.$$  

(12)

Herewith the formula for the first-order energy is already obtained:

$$\epsilon_1 = \langle A\phi_0 | AV\phi_0 \rangle / \langle A\phi_0 | A\phi_0 \rangle.$$  

(13)

To find the higher-order expressions, $T$ is expanded in powers of $V$. We choose the expansion that yields the Schrödinger-type perturbation formulas. Since $H_0$ does not commute with $P$ we have to deviate from the usual procedure, which introduces the operator $R_0$.
We define

$$R_0 = \sum_{k \neq 0} | \phi_k \rangle \langle \phi_k | / (E_0 - E_k), \quad (14)$$

where $\phi_k$ are the eigenfunctions and $E_k$ the eigenvalues of the operator $H_0$. $R_0$ is a nonpositive operator if $E_0$ is the ground-state energy; it is defined in the whole $|\phi\rangle$, and consequently in $|\psi\rangle$. $H_0$ is Hermitian; its eigenfunctions form a complete, orthonormal set in $|\phi\rangle$:

$$\sum_k | \phi_k \rangle \langle \phi_k | = I \text{ [the identity operator in } |\phi\rangle]. \quad (15)$$

We write

$$P(E-H) = A(E-H)$$

and the result, substituted into (11) yields, after using (9),

$$(E_0 - H_0)T - UT = P. \quad (17)$$

Multiplying this equation to the left by $PR_0$, $R_0$ given by (14), we obtain

$$T = PR_0P + PR_0UT. \quad (18)$$

We have used the fact that

$$PR_0(E_0 - H_0)T = P \sum_{k \neq 0} [ | \phi_k \rangle \langle \phi_k | (E_0 - H_0) / (E_0 - E_k) ] T$$

$$= P \sum_{k \neq 0} | \phi_k \rangle \langle \phi_k | T$$

$$= P(I - | \phi_0 \rangle \langle \phi_0 | ) T$$

$$= PT$$

$$= T.$$

With the aid of Relation (18) $T$ is expanded in an infinite series:

$$T = \sum_{n=0}^{\infty} (PR_0U)^n PR_0P. \quad (19)$$

We do not derive the criteria for this series to be convergent; we just assume that they are fulfilled. Formula (19) yields immediately the expressions for the perturbed energies and wavefunctions $|\psi\rangle$: 

$$\langle \psi | = (PR_0U)^n - 1 PR_0P V \phi_0$$

$$\epsilon^{(n+1)} = \frac{\langle AV \phi_0 | (PR_0U)^n - 1 PR_0P | AV \phi_0 \rangle}{\langle A \phi_0 | A \phi_0 \rangle}. \quad (20)$$

We use $\phi_k$ and $\phi_1$ eigenfunctions of $H_0$ with the real eigenvalues $E_k$ and $E_1$. We have used the relations $AH = HA$, substituted $AH = H_0 + V$, and define $V' = V - (E_0 - H_0)$, and resolves this operator into its spectrum. We define

$$R_0 = \sum_{k \neq 0} | \phi_k \rangle \langle \phi_k | / (E_0 - E_k),$$

where $\phi_k$ are the eigenfunctions and $E_k$ the eigenvalues of the operator $H_0$. $R_0$ is a nonpositive operator if $E_0$ is the ground-state energy; it is defined in the whole $|\phi\rangle$, and consequently in $|\psi\rangle$. $H_0$ is Hermitian; its eigenfunctions form a complete, orthonormal set in $|\phi\rangle$:

$$\sum_k | \phi_k \rangle \langle \phi_k | = I \text{ [the identity operator in } |\phi\rangle].$$

We write

$$P(E-H) = A(E-H)$$

and the result, substituted into (11) yields, after using (9),

$$(E_0 - H_0)T - UT = P. \quad (17)$$

Multiplying this equation to the left by $PR_0$, $R_0$ given by (14), we obtain

$$T = PR_0P + PR_0UT. \quad (18)$$

We have used the fact that

$$PR_0(E_0 - H_0)T = P \sum_{k \neq 0} [ | \phi_k \rangle \langle \phi_k | (E_0 - H_0) / (E_0 - E_k) ] T$$

$$= P \sum_{k \neq 0} | \phi_k \rangle \langle \phi_k | T$$

$$= P(I - | \phi_0 \rangle \langle \phi_0 | ) T$$

$$= PT$$

$$= T.$$

With the aid of Relation (18) $T$ is expanded in an infinite series:

$$T = \sum_{n=0}^{\infty} (PR_0U)^n PR_0P. \quad (19)$$

We do not derive the criteria for this series to be convergent; we just assume that they are fulfilled. Formula (19) yields immediately the expressions for the perturbed energies and wavefunctions $|\psi\rangle$: 

$$\langle \psi | = (PR_0U)^n - 1 PR_0P V \phi_0$$

$$\epsilon^{(n+1)} = \frac{\langle AV \phi_0 | (PR_0U)^n - 1 PR_0P | AV \phi_0 \rangle}{\langle A \phi_0 | A \phi_0 \rangle}. \quad (20)$$

Remark that the perturbed functions have the proper symmetry.

The formula for the second-order energy is

$$\epsilon_2 = \langle AV \phi_0 | PR_0P | AV \phi_0 \rangle / \langle A \phi_0 | A \phi_0 \rangle$$

$$= \langle A \phi_0 | A \phi_0 \rangle^{-1}$$

$$\times \sum_k \langle A(V - E_1) \phi_0 | A \phi_k \rangle \langle A \phi_k | A(V - E_1) \phi_0 \rangle / (E_0 - E_k). \quad (21)$$

The expressions for higher orders can also be obtained easily, but are not written here explicitly.

**GENERAL PROPERTIES OF THIS PERTURBATION THEORY, COMPARISON TO OTHER THEORIES**

All energy expressions are real quantities. In second order this is seen immediately. In all other orders we make use of the following equation:

$$\langle AV \phi_k | A \phi_1 \rangle = \langle AH \phi_1 | A \phi_1 \rangle - \langle AH \phi_1 | A \phi_1 \rangle$$

$$= \langle A \phi_k | AH \phi_1 \rangle - E_k \langle A \phi_k | A \phi_1 \rangle$$

$$= \langle A \phi_k | AV \phi_1 \rangle + (E_1 - E_k) \langle A \phi_k | A \phi_1 \rangle. \quad (22)$$

$$(\phi_k \text{ and } \phi_1 \text{ are eigenfunctions of } H_0 \text{ with the real eigenvalues } E_k \text{ and } E_1.)$$

We have used the relations $AH = HA$ and $H^t = H$.

In first order the proof is trivial. In third and higher orders we prove that

$$PR_0UPR_0P = PR_0PU^t R_0P. \quad (23)$$

From (23) it follows that $(PR_0U)^n PR_0P$ is self-adjoint for all $n \geq 0$ (for the detailed proof, see Appendix). By consequence all energy expressions are real. Moreover it follows from (23) that all energies of even order are negative definite if $E_0$ is the ground-state energy of the unperturbed system. (See also Appendix.)

Also using Eq. (22) we have found that the energy expressions up to and including third order are in exact agreement with the Eisenschitz–London results, if $A$ consists of electron exchange operators only. This may be valid for higher orders too, but we did not verify it.

The first-order energy in our theory corresponds to those theories which also yield an explicit second order expression. Our second-order energy contains some extra exchange terms compared to those theories which also yield an explicit second order expression. If the intermolecular overlap is neglected, our formula changes into the formula of Salem.
ACKNOWLEDGMENTS

Stimulating discussions with Professor L. Jansen, Dr. M. H. Boon, Dr. R. Ritter, and Dr. F. Hofelich are gratefully acknowledged. We would also like to express our thanks to Dr. G. Shaw and Professor J. I. Musher for sending their manuscripts prior to publication.

APPENDIX

The relation (23) can be proved in two different ways. The first proof starts with Eq. (18):

\[ T = P R_0 P + P R_0 U T. \]  \( \text{(A1)} \)

Since \( P, T, \) and \( R_0 \) are self-adjoint, we obtain as the adjoint of this equation

\[ T = P R_0 P + T U^\dagger R_0 P. \]  \( \text{(A2)} \)

Substituting (A2) into (A1) yields

\[ T = P R_0 P + P R_0 U P R_0 P + P R_0 U T U^\dagger R_0 P; \]  \( \text{(A3)} \)

substituting (A1) into (A2),

\[ T = P R_0 P + P R_0 P U R_0 P + P R_0 U T U^\dagger R_0 P. \]  \( \text{(A4)} \)

Subtracting (A3) and (A4) gives the desired result

\[ P R_0 U P R_0 P = P R_0 P U^\dagger R_0 P. \]

The second way to prove (23) by substituting the definitions of \( P, R_0, \) and \( U \) is very illustrative, since it shows also the way in which the results of this perturbation theory can be compared to the Eisenschitz–London expressions. We first remark that \( V = H - H_0 \) is self-adjoint and that Eq. (22) is also valid if we replace \( V \) by \( V' = V - (E - E_0) \).

We then write

\[ R U P R_0 = \sum_{k \neq 0, l \neq 0} [(E_0 - E_k)(E_0 - E_l)]^{-1} \left( | \phi_k \rangle \langle \phi_k | V'A | \phi_l \rangle \langle \phi_l | - | \phi_k \rangle \langle \phi_k | A | \phi_0 \rangle \langle \phi_0 | V'A | \phi_l \rangle \langle \phi_l | \right) \]

Substituting (22) into the above equation yields the same expression with \( V'A \) replaced by \( AV' \), plus a remainder. The above expression with \( V'A \) replaced by \( AV' \) is equal to \( R_0 P U^\dagger R_0 \). Therefore,

\[ R U P R_0 = R_0 P U^\dagger R_0 + \text{remainder}, \]

remainder = \[ \sum_{k \neq 0, l \neq 0} [(E_0 - E_k)(E_0 - E_l)]^{-1} \left( (E_l - E_0) | \phi_k \rangle \langle \phi_k | A | \phi_l \rangle \langle \phi_l | - (E_l - E_0) + (E_0 - E_k) \right) \times \left( | \phi_k \rangle \langle \phi_k | A | \phi_0 \rangle \langle \phi_0 | A | \phi_l \rangle \langle \phi_l | \right) \]

\[ = \sum_{k \neq 0, l \neq 0} (E_0 - E_l)^{-1} \left( | \phi_k \rangle \langle \phi_k | A | \phi_l \rangle \langle \phi_l | - | \phi_k \rangle \langle \phi_k | A | \phi_0 \rangle \langle \phi_0 | A | \phi_l \rangle \langle \phi_l | \right) \]

\[ - \sum_{k \neq 0, l \neq 0} (E_0 - E_k)^{-1} \left( | \phi_k \rangle \langle \phi_k | A | \phi_l \rangle \langle \phi_l | - | \phi_k \rangle \langle \phi_k | A | \phi_0 \rangle \langle \phi_0 | A | \phi_l \rangle \langle \phi_l | \right). \]

Into the first summation we substitute

\[ \sum_{k \neq 0} | \phi_k \rangle \langle \phi_k | = I - | \phi_0 \rangle \langle \phi_0 |, \]

and into the second one

\[ \sum_{l \neq 0} | \phi_l \rangle \langle \phi_l | = I - | \phi_0 \rangle \langle \phi_0 |. \]

The result is

remainder = \( P R_0 - R_0 P \).

So we have proved that

\[ R_0 U P R_0 = R_0 P U^\dagger R_0 + P R_0 - R_0 P \]

and therefore that \( P R_0 U P R_0 P = P R_0 P U^\dagger R_0 P \).
With the aid of Eq. (23) we prove that \((PR_0U)^nPR_0P\) is self-adjoint:

\[
(PR_0U)^nPR_0P = (PR_0U)^{-1}PR_0U^\dagger R_0P
\]

\[
= (PR_0U)^{-1}PR_0P(U^\dagger R_0P)
\]

\[
= (PR_0U)^{-2}PR_0UPR_0P(U^\dagger R_0P)
\]

etc. Continuing in this manner we find that

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

If \(n\) is even, we write

\[
(PR_0U)^nPR_0P = (PR_0U)^{n/2}PR_0P(U^\dagger R_0P)^{n/2},
\]

from which result follows that the energies of even order are negative definite or zero if \(R_0\) is a nonpositive operator. \(R_0\) is nonpositive for perturbations of the ground state.

**THE JOURNAL OF CHEMICAL PHYSICS**

**VOLUME 47, NUMBER 9 1 NOVEMBER 1967**

**Mechanisms of Energy Transfer Involving Trivalent Er and Tb or Tm in Sodium Rare-Earth Tungstates**

L. G. Van Uitert, E. F. Dearborn, and J. J. Rubin

*Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey*  
(Received 2 May 1967)

Emission is observed from six manifolds of Er in the tungstates at 77°K. Their signatures and intrinsic lifetimes in microseconds are: Er\(2\)\(\text{H}_{9/2}\), \(<5\); Er\(4\)\(\text{S}_{7/2}\), \(25\); Er\(4\)\(\text{F}_{9/2}\), \(\sim 5\); Er\(4\)\(\text{I}_{11/2}\), \(\sim 13\); Er\(4\)\(\text{I}_{13/2}\), \(120\); and Er\(4\)\(\text{I}_{15/2}\), \(\sim 4500\). A seventh manifold (Er\(2\)\(\text{S}_{7/2}\)) emits when thermally populated from Er\(4\)\(\text{S}_{3/2}\) at 295°K. The principal transitions from all of these manifolds are to the ground manifold (Er\(4\)\(\text{I}_{15/2}\)); as a result, radiation reabsorption is strong for each manifold and random migration of excitation between Er\(4\)\(\text{I}_{15/2}\) manifolds is possible at low Er concentrations. Further, due to the small spacings between the various manifolds of Er, relaxation by internal conversion processes is prevalent. Taking these factors and self-quenching interactions of Tb\(3\)\(\text{D}_{3}\) and Er into account, the nonradiative transfer of energy from Tb\(3\)\(\text{D}_{3}\) or Tb\(3\)\(\text{D}_{3}\) to Er, from Er\(4\)\(\text{I}_{15/2}\), Er\(4\)\(\text{S}_{7/2}\), Er\(4\)\(\text{F}_{9/2}\), Er\(4\)\(\text{I}_{11/2}\), or Er\(4\)\(\text{I}_{13/2}\) to Tb, and the equivalent self-quenching interactions of Er are all indicated to be by dipole–dipole in character.

**INTRODUCTION**

Early work on the elucidation of mechanisms of energy transfer between cations in luminescent solids has been discussed by Botden. More recent work involving rare-earth ion interactions has been summarized elsewhere. Energy transfer is generally associated with radiation reabsorption, multipolar interactions, and/or exchange. Multipolar processes can be responsible for remote interactions (e.g., 20 Å) while exchange may be important for interactions involving near neighbors. Multipolar transfer interactions between trivalent Tb and Sm, Eu, Dy, Pr, and/or Nd and between Eu and Nd in the sodium rare-earth tungstates has been analyzed previously. The present work is concerned with radiative and nonradiative interactions between trivalent Er and Tb or Tm ions.

**MATERIALS AND MEASUREMENTS**

Crystals of various members of the series Na\(_{0.5}\)(Y, Tb, Er)\(_{0.5}\)WO\(_4\) in the combinations indicated in the accompanying figures were grown from an Na\(_2\)W\(_6\)O\(_{18}\).