INTERMOLECULAR INTERACTIONS BY PERTURBATION THEORY
INCLUDING EXCHANGE EFFECTS

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A perturbation theory for intermolecular interactions is developed with wave functions of arbitrary symmetry. First- and second-order expressions are written out. For the sake of simplicity in practical calculations, the Unsöld approximation is introduced in the second-order energy.

1. INTRODUCTION

Intermolecular and interatomic interactions are usually distinguished in two types: At small distances the "chemical" interactions are important. They are calculated in first-order perturbation theory, taking the Pauli exclusion principle into account by using properly antisymmetrized wave functions (e.g., Heitler-London). At distances large compared to the molecular, atomic diameters these interactions are negligibly small compared to the, "physical", Van der Waals interactions. The latter are calculated in second-order perturbation theory with wave functions that are simple products of molecular, atomic wave functions.

Since both types of interactions are of quantum theoretical nature this distinction has to be justified and it will certainly not be valid for intermediate distances.

The first to develop a perturbation theory for interatomic interactions with antisymmetric wave functions were Eisenschitz and London [1]. After them such a perturbation theory or a variational procedure that is quite similar to it was used by Margenau [2], Moffitt [3], McGinnies and Jansen [4], Dalgarno and Lynn [5], Hirschfelder and Silbey [6]. We think that the treatment of Eisenschitz and London is so complete and mathematically elegant that it deserves to be written out in a more modern, somewhat generalized language.

There are two basic differences that distinguish this perturbation theory with antisymmetric wave functions from the usual perturbation theory. The unperturbed Hamiltonian, $H_0$, is a sum of

molecular, atomic operators; its eigenfunctions are products of the molecular, atomic eigenfunctions. In the product functions the electron coordinates are ordered in correspondence with the ordering of the coordinates in $H_0$. To satisfy the Pauli principle for electrons, antisymmetrized product functions are chosen as unperturbed functions. Firstly, these functions are not eigenfunctions of $H_0$. Secondly, if the total set of product eigenfunctions of $H_0$ spans the entire function space, the antisymmetrized products span the antisymmetric function space. However, they are linearly dependent, so that, if a general antisymmetric function is expanded as a linear combination of antisymmetrized products, the coefficients of the expansion are not uniquely determined. This second property was used by Eisenschitz and London to select a mathematically convenient set of expansion coefficients.

2. PERTURBATION THEORY

The theory is somewhat generalized by, instead of assuming that the wave functions are antisymmetric with respect to permutations of the electron coordinates, ascribing them some general symmetry properties. They may be symmetric or antisymmetric in the nuclear coordinates, in the electronic coordinates, or even possess some special symmetries with respect to permutations of the space or spin coordinates only. All these properties can be expressed in a projection operator $P$, an operator that projects the $N$-particle function space, $\{\phi\}$, onto the subspace of functions with the desired symmetry properties, $\{\psi = P\phi\}$.

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P has the usual properties of a projection operator. It is

\[ P^2 = P \]

and

\[ P^\dagger = P. \] (1)

If we treat a certain physical problem the symmetry of the system is reflected in its Hamiltonian. Therefore the Hamiltonian is invariant under operations of the symmetry group of the system and, as a consequence, under the projection operator \( P \), which is a linear combination of such operations. Moreover, \( H \) is self-adjoint. Expressed mathematically:

\[ PH = HP, \quad H^\dagger = H. \] (2)

If we separate \( H \) in a Hamilton operator of an unperturbed system, \( H_0 \), and a perturbation, \( V \), both parts are not necessarily invariant under \( P \). In the case we are interested in, \( H_0 \) represents the sum of the intramolecular, intra-atomic interactions and \( V \) the intermolecular, interatomic interaction. Both \( H_0 \) and \( V \) correspond to a certain ordering of the nuclear and electronic coordinates. Therefore

\[ PH_0 \neq H_0 P, \quad PV \neq VP. \] (3)

3. INTERMEZZO: EXPANSION OF FUNCTIONS
   IN THE SUBSPACE \( \{ \psi \} \)

A basis for the function space \( \{ \phi \} \) is given by the eigenfunctions of \( H_0 \):

\[ H_0 \phi_k^{(0)} = E_k^{(0)} \phi_k^{(0)}. \] (4)

The \( \phi_k^{(0)} \) are assumed to be orthonormal:

\[ \langle \phi_k^{(0)} | \phi_l^{(0)} \rangle = \delta_{kl}. \]

A resolution of the identity operator in \( \{ \phi \} \) is given by

\[ I = \sum_k | \phi_k^{(0)} \rangle \langle \phi_k^{(0)} |. \]

Or, in other words, each function that satisfies some well-behaviour conditions can be expressed in this basis,

\[ \phi = \sum_k \phi_k^{(0)} c_k, \]

with the coefficients:

\[ c_k = \langle \phi_k^{(0)} | \phi \rangle. \]

The functions \( \psi_k^{(0)} = P\phi_k^{(0)} \) span the subspace \( \{ \psi \} \) but they are linearly dependent. (Because of \( P \)) they are not eigenfunctions of \( H_0 \). If a function \( \psi \) is expanded as a linear combination of \( \psi_k^{(0)} \),

\[ \psi = \sum_k \psi_k^{(0)} a_k, \]

the coefficients \( a_k \) are not uniquely determined. One may still write, due to the completeness of the \( \phi_k^{(0)} \) in the function space \( \{ \phi \} \):

\[ P = \sum_k | P\phi_k^{(0)} \rangle \langle P\phi_k^{(0)} | = \sum_k | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} |. \] (5)

If a function \( \psi \) belonging to the subspace \( \{ \psi \} \) is expressed in the \( \psi_k^{(0)} \) with the help of this resolution of \( P \):

\[ \psi = P\psi = \sum_k | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \psi = \sum_k \psi_k^{(0)} b_k, \] (6)

the set of coefficients \( b_k = \langle \psi_k^{(0)} | \psi \rangle \) is uniquely determined and represents a special set in the collection of all sets of expansion coefficients \( a_k \).

4. PERTURBATION THEORY

We proceed according to the Rayleigh-Schrödinger perturbation theory. The Hamiltonian is written as

\[ H = H_0 + \lambda V. \] (7)

The eigenfunctions and eigenvalues of the equation for the total system, \( H \psi = E \psi \), are expanded as power series of \( \lambda \):

\[ \psi = \sum_{n=0}^\infty \lambda^n \psi^{(n)}, \quad E = \sum_{n=0}^\infty \lambda^n \epsilon^{(n)}. \] (8)

The perturbed functions \( \psi^{(n)} \), belonging to the subspace \( \{ \psi \} \) are expanded in the \( \psi_k^{(0)} \):

\[ \psi^{(n)} = \sum_k a_k^{(n)} \psi_k^{(0)}. \] (9)

As we want to consider the ground state for the assumed symmetry we choose as the zeroth order function \( \psi^{(0)} = \psi_0^{(0)} \). This means

\[ a_k^{(0)} = \delta_{k0}. \] (10)

(8) and (9) are then substituted in \( H \psi = E \psi \):

\[ \sum_{n=0}^\infty \lambda^n \sum_k a_k^{(n)} H \psi_k^{(0)} = \sum_{m,n=0}^\infty \lambda^{m+n} \epsilon^{(m)} \sum_k a_k^{(n)} \psi_k^{(0)}. \]

In the left-hand side of this equation \( \psi_k^{(0)} = P\phi_k^{(0)} \) is introduced, use is made of the commutation re-
lation (2), and (7) is substituted. Then (4) is used and terms are somewhat rearranged to obtain:

\[
\sum_{n=0}^{\infty} \sum_{k} \chi^{n} a_{k}^{(n)} E_{k}^{(o)} P_{k}^{(o)} + \sum_{n=1}^{\infty} \sum_{k} \chi^{n} a_{k}^{(n-1)} u_{k}^{(o)} = \sum_{n=0}^{\infty} \sum_{m=0}^{n} \chi^{m} a_{k}^{(n-m)} \psi_{k}^{(o)}.
\]

Putting the coefficients of the different powers of \( \chi \) equal to zero yields; for \( n = 0 \), substituting (10):

\[
E_{o}^{(o)} \psi_{o}^{(o)} = \epsilon^{(o)} \psi_{o}^{(o)}, \quad \epsilon^{(o)} = E_{o}^{(o)},
\]

for \( n = 1 \), with the help of (10) and (11):

\[
\sum_{k} a_{k}^{(1)} [E_{k}^{(o)} - E_{o}^{(o)}] \psi_{k}^{(o)} = \epsilon^{(1)} \psi_{o}^{(o)} - PV \psi_{o}^{(o)}
\]

for \( n = 2 \):

\[
\sum_{k} a_{k}^{(2)} [E_{k}^{(o)} - E_{o}^{(o)}] \psi_{k}^{(o)} = \epsilon^{(2)} \psi_{o}^{(o)} + \sum_{k} a_{k}^{(1)} [\epsilon^{(1)} \psi_{k}^{(o)} - PV \psi_{k}^{(o)}]
\]

etc.

The right-hand sides of these equations are expanded as linear combinations of the \( \psi_{k}^{(o)} \) according to formula (6). The first-order equation (12) becomes:

\[
\sum_{k} a_{k}^{(1)} [E_{k}^{(o)} - E_{o}^{(o)}] \psi_{k}^{(o)} = \sum_{k} \langle \psi_{k}^{(o)} | \epsilon^{(1)} \psi_{o}^{(o)} - PV \psi_{o}^{(o)} \rangle \psi_{k}^{(o)}.
\]

A solution to this equation is found by equating the coefficients of \( \psi_{k}^{(o)} \). This yields, introducing the notations

\[
V_{k} = \langle P \psi_{k}^{(o)} | PV \psi_{k}^{(o)} \rangle, \quad \Delta_{k} = \langle P \psi_{k}^{(o)} | P \psi_{k}^{(o)} \rangle
\]

for \( k = 0 \)

\[
\epsilon^{(1)} = \frac{\langle P \psi_{k}^{(o)} | PV \psi_{k}^{(o)} \rangle}{\langle P \psi_{k}^{(o)} | P \psi_{k}^{(o)} \rangle} = \frac{V_{oo}}{\Delta_{oo}},
\]

for \( k \neq 0 \)

\[
a_{k}^{(1)} = \frac{V_{k} - \epsilon^{(1)} \Delta_{k}}{E_{k}^{(o)} - E_{o}^{(o)}}.
\]

Choose \( a_{0}^{(1)} = 0 \).

Proceeding analogously with the second-order equation (13) one obtains:

\[
\epsilon^{(2)} = \frac{1}{\Delta_{oo}} \sum_{k} a_{k}^{(1)} (V_{k} - \epsilon^{(1)} \Delta_{k})
\]

\[
= \frac{1}{\Delta_{oo}} \sum_{k=0}^{\infty} \frac{(V_{k} - \epsilon^{(1)} \Delta_{k})}{E_{k}^{(o)} - E_{o}^{(o)}}.
\]

In this manner one finds all the terms in perturbation theory, but here we are only interested in first- and second-order. The first-order energy is expressed in the unperturbed ground state wave function. To get rid of the excited state functions in the second-order energy we have to apply the Unsöld approximation [7]. Formula (16) becomes

\[
\epsilon^{(2)} = -\frac{1}{\Delta_{av}} \sum_{k=0}^{\infty} (V_{k} - \epsilon^{(1)} \Delta_{k})
\]

\[
\times (V_{k} - \epsilon^{(1)} \Delta_{k})
\]

where \( \Delta_{av} \) is an "average excitation energy".

In order to apply (5) the term \( V_{k} \) has to be rewritten, with the help of \( V = H - H_{o} \) (\( \lambda \) is now contained in \( V \)):

\[
V_{k} = \langle P \psi_{k}^{(o)} | PV \psi_{k}^{(o)} \rangle
\]

\[
= \langle P \psi_{k}^{(o)} | PH \psi_{k}^{(o)} \rangle - \langle P \psi_{k}^{(o)} | PH_{o} \psi_{k}^{(o)} \rangle.
\]

Using (2) and (4) and once again \( H = H_{o} + V \) this expression becomes:

\[
V_{k} = \langle PV \psi_{k}^{(o)} | P \psi_{k}^{(o)} \rangle + [E_{k}^{(o)} - E_{o}^{(o)}] \langle P \psi_{k}^{(o)} | P \psi_{k}^{(o)} \rangle.
\]

After substituting this in (17) equation (5) is used (N. B. the summation over \( k \) does not contain the term \( k = 0 \)).

Introducing the first-order result (15) many terms cancel and we are left with

\[
\epsilon^{(2)} = -\frac{1}{\Delta_{av}} \sum_{k} \frac{V_{k} - \epsilon^{(1)} \Delta_{k}}{E_{k}^{(o)} - E_{o}^{(o)}}
\]

\[
\left[ \frac{\langle PV \psi_{k}^{(o)} | PV \psi_{k}^{(o)} \rangle}{\langle P \psi_{k}^{(o)} | P \psi_{k}^{(o)} \rangle} - \frac{\langle P \psi_{k}^{(o)} | PV \psi_{k}^{(o)} \rangle}{\langle P \psi_{k}^{(o)} | P \psi_{k}^{(o)} \rangle} \right]^{2}
\]

Remark: to calculate expressions of the form \( \langle P \psi^{(o)} | P \psi^{(o)} \rangle \) the following simplification is obtained by using (1):

\[
\langle P \psi^{(o)} | P \psi^{(o)} \rangle = \langle P \psi^{(o)} | P \psi^{(o)} \rangle = \langle \psi^{(o)} | \psi^{(o)} \rangle.
\]

Analyzing the formulas (15) and (18) for the
case of intermolecular, interatomic interactions the following conclusions may be made: The formula (15) for the first-order energy corresponds exactly to the Heitler-London or first-order chemical binding energy. The contribution to this energy due to the identity part of the projection operator $P$ is small compared to the terms resulting from permutations in $P$, the so-called exchange terms. The second-order result (18) contains the Van der Waals energy as the identity term, the rest may be called second-order exchange energy. This second-order exchange energy can yield an important contribution at intermediate distances.

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