Perturbation Theory of the Intermolecular Forces at Finite Orbital Overlap

A. Ažman*

King's College, Cambridge, England

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Very recently there has been a great interest in the application of the perturbation theory to the calculation of the intermolecular forces when the overlap is small but finite \(^1-^4\). We present a different approach which leads to similar results as obtained by other investigators.

Consider two separate systems \(i\) and \(j\) whose wavefunctions are \(a(i)\) and \(b(j)\) and satisfy:

\[
H_a(i) a(i) = E_a a(i) \\
H_b(j) b(j) = E_b b(j)
\]

The total Hamiltonian for the two systems together is:

\[
H = H_a(i) + H_b(j) + V = H_0 + V
\]

where the eigenfunction of \(H_0\) is \(a(i) b(j)\) with the eigenvalue

\[
E_a + E_b = E_{ab}^t
\]

To develop the perturbation theory we have to choose antisymmetric product of \(a(i)\) and \(b(j)\) as a basis for the perturbation development of the exact function \(\psi >\). Formally we can find the Hamiltonian which eigenfunction is \(\Phi_t > = A a(i) b(j)\) where \(A\) is antisymmetrizing operator:

\[
A H_0 a(i) b(j) = E_{ab}^t A a(i) b(j)
\]

\[
\overline{H_0} A a(i) b(j) = E_{ab}^t A a(i) b(j) \quad \text{with} \quad \overline{H_0} = A H_0 A^{-1}
\]

Total Hamiltonian is \(H = H_0 + V\), where \(V = A V A^{-1}\), using the fact that \(H\) and \(A\) commute.

Perturbation theory can now be used in its usual way:

\[
\psi > = \Phi_t > + \psi_1 > + \psi_2 > + \ldots
\]

\[
E = E_{ab}^t + E_1 + E_2 + \ldots \quad \text{with the normalization}
\]

\[
< \Phi_0 | \psi > = < \Phi_0 | \Phi_0 > \\
< \Phi_0 | \psi_1 > = < \Phi_0 | \psi_2 > = 0
\]

* Present address: Department of Chemistry, University of Ljubljana, Ljubljana, Slovenia, Yugoslavia.
Corrections to the energy and wavefunction can be obtained using the prescription of the ordinary perturbation theory:

\[
E_1 = \frac{\langle \Phi_0 | \nabla | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle}
\]

\[
E_2 = \frac{\langle \Phi_0 | \nabla | \psi_1 \rangle}{\langle \Phi_0 | \Phi_0 \rangle}
\]

\[
|\psi_1\rangle = \sum_{t \neq o} \frac{\langle \Phi_t | E_t - \nabla | \phi_0 \rangle}{E_{ab}^t - E_{ab}^0} |\phi_t\rangle
\]

Keeping terms to the first order in the exchange only one obtains: the prime indicates terms which involve electron exchange:

\[
E_1 = V_{oo} + (V'_o - V_{oo} S'_{oo})
\]

\[
E_2 = \sum_{t \neq o} V_{to}^2 + \sum_{t \neq o} E_{ab}^o - E_{ab}^t (V'_{to} - V_t S'_{to} - V_{oo} S_{to} -
\]

\[
-(E_{ab}^t - E_{ab}^o) S'_{to})
\]

\[
|\psi_1\rangle = \sum_{t \neq o} \frac{N (V_{to} + V'_t - V_{oo} S_{to}')}{E_{ab}^o - E_{ab}^t} |\phi_t\rangle
\]

The prime indicates terms which involve electron exchange, \( V_{to} = \langle (ab)_t | V | (ab)_o \rangle \), and \( S'_{to} \) is overlap matrix element.

The results are similar to the results obtained by Murrell and Shaw\(^4\) using modified Yaris perturbation method.

Note added in proof: Very recently Amos and Musher\(^6\) pointed out that it is not necessary to use antisymmetrized functions \( |\psi_i\rangle \), \( |\psi_2\rangle \) ..., though the corrections are equal as obtained with the function where only \( |\phi_o\rangle \) is antisymmetrized.

REFERENCES


IZVLEČEK

Perturbacijska teorija medmolekulnih sil pri končnem prekrivanju orbital

A. Azman

Z vpeljavo nehermitskega operatorja smo pokazali, da lahko rešimo problem interakcije med molekulami v okviru standardne perturbacijske metode.

KING'S COLLEGE, CAMBRIDGE, ENGLAND