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Note

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

$$E_a + E_b = E^t_{ab}$$

To develope 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 $|\,\psi>$. Formaly we can find the Hamiltonian which eigenfunction is $|\,\Phi_t> = \mathcal{A}\,a\,(i)\,b\,(j)$ where $\mathcal{A}$ is antisymmetrizing operator:

$$\mathcal{A}\;\; H_0 a\,(i)\,b\,(j) = E^t_{ab}\;\mathcal{A}\,a\,(i)\,b\,(j)$$

$$\overline{H}_0\,\mathcal{A}\;\;a\,(i)\,b\,(j) = E^t_{ab}\;\mathcal{A}\,a\,(i)\,b\,(j)\;\;\text{with}\;\;\overline{H}_0 = \mathcal{A}\,H_0\,\mathcal{A}^{-1}$$

Total Hamiltonian is $H = \overline{H}_0 + \overline{V}$, where $\overline{V} = \mathcal{A}\,V\,\mathcal{A}^{-1}$, using the fact that H and $\mathcal{A}$ commute.

Perturbation theory can now be used in its usual way[5]:

$$|\,\psi> = |\,\Phi_0> + |\,\psi_1> + |\,\psi_2> + \ldots$$

$E = E^t_{ab} + E_1 + E_2 + \ldots$ with the normalization

$$<\Phi_0\,|\,\psi> = <\Phi_0\,|\,\Phi_0> \cdot$$

$$<\Phi_0\,|\,\psi_1> = <\Phi_0\,|\,\psi_2> = 0$$

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* 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:

$$E_1 = \frac{<\Phi_o | \overline{V} | \Phi_o>}{<\Phi_o | \Phi_o>}$$

$$E_2 = \frac{<\Phi_o | \overline{V} | \psi_1>}{<\Phi_o | \Phi_o>}$$

$$| \psi_1 = \sum_{t \neq o} \frac{<\Phi_t | E_1 - \overline{V} | \Phi_o>}{E^t_{ab} - E^o_{ab}} | \Phi_t >$$

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

$$E_1 = V_{oo} + (V'_{oo} - V_{oo} S'_{oo})$$

$$E_2 = \sum_{t \neq o} \frac{V^2_{to}}{E^o_{ab} - E^t_{ab}} + \sum_{t \neq o} \frac{V_{to}}{E^o_{ab} - E^t_{ab}} (V'_{to} - V_{to} S'_{oo} - V_{oo} S'_{to} - (E^t_{ab} - E^o_{ab}) S'_{to})$$

$$| \psi_1 > = \sum_{t \neq o} \frac{N (V_{to} + V'_{to} - V_{oo} S'_{to})}{E^o_{ab} - E^t_{ab}} | \Phi_t >$$

The prime indicates terms which involve electron exchange, $V_{to} = <<(ab)_t | V | (ab)_o>>$, 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 $| \psi_1 >$, $| \psi_2 > \ldots$, though the corrections are equal as obtained with the function where only $| \Phi_o >$ is antisymmetrized.

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IZVLEČEK

Perturbacijska teorija medmolekularnih sil pri končnem prekrivanju orbital

A. Ažman

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

KING'S COLLEGE, CAMBRIDGE,
ENGLAND

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