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Note

Perturbation Theory of Intermolecular Forces Using an »Effective« Hamiltonian

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Recently H. Ezawa and M. Luban[1] proposed an interesting approach for the diagonalization of the Hamiltonian describing two interacting systems. The main idea is this: with the knowledge of one of the Hamiltonian describing system A one can construct an effective Hamiltonian for the system B with respect to its interaction with the subsystem A. The aim of our note is to show that the perturbation treatment of the proposed method leads to the corrections (first and second order) in energy of the system which are the same as obtained by Rayleigh-Schrödinger perturbation theory[2].

The Hamiltonian we have to diagnolize is:

$$H = H_A + H_B + H_I \tag{1}$$

and the solutions of the Hamiltonians H_A and H_B are known. The "Effective" Hamiltonian H is determined by (2):

$$(H_A + H_B + H_I)\,\Psi = \Psi\,H \tag{2}$$

This is the first step of the diagonalization. The second one is:

$$H\,|\,\Phi> = E\,|\,\Phi> \tag{3}$$

The wavefunction $\overline{\Psi}$ of H is:

$$\overline{\Psi} = \Psi\,|\,\Phi> \tag{4}$$

and the corresponding eigenvalue is E (eq. (3). The perturbation expansions are made in both steps of the diagonalization. In the first step we have:

$$\Psi = \Psi_0 + \Psi^1 + \Psi^2 + \ldots \tag{5}$$

$$H = H_0 + H^1 + H^2 + \ldots$$

where $H_A\,\Psi_0 = e_0\,\Psi_0$

From eq. (5) the following set of equations are obtained:

$$(H_A + H_B)\,\Psi_0 = \Psi_0\,H_0 \tag{6}$$

$$(H_A + H_B)\,\Psi^1 + H_I\,\Psi_0 = \Psi^1\,H_0 + \Psi_0\,H^1 \tag{7}$$

$$(H_A + H_B)\,\Psi^2 + H_I\,\Psi^1 = \Psi^1\,H^1 + \Psi^2\,H_0 + \Psi_0\,H^2 \tag{8}$$

$$H_0 = e_0 + H_B \tag{9}$$

$$H^1 = (\Psi_0\,|\,H_I\,|\,\Psi_0) \tag{10}$$

$$H^2 = (\Psi_0 \mid H_I \mid \Psi^1) \tag{11}$$

In the deriving of the useful equation for Ψ^1 the following expansion is used[1]:

$$\Psi^1 = \sum_i \Psi_i C_i \tag{12}$$

where Ψ_i form a complete set for the Hamiltonian H_A and C_i are operators from the Hilbert space of the system B. From eq. (7) the commutator equation results for the coefficient C_i:

$$[H_B, C_i] + (e_i - e_0) C_i = K \tag{13}$$

$$\text{with } K = \delta_{i0} (\Psi_0 \mid H_I \mid \Psi_0) - (\Psi_i \mid H_I \mid \Psi_0)$$

Eq. (13) can be solved using a complete set of the wavefunctions $\mid \Phi_i >$ and eigenvalues E_i of H_B. The matrix elements of C_i are given by:

$$(E_j - E_k + e_i - e_0) < \Phi_j \mid C_i \mid \Phi_k > = < \Phi_j \mid K \mid \Phi_k > \tag{14}$$

The perturbation expansion is made in the usual way on the eq. (3) with the results:

$$E_0 = e_0 + E_0 \tag{15}$$

$$E^1 = < \Phi_0 \mid H^1 \mid \Phi_0 > \tag{16}$$

$$E^2 = < \Phi_0 \mid H^1 \mid \Phi^1 > + < \Phi_0 \mid H^2 \mid \Phi_0 > \tag{17}$$

$$\mid \Phi^1 > = \sum \frac{< \Phi_i \mid H^1 \mid \Phi_0 >}{E_0 - E_i} \mid \Phi_i > \tag{18}$$

Eq. (15) and (16) are known expressions from the standard theory. The first term of the second order correction to the energy eq. (17) is the induction energy term (A polarizes B). The second term of the eq. (17) contains: the induction term (B polarizes A) when Ψ^1 has not operator character and dispersion energy term. This is easily seen using eq. (11), (12) and (14).

We have shown that the proposed method though using unusual mathematical suppositions gives the same corrections in the perturbation treatment as the Rayleigh-Schrödinger perturbation theory.

REFERENCES

1. H. Ezawa and M. Luban *J. Math. Phys.* **8** (1967) 1285.
2. J. O. Hirschfelder and W. J. Meath in *Advances in Chemical Physics*, Vol. 12, p. 3, Ed. J. O. Hirschfelder, Interscience Publisher, 1967.

IZVLEČEK

Perturbacijska teorija medmolekulskih sil z uporabo »Efektivnega Hamiltoniana«

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Pokazali smo, da perturbacijska teorija z »Efektivnim Hamiltonianom« H. Ezawa in M. Lubana, da iste popravke za energijo med molekulami kot Rayleigh-Schrödingerjeva perturbacijska metoda

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