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CLUSTER EXPANSION OF THE MOLECULAR ENERGY WITH THE CORRELATED WAVE FUNCTION

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It is well known that the electronic configuration of many-electron system is best described by a wave function containing explicit interelectronic distances. The computational complexity of this approach, however, prevents its application to larger molecular systems. The aim of the present paper is to use the correlated wave function in a molecular problem but to carry out actual calculation of the energy by its cluster expansion. In this attempt we have employed the expansion given by van Kampen [1, 2].

Van Kampen's expression for the energy [3] of N particles is

$$E_0 = \sum_{n}^{N} E_{0n}\,, \tag{1}$$

where in particular

$$E_{01} = \sum_{i}^{N} C_1(i) \tag{2}$$

with

$$C_1(i) = \langle \psi_1(i)\, H_1\, \psi_1(i) \rangle / \langle \psi_1(i)\, \psi_1(i) \rangle,$$

and

$$E_{02} = \sum \sum_{i<j}^{N} C_2(ij)$$

with

$$C_2(ij) = \langle \psi_2(ij)\, H_2\, \psi_2(ij) \rangle \; \langle \psi_2(ij)\, \psi_2(ij) \rangle - C_1(i) - C_1(j). \tag{3}$$

E_{01} is the energy of N independent particles and E_{02} is the energy of the cluster composed by two particles. In the calculation only these two terms were taken into account.

The wave function $\psi_\lambda(ij)$ is of the form

$$\psi_2(ij) = \{\Phi_p(i)\,\Phi_q(j) \pm \Phi_q(i)\,\Phi_p(j)\}\ \{\alpha(i)\,\beta(j) \mp \alpha(j)\,\beta(i)\}\,f(r_{ij}), \tag{4}$$

where $f(r_{ij})$ is the function of the interelectronic distances r_{ij}.

The above procedure was used to calculate the ground state energy (π-electrons) of trans-butadiene. The functions $\psi(i) \equiv \Phi(i)$ were the Hückel molecular orbital functions calculated with theoretical parameters from [4]. In Eq. (2) H_1 is the core Hamiltonian and

$$H_2(ij) = H_1(i)+H_1(j)+\frac{1}{r_{ij}}\,.$$

The function $f(r_{ij})$ was taken in the form

$$f(r_{ij}) = 1 + cr_{ij}\,. \tag{5}$$

This form has been used extensively in the application of the correlated wave function to atoms [5]. c is the variation parameter and was determined by minimization of E_0 from Eq. (1). Besides the Coulomb integrals, integrals of the form

$$\langle\Phi_p(i)\,\Phi_q(j)\,r_{ij}\,\Phi_r(i)\,\Phi_s(j)\rangle$$

and

$$\langle\Phi_p(i)\,\Phi_q(j)\,r_{ij}^2\,\Phi_r(i)\,\Phi_s(j)\rangle$$

appear. Analytical expressions for $p = q$, $r = s$ can be found for the former integrals and $p = q$, $r = s$; $p = r$, $q = s$ for the latter. Though the exchange integrals with operator r_{ij}^2 are not small, they do not contribute significantly to E_0, and for this reason, as well as to retain the approximation inherent in P—P—P method, were neglected. Energy E_{02} contain terms of the form $\langle\psi_2\,r_{ij}\,H_1\,r_{ij}\,\psi_2\rangle$; these elements were calculated by using the complete set consisting of molecular orbitals.

Results

The truncate dcluster expansion from Eq. (1) gives the energy -91.48 eV at $c = 0.11$ a.u. The antisymmetrized product of the Hückel molecular orbitals gives the value -85.98 eV and SCF method -93.79. The result obtained by cluster expansion is thus disappointing. The reason for this can be explained by the fact [6] that $f(r_{ij})$ does not have the right asymptotic value at $r_{ij} \to 0$, which means that E_0 from Eq. (1) cannot be approximated by E_{01} and E_{02} only. As $f(r_{ij})$ in Eq. (5) does not fulfil the asymptotic condition, the higher order in Eq. (1) has to be included. Very rough calculation shows that the third order E_{03} lowers the energy by about 3 eV. It is interesting to note that none of the $f(r_{ij})$ so far proposed [5] displays the correct asymptotic behaviour.

In spite of the unsatisfactory result, we believe that cluster expansion offers a simple way of treating the energy of complex molecular systems with the correlated wave function.

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