Electronic Correlation in Molecular Systems: An Effective Interaction Approach

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Numerous methods have been proposed which can account for the correlation between electrons. The aim of this note is to use one of them that has been used in nuclear physics[1] with some success. The mathematical procedure is as follows: The Hamiltonian of the molecular system is given by

$$H = \sum_i t_i + \sum_{i<j} v_{ij} \tag{1}$$

with the known zero order equation

$$H_o \Phi = E_o \Phi \tag{2}$$

In order to solve

$$H \Psi = E \Psi$$

the hermitian operator S is introduced[2]

$\Psi = e^{iS} \Phi$ and determined from

$$E = \langle \Psi | H | \Psi \rangle = \langle \Phi | \bar{H} | \Phi \rangle = \min. \tag{3}$$

with $\bar{H} = e^{-iS} H e^{iS}$

The cluster expansion of $\bar{H}$ includes clusters of one, two, three, *etc.* particles. The simplest approximation to the many-body operator H is the operator that retains only clusters of two particles. S takes then the form:

$$S = \sum_{i<j} S_{ij}$$

The Hamiltonian $\bar{H}$ is

$$\bar{H} = \bar{H}^1 + \bar{H}^2 + \bar{H}^3 + \ldots \tag{4}$$

where

$$\bar{H}^1 = \sum_i t_i = \sum_{ij} a_i^+ a_j \langle i | t | j \rangle$$

$$\bar{H}^2 = \frac{1}{2} \sum_{ijkl} a_i^+ a_j^+ a_l a_k [\langle ij | e^{-iS_{12}} (t_1 + t_2 + v_{12}) e^{iS_{12}} | kl \rangle - \langle ij | t_1 + t_2 | kl \rangle]$$

If the model function Φ is a single Slater determinant, the trial energy of the system can be written (neglecting three-particle $\bar{H}^3$ and higher terms)

$$E = \sum_i^{occ.} <i\,|\,t\,|\,i> + \frac{1}{2}\sum_{ij}^{occ.} <ij\,|\,\bar{v}\,|\,ij - ji> \tag{5}$$

with $\bar{v}$ (the effective potential)

$$\bar{v} = e^{-iS_{12}}\,(t_1 + t_2 + v_{12})\,e^{iS_{12}} - (t_1 + t_2) \tag{6}$$

Instead of determining the operator $e^{-iS_{12}}$ from eq. (5) and keeping it to be unitary, it is simpler to introduce the correlated two-particle wave function $\psi\,(1,2)$ and to rewrite E using it. $\psi\,(1,2)$ is defined as $e^{iS_{12}}\,i\,(1)\,j\,(2) = \psi\,(1,2)$ and has to be determined from eq. (3) with the subsidiary condition $\int\!\!\int\,|\psi\,(1,2)|^2\,dV_1\,dV_2 = 1$. It is appropriate to notice that this procedure is not completely but only approximately equivalent to the procedure for determining the operator $e^{iS_{12}}$. Eq. (3) and eq. (5) give the equation

$$\langle \psi^*\,(1,2)\,|\,t_1 + t_2 + t_{12}\,|\,\psi\,(1,2)\rangle \equiv F = min.$$

and $\psi\,(1,2)$ is obtained from

$$\frac{\partial F}{\partial \psi^*} = 0 \tag{7}$$

The above described procedure has been applied to calculate the energy of *trans*-butadiene. H_o was chosen in two different ways:

$$i)\; H_o = \sum_i t_i \qquad ii)\; H_o = \sum_i t_i + v_{H.F.}$$

where $V_{H.F.}$ is the *SCF* potential deduced from the semiempirical Pariser-Parr-Pople method. (ref. 3, parameters with theoretical values). In both calculations $\psi\,(1,2)$ was expanded into molecular orbitals φ_i, φ_j (the eigenfunctions of H_o)

$$\psi_m\,(1,2) = \sum_{ij} d_{mij}\,\varphi_i\,(1)\,\varphi_j\,(2)$$

with the coefficients d_{mij} which resulted from eq. (7).

The calculated energies are -93.59 eV and -96.25 eV when the molecular orbitals from $i)$ or $ii)$ are used. These values have to be compared with values -93.79 eV and -96.15 eV obtained by the *SCF* or *SCF* configuration interaction method[3]. The present approach is equivalent[4] to the Brueckner (Bethe-Goldstone) theory of the many-particle system. The variational approach of the Brueckner theory with independent pairs overestimates the correlation energy[5]. The present result with molecular orbitals from $ii)$ is in accordance with this statement. The direct solution[6] of the Bethe-Goldstone equation with molecular orbitals from $i)$ agrees closely with the value obtained by the present approach (*MO* from i).

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IZVLEČEK

Elektronska korelacija v molekulah: metoda efektivnega potencijala

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V delu je uporabljena metoda efektivnega potencijala[1]. Rezultati potrjujejo dejstvo, da metode z osnovo neodvisne parske korelacije dajo prevelike vrednosti za korelacijsko energijo.

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