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A New Approach to Variational CI Calculations on Systems Containing Non-Interacting Molecules

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A new method to perform variational CI calculations on systems containing non-interacting molecules is presented.

Key words: Non-interacting molecules, systems containing ~

1. Introduction

With the present efficiency of *ab initio* molecular orbital methods it has become feasible to calculate accurate energies for small molecular systems. By doing such calculations for a limited number of molecules the thermodynamic ΔU and ΔH values can be determined for a large number of chemical reactions. Such schemes have been extensively used within the Hartree-Fock approximation [1-5]. The extension of these calculations to include correlation effects, which may be essential for accurate ΔU and ΔH values [6-8] is not straightforward. It can, in principle, be done by two methods. Either one uses some form of electron pair approximation which gives estimates of total molecular correlation energies, or one calculates a variationally determined upper limit to the correlation energy. If we consider a chemical reaction A + B → AB, the advantage of the electron pair approximations is that the sum of the correlation energies for molecules A and B could be compared with the correlation energy for system AB and thus give an estimate of the correlation energy contribution to the ΔE value of the chemical reaction. The drawback of these methods is that the calculated correlation energies are not variationally determined [9].

If, on the other hand, we adopt a variational approach, problems arise since we must truncate our expansion of the wave function into Slater determinants. The standard choice is to include all singly and doubly replaced configurations. It is, however, known that the energy for non-interacting systems are not additive within this approximation. For example, to calculate the correlation energy contribution to the ΔE value for the reaction mentioned above in a consistent way one is forced to perform a configuration interaction (CI) calculation on A + B regarded as one system with two fragments far apart. This procedure has two major drawbacks. The size of the CI calculation increases considerably and, more important, it cannot be fitted into a scheme with calculations on a few molecules giving ΔU and ΔH for a larger number of reactions. In the present work a simple variationally correct procedure is presented which circumvents these two drawbacks in a simple, although approximative, way.

2. Theory

Consider a system A in a quantum mechanical state which, to a good approximation, can be described by a single Slater determinant Φ_A built up from orthonormal spin orbitals χ_i (iE 1, 2, . . . n). The set of occupied spin orbitals χ_i is completed by other spin orbitals χ_a such that χ_i, together with χ_a, form an orthonormal set. We may define "singly substituted" determinants $\Phi^a_{\mathrm{A}'i}$ as those obtained from Φ_A by replacing χ_i by χ_a. "Doubly" and higher substituted determinants $\Phi^{a,b}_{\mathrm{A},i,j}$, $\Phi^{a,b,c}_{\mathrm{A},i,j,k}$ etc., are similarly defined. The configuration interaction expansion of the wave function for the considered state can be written [11]:

$$\Psi_\mathrm{A} = \Phi_\mathrm{A} + \sum_{i,a} C^a_{\mathrm{A},k}\Phi^a_{\mathrm{A},i} + \sum_{\substack{i<j\\a<b}} C^{a,b}_{\mathrm{A},i,j}\Phi^{a,b}_{\mathrm{A},i,j} + \ldots . \tag{1}$$

Now assume that the expansion of the wave function is truncated to contain only terms expressed explicitly in Eq. (1). This procedure is usually adopted in the direct CI method [10]. Further it has been shown that the contribution to the total energy of a system from singly substituted determinants is small, so we may assume that the wave function can be written

$$\Psi_\mathrm{A} = \Phi_\mathrm{A} + \sum_{\substack{i<j\\a<b}} C^{a,b}_{\mathrm{A},i,j}\Phi^{a,b}_{\mathrm{A},i,j} = \Phi_\mathrm{A} + C_\mathrm{A}\Phi'_\mathrm{A} \tag{2}$$

where

$$\Phi'_\mathrm{A} = \sum_{\substack{i<j\\a<b}} \frac{C^{a,b}_{a,i,j}}{C_\mathrm{A}} \cdot \Phi^{a,b}_{\mathrm{A},i,j}. \tag{3}$$

Defined in this way Φ_A and Φ'_A will be orthonormal if we choose C_A properly. If we know the best variational function in a given finite basis according to Eq. (2) then

$$\bar{H}_\mathrm{A}\Psi_\mathrm{A} = E_\mathrm{A}\Psi_\mathrm{A}, \tag{4}$$

where $\bar{H}_\mathrm{A}$ is the projected Hamiltonian for the system A [12] defined by

$$\bar{H}_\mathrm{A} = \pi H_\mathrm{A}\pi. \tag{5}$$

H_A is the true Hamiltonian for the system and π is a projection operator corresponding to the used basis. Multiplying Eq. (4) from the left by Φ_A we obtain:

$$\langle \Phi_\mathrm{A} | H_\mathrm{A} | \Psi_\mathrm{A} \rangle = E_\mathrm{A} \tag{6}$$

or

$$\langle \Phi_\mathrm{A} | H_\mathrm{A} | \Phi_\mathrm{A} \rangle + C_\mathrm{A} \langle \Phi_\mathrm{A} | H_\mathrm{A} | \Phi'_\mathrm{A} \rangle = E_\mathrm{A}. \tag{6b}$$

If we define the correlation energy for system A ($E_{\mathrm{A}}^{\mathrm{corr}}$) as the difference between the total energy E_{A} and the energy corresponding to the determinant $\Phi_{\mathrm{A}}(E_{\mathrm{A}}^0)$ this may be written:

$$E_{\mathrm{A}}^{\mathrm{corr}} = E_{\mathrm{A}} - E_{\mathrm{A}}^0 = C_{\mathrm{A}} \langle \Phi_{\mathrm{A}} | H_{\mathrm{A}} | \Phi'_{\mathrm{A}} \rangle. \tag{7}$$

If we multiply Eq. (4) from the left by Φ'_{A} we obtain:

$$\langle \Phi'_{\mathrm{A}} | H_{\mathrm{A}} | \Phi_{\mathrm{A}} \rangle + C_{\mathrm{A}} \langle \Phi'_{\mathrm{A}} | H_{\mathrm{A}} | \Phi'_{\mathrm{A}} \rangle = C_{\mathrm{A}} E_{\mathrm{A}}. \tag{8}$$

Using Eq. (7) we obtain:

$$\langle \Phi'_{\mathrm{A}} | H_{\mathrm{A}} | \Phi'_{\mathrm{A}} \rangle = E_{\mathrm{A}}^0 + (C_{\mathrm{A}}^2 - 1) \cdot E_{\mathrm{A}}^{\mathrm{corr}} / C_{\mathrm{A}}^2. \tag{9}$$

If we now form a new system AB out of two non-interacting systems A and B we may write the wave function for the system AB with the same approximation as used in Eq. (2):

$$\Psi_{\mathrm{AB}} = \Phi_{\mathrm{A}} \Phi_{\mathrm{B}} + \left(\sum_{\substack{i<j \\ a<b}} C_{\mathrm{A},i,j}^{a,b} \Phi_{\mathrm{A},i,j}^{a,b} \right) \Phi_{\mathrm{B}} + \Phi_{\mathrm{A}} \cdot \left(\sum_{\substack{k<l \\ d<e}} C_{\mathrm{B},k,l}^{d,e} \Phi_{\mathrm{B},k,l}^{d,e} \right). \tag{10}$$

We now approximate $\sum_{i<j} C_{\mathrm{A},i,j}^{a,b} \Phi_{\mathrm{A},i,j}^{a,b}$ with $a \cdot \Phi'_{\mathrm{A}}$ where Φ'_{A} is taken from Eq. (2) and using a similar approach for system B we may write

$$\Psi_{\mathrm{AB}} = \Phi_{\mathrm{A}} \Phi_{\mathrm{B}} + a \Phi'_{\mathrm{A}} \Phi_{\mathrm{B}} + b \Phi_{\mathrm{A}} \Phi'_{\mathrm{B}}. \tag{11}$$

Now we may solve the secular equation for a wave function according to Eq. (11). The matrix elements needed were obtained from Eqs. (7) and (9). We obtain

$$E_{\mathrm{AB}}^{\mathrm{corr}} = \frac{(E_{\mathrm{A}}^{\mathrm{corr}})^2}{C_{\mathrm{A}}^2 \left(E_{\mathrm{AB}}^{\mathrm{corr}} + \frac{(1 - C_{\mathrm{A}}^2)}{-C_{\mathrm{A}}^2} \cdot E_{\mathrm{A}}^{\mathrm{corr}} \right)} + \frac{(E_{\mathrm{B}}^{\mathrm{corr}})^2}{C_{\mathrm{A}}^2 \left(E_{\mathrm{AB}}^{\mathrm{corr}} + \frac{1 - C_{\mathrm{A}}^2}{C_{\mathrm{B}}^2} E_{\mathrm{B}}^{\mathrm{corr}} \right)}. \tag{12a}$$

Here we have used the notation $E_{\mathrm{AB}}^{\mathrm{corr}} = E_{\mathrm{AB}} - E_{\mathrm{A}}^0 - E_{\mathrm{B}}^0$. E_{AB} is the total energy for a wave function according to Eq. (11). Eq. (12a) is of the third degree in $E_{\mathrm{AB}}^{\mathrm{corr}}$, and since all other quantities can easily be obtained from calculations on system A and B, it can be solved e.g. iteratively. Following the same principle the constants a and b may be determined and thus an approximative value for C_{AB} calculated. In this way many systems can be added together. One obtains

$$C_{\mathrm{AB}}^2 = \left[\frac{E_{\mathrm{A}}^{\mathrm{corr}}}{C_{\mathrm{A}} \left(E_{\mathrm{AB}}^{\mathrm{corr}} + \frac{1 - C_{\mathrm{A}}^2}{C_{\mathrm{A}}^2} E_{\mathrm{A}}^{\mathrm{corr}} \right)} \right]^2 + \left[\frac{E_{\mathrm{B}}^{\mathrm{corr}}}{C_{\mathrm{B}} \left(E_{\mathrm{AB}}^{\mathrm{corr}} + \frac{1 - C_{\mathrm{B}}^2}{C_{\mathrm{A}}^2} E_{\mathrm{B}}^{\mathrm{corr}} \right)} \right]^2 . \tag{12b}$$

3. Approximations

To derive Eq. (12) two approximations have been made relative to a direct CI calculation on the united systems. Firstly it is assumed that the relative weights of all the excited determinants for one of the sub-systems are unchanged when a second non-interacting sub-system is introduced. Certainly this approximation is good since the changes in the coefficients are very small. Secondly it is assumed that the CI expansion for the sub-systems does not contain any determinants with single replacements. If we define Φ'_{A} a little differently,

$$\Phi'_{\mathrm{A}} = \sum_{i,a} C^{a}_{\mathrm{A},i}/C_{\mathrm{A}}\Phi^{a}_{\mathrm{A},i} + \sum_{i<j} C^{a}_{\mathrm{A},i,j}/C_{\mathrm{A}}\Phi^{a,b}_{\mathrm{A},i,j}, \tag{13}$$

it can be seen that this change only introduces one extra term,

$$\sum_{i,a} C^{a}_{\mathrm{A},i} \sum_{k,d} C^{d}_{\mathrm{B},k}\Phi^{a}_{\mathrm{A},i}\Phi^{d}_{\mathrm{B},k},$$

in the wave function of the system AB. This term will only have matrix elements with itself and will cause only a slight lowering of the total energy of the system since the matrix elements will be quadratic in both $C^{a}_{\mathrm{A},i}$ and $C^{d}_{\mathrm{B},k}$. Thus we may conclude that the energy calculated using this approximative formalism is a true upper limit to the energy calculated in a direct configuration interaction calculation.

4. Results

In order to check the validity of the approximations made, some test calculations have been performed using the program system MOLECULE-CI [10]. A basis set consisting of 7*s* and 3*p* Gaussian basis functions contracted to 4,2 [13] has been used for oxygen and carbon, and 4*s* functions multiplied by 1.34 contracted to 2 [14] have been used for hydrogen in the SCF calculations. In the configuration interaction calculation all singly and doubly replaced determinants that could be constructed according to Eq. (1) were used except that the oxygen and carbon 1*s* orbitals and corresponding part of the virtual orbital space were deleted in the expansion.

The results obtained are shown in Table 1 together with accurately calculated values in an expansion containing both sub-systems.

5. Discussion

From Table 1 it can be seen that the difference between the approximate and the exact value for ΔE within the given basis set is nowhere larger than $1.26 \cdot 10^{-4}$ Hartree corresponding to 80 cal/mol. This is clearly smaller than the errors expected from other sources. It is also clear that the correction introduced by Eq. (12a) is substantial. It is thus clear that variational CI calculations on individual molecules can be used to estimate ΔU and ΔH values for chemical reactions. If the effect of higher substituted determinants are considered to be vital for the correlation energy part of ΔE it could be introduced in an approximative but fairly consistent way using the renormalization equation $E_{\mathrm{u.c.}} = (1 - c_0^2)E_2$ where $E_{\mathrm{u.c.}}$ is the considered effect, c_0 the coefficient of the leading determinant and E_2 is the correlation energy calculated with singly and doubly replaced determinants.

Table 1

	Direct CI		Equations (12a) (12b)		
System	Corr. Energy (a.u.)	C_A	Corr. Energy (a.u.)	C_A	ΔE^{corr} (a.u.)
H_2	−0.024830	0.1216606	–	–	–
$CO + H_2$	−0.218080	0.2932754	–	–	–
CH_3OH	−0.218172	0.2726204	–	–	–
H_2O	−0.126162	0.1895858	–	–	–
CH_4	−0.114144	0.2249407	–	–	–
$H_2 + H_2$	−0.048956	0.1692455	−0.048955	0.1696150	0.000001
$(CO + H_2) + H_2$	−0.238432	0.3087531	−0.238375	0.3103180	0.000057
$(CO + H_2) + H_2 + H_2$	−0.258397	0.3228767	−0.258271	0.3258433	0.000126
$(CO + H_2) + 2H_2$	−0.258397	0.3228767	−0.258289	0.3256990	0.000108
$CH_3OH + H_2$	−0.238722	0.2904648	−0.238681	0.2914418	0.000041
$H_2O + CH_4$	−0.231065	0.2800637	−0.231028	0.2821772	0.000037

In the calculations presented in Table 1 the atomic basis sets are not large enough to ensure reliable ΔE values. The need of large basis sets makes it even more important to avoid CI calculations on combined non-interacting systems.

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