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A multireference energy decomposition scheme with respect to fragment valence states

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In this paper we describe a multi-reference energy decomposition scheme defined with respect to specific "valence states" of the interacting fragments. The orbitals of these fragments are computed with a new iterative procedure involving MC-SCF computations with the fragments at infinite separation and CI computations at the internuclear distance of interest. This procedure is applied here for the analysis of the rotational barrier in methylamine.

Key words: Energy decomposition—MC-SCF computation—Valence state.

1. Introduction

In a recent paper [1] we have proposed a decomposition scheme of the molecular interaction energy computed with a multi-reference expansion of the wavefunction. In this scheme the decomposition analysis is performed relative to specific spectroscopic states of the isolated fragments. However in many chemical problems, in particular in the vast majority of structural problems, the chemically relevant states of the interacting fragments are the valence states, which can be expressed as appropriate linear combinations of spectroscopic states.

In this paper we describe a procedure for the computation of the valence states of molecular fragments arising from the dissection of a supermolecule and a multi-reference energy decomposition scheme with respect to specific valence states. For illustrative purposes, these procedures are used here to analyse the factors controlling the conformational preference in methylamine.

2. Methods

In the approach used here, the wavefunction for the supermolecule A-B is represented by the following expansion:

$$\Psi = \sum_k C_k \Phi_k \tag{1}$$

where the Φ_k are configuration state functions constructed from the orbitals of the non-interacting subsystems. The orbitals occurring in the Φ_k are classified as: (i) core orbitals, which are doubly occupied in all configurations; (ii) valence orbitals, which have all possible occupancies and (iii) virtual orbitals which are unoccupied in all configurations. The individual Φ_k, built from the orbitals of the non interacting fragments, can be either no-bond configurations (NBC) corresponding to the correctly antisymmetrized product of two isolated fragment configurations or charge transfer configurations (CTC) corresponding to configurations derived from the NBC by electron transfer between fragments.

In this approach, we define the valence state of a given fragment A arising from the dissection of a supermolecule A-B through the following computational procedure:

(1) we perform first a CI computation for the supermolecule A-B at the geometry of interest, including the NBC involving the fragment configurations associated with the relevant spectroscopic states and related CTC.
(2) then, we perform an MC-SCF computation with the fragments at infinite separation and with the coefficients of the various spectroscopic states associated with a given fragment from the previous CI computation. This procedure provides the orbital basis for the subsequent CI computation (1). In the first iteration the choice of the fragment orbital basis is not very critical: in our computations we have used the MC-SCF orbitals of the isolated fragments in their lowest spectroscopic states.
(3) we repeat (1) and (2) until the difference between the coefficients which define a fragment valence state in two successive iterations is less than 10^{-4}.

The decomposition scheme of the interaction energy between two interacting fragments in their appropriate valence states, involves the computation of the following total energy values and energy differences:

(1) The energy E_0 of the isolated fragments in their valence states.
(2) The energy E_1 corresponding to the antisymmetrized product of the configurations of the isolated fragments in their valence states. The difference between this energy computed at a given interfragment separation and the energy of the isolated fragments (E_o) gives the electrostatic and exchange repulsion energy at a given r_{AB};

$$\Delta E_{\mathrm{ES+EX}} = E_1 - E_0 \tag{2}$$

(3) The energy E_2, corresponding to the subsequent inclusion of the CTC and therefore associated with the full CI expansion. Thus the energy difference

$$\Delta E_{\mathrm{VAL}} = E_2 - E_1 \tag{3}$$

gives the stabilization due to "valence" charge transfer.

(4) The energy E_T, associated with the subsequent inclusion of orbital mixing between core and valence orbitals with the virtual orbitals and between core and valence orbitals. The following energy difference:

$$\Delta E_{\mathrm{CT+PL}} = E_T + E_2 \tag{4}$$

gives the energy associated with the orbital polarization and charge transfer effects.

The matrix elements for the CI calculations are computed using the Unitary Group method described by Hegarty and Robb [2]. The orbital polarization and charge transfer effects are computed in the same manner as in Ref. [1], using second order perturbative approximation to MC-SCF theory [3]. It is also possible to separate the contribution of charge transfer and polarization effects and further to decompose these into the various orbital pairs contribution.

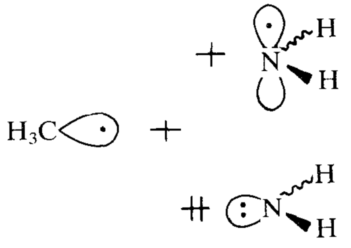
3. Applications

For illustrative purposes, in this section we describe the application of this procedure to the analysis of the factors controlling the conformational preference in methylamine. All computations have been performed at the STO-3G level [4], using for the computation of the SCF energy values the GAUSSIAN 80 series of programs [5].

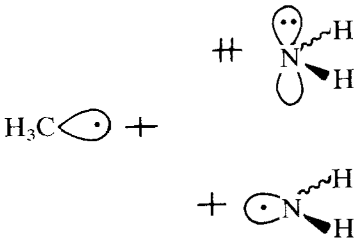
Methylamine has been dissected in the two fragments H_3C— and —NH_2. The H_3C fragment has only one valence orbital, a σ-type singly occupied orbital, and therefore the valence state here corresponds just to the spectroscopic state with a distorted geometry. For the H_2N fragment there are two valence orbitals, a σ and a p_π orbital and therefore two spectroscopic states, the ground B_1 state where the σ orbital is doubly occupied and the p-orbital singly occupied and the excited ${}^2A_1$ state where the occupations of the two orbitals are reversed. Therefore the valence state of the —NH_2 fragment in methylamine will be described as a linear combination of the two spectroscopic states

$$VS(NH_2) = C_1{}^2B_1 + C_2{}^2A_1 \tag{5}$$

The values of the two coefficients C_1 and C_2 have been computed using the procedure previously outlined. The computations have been performed at the staggered STO-3G optimized geometry. This CI problem involves the following two NBC



NBC I



NBC II

and four related CTC, with a total of six configurations.

Table 1. Valence State Coefficients (see Eq. (5)) for the NH$_2$ Fragment in the Staggered Conformation of Methylamine at the STO-3G geometry[a]

	C_1	C_2
Iteration 1	0.873381	0.487038
Iteration 2	0.660272	0.751026
Iteration 3	0.516309	0.856403
Iteration 4	0.505663	0.862731
Iteration 5	0.508224	0.861225
Iteration 6	0.507563	0.861615
Iteration 7	0.507733	0.861515

[a] See Ref. [6]

We have performed first an MC-SCF computation including only NBC I with the two fragments at a separation of 20 Å to determine the starting orbital basis. Then, with these orbitals, we have performed a CI computation in the space of the six configuration at the optimized geometry. The coefficients of the two NBC, properly renormalised, provide now a first estimate of the valence state coefficients C_1 and C_2. For this combination of the two NBC we have performed an MC-SCF computation with the two fragments at a separation of 20 Å. Again, with the resulting orbitals, we have performed the six configuration CI and determined two new values for C_1 and C_2. This procedure has been repeated till the difference between the values of the coefficients in two successive calculations is less than 10^{-4}. The values of C_1 and C_2 obtained at the various iterations are shown in Table 1.

For other conformations this procedure provides values of the coefficients very near but not exactly equal to the values listed in Table 1. However in a comparative analysis of various points of the same hypersurface it is convenient to use the same valence state for all points. The various energy values, and in particular the energy differences, are not very sensitive to slight changes in the valence state coefficients.

The results of the energy decomposition are listed in Table 2. The computations have been performed at three different geometries: (1) at the STO-3G staggered optimized geometry [6]; (2) at the eclipsed geometry obtained through a rigid

Table 2. Energy Decomposition Analysis for the Conformers and Rotational Barrier in Methyl-amine, Computed at the STO-3G Level

		Eclipsed		Barrier[b]	
	Staggered	Rig. Geom.	Opt. Geom.	Rig. Geom.	Opt. Geom.
E_0^a	−93.87446	−93.87446	−93.87351	0.000	0.596
E_1^a	−93.42749	−93.42272	−93.43287	2.993	−3.376
E_2^a	−94.03270	−94.02771	−94.03003	3.131	1.675
E_T^a	−94.05283	−94.04720	−94.04850	3.533	2.717
$\Delta E_{\text{ES+EX}}^b$	280.474	283.467	276.502	2.993	−3.972
ΔE_{VAL}^b	−379.769	−379.631	−374.718	0.138	5.051
$\Delta E_{\text{CT+PL}}^b$	−12.632	−12.230	−11.590	0.402	1.042

[a] Energy values in a.u.

[b] Energy values in Kcal/mol

rotation of the staggered conformer with optimized geometry and (3) at the STO-3G eclipsed optimized geometry [6]. Let we examine the various contributions to the rotational barrier which is given here by the difference E_T (Eclipsed) – E_T (staggered).

In the rigid model the largest contribution arises from the electrostatic and exchange repulsion energy (2.993 Kcal/mol) while those associated with the valence charge transfer (0.138 Kcal/mol) and with the orbital polarization and charge transfer effects (0.402) are significantly less important. These results are in good agreement with those obtained with the energy decomposition scheme suggested by Kitaura–Morokuma [7] and also with a quantitative *PMO* analysis [6].

The comparison with the results obtained in the optimized model shows that in the eclipsed conformation the geometry tends to change in order to reduce the large effect associated with the electrostatic and exchange repulsion energy. The comparison of the E_1 values obtained at the rigid and optimized eclipsed geometries shows a significant lowering of this energy term with geometry relaxation (6.27 Kcal/mol). This result is obtained mainly through a lengthening of the C—N bond and changes of the bond angles, which reduce the overlap between the mutually eclipsing bond MOs. However this energy variation is largely counterbalanced by the following effects which accompany the geometry relaxation:

(1) a destabilization of the various fragments MO's (0.59 Kcal/mol), as indicated by the increase of E_0;
(2) a decrease of the stabilizing effects associated with the valence charge transfer (4.91 Kcal/mol), as indicated by the trend of the ΔE_{VAL} values;
(3) a decrease of the stabilizing effects associated with the orbital polarization and charge transfer effects (0.64 Kcal/mol) as indicated by the trend of the $\Delta E_{\mathrm{CT+PL}}$ values.

Therefore, in the optimized model, the rationalization of the rotational barrier becomes much more complicated than in the rigid model, in agreement with previous suggestions [6]. All the various terms provide large contributions, some of opposite sign, so that the rotationale barrier results from large cancellations.

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