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Molecular interactions in a homogeneous electric field: the $(HF)_2$ complex

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Summary. The interaction energy of two HF molecules, subjected to a static external field, is analyzed. The analysis aims at the elaboration of simple expressions able to reproduce environmental and substitution effects on non-covalent molecular interactions.

Key words: Hydrogen bond – External electric field – BSSE corrections – Environmental effects

1 Introduction

A considerable part of the effects experienced by molecules in the laboratory and in the real world may be interpreted in terms of classical electric (and/or magnetic) fields acting on the molecular system. In some cases the description of the molecular system may be reduced to the classical level, in others a quantum description is necessary. The semiclassical approximation, i.e. the use of classical interactions on a quantum object, has a remarkable heuristic potentiality for the interpretation of chemical effects, and for this reason it represents the basis for many models in chemistry.

Formally the simplest category of interactions is that produced by static electric fields (SEF). The actual shape of a SEF representing a realistic interaction phenomenon may be rather complex (consider, for example, the fields necessary to describe biomolecular processes) but important insight may be obtained looking at the effect of fields of very simple shape, like that produced by a point charge, or that produced by an infinite uniformly charged plate.

In our past work we have often employed the examination of the effects of fields of complex shape giving realistic and detailed descriptions of local molecular effects [1], but in the present paper we consider the simple case of a constant electric field.

The main reason for this revisitation of a simple model lies in our interest in solvent reaction fields [2]. In our attempts to interpret solvation effects we have found profitable, for heuristic reasons, to also use simple models like that employed here [3]. The present report is thus focussed on some topics of interest for phenomena occurring in solution, and in particular those related to the effect of a SEF on the association properties of hydrogen bonded dimers.

The study is centred on the analysis of the components of the hydrogen bond energy, performed at the SCF level with basis sets (BSs) of moderate dimensions. The use of BSs of moderate dimensions is suggested by the size of the material systems to which this study is ultimately addressed: large molecular aggregate reaching the mesoscopic size, for which the use of large BSs is impossible. We shall supplement, however, the study with some calculations performed with larger BSs (vide infra). The results may be affected by the basis set superposition error (BSSE), and part of the paper is addressed to the examination of the *CP* correction to the BSSE, performed in the presence of an external field: little is known about the effect of a SEF on the BSSE. Interpretations of the effects due to the SEF on the association energy components and on the *CP* corrections to these components are searched, having in view the elaboration of models to be applied to classical fields of other origin and other shapes (e.g. fields in solution produced by biological membranes or polyions).

There is a large number of theoretical and computational papers considering the effects of SEFs on molecular systems, addressed to the study of a wide spectrum of problems.

We report in Refs. [4–38] a selection of papers having some points in common with the present research. This listing is very far from being complete, but in its variety should be sufficient to give bibliographical clues to the interested reader.

A part of these papers deals with the examination of the effects of external fields on the geometry [4–9] and on the electronic distribution [4–12] of isolated molecules. Some papers are more directly addressed to specific properties of the systems, like vibrations [13–17], photoionization [18], chemical shifts [17], light scattering [19], Stark effect [20], emission spectra [21].

Other papers of our bibliographical selection consider the behaviour of couples, or larger collections, of molecules under the action of an additional SEF (often that produced by a charged component of the material system); the attention is focussed on molecular interactions and chemical reactions [22–35] or on the collective properties of the matter in a condensed phase [36–38].

The theory of non-covalent interactions in the presence of static fields is generally cast in the form of perturbation theory with multipole expansion of the interaction [39–41]; we are not acquainted of systematic studies based on the analysis of variational *ab initio* calculations of the type performed here.

2 Methodological aspects

The main calculations have been performed with standard RHF procedures, followed by analyses, in which we have used transformations of the canonical MO's into localized ones (Boys LO's [42]), decomposition of the LO's into main component and secondary contributions; reformulation of the total energy E into LO components; decomposition of the interaction energy ΔE according to the Kitaura–Morokuma analysis [43], *CP* correction of ΔE and of its components for the BSSE.

All the methodological and computational features of the tools we have elaborated in the past to analyze inter- and intramolecular interactions, and we are using here, have been documented in previous papers. Since the reference to all the source papers is too long, we signal a recent review in which all the required information may be found [44].

The only point which has not explicitly been presented in preceding papers is the *CP* correction scheme to the ΔE components for a dimerization act in the presence of an external field. A short summary of the procedure we have adopted is reported here below.

It is conveneint to introduce the following notations:

$$\Delta E'_{AB}(R_{AB}) = E^{\mathrm{TOT}}(\vec{F}; \theta_A, \theta_B; \boldsymbol{R}_{AB}) - E'_A(\vec{F}; \theta_A) - E'_B(\vec{F}; \theta_B) \tag{1}$$

E'_A and E'_B are the energies of the monomers under the action of the homogeneous electric field $\vec{F}$; θ_A and θ_B denote the orientation of the two partners with respect to the electric field; $\boldsymbol{R}_{AB}$ denotes the mutual spatial position of A and B in AB. Remark that the isolated A and B have the same internal geometry and orientation with respect to $\vec{F}$ they exhibit in the dimer $AB(R_{AB})$. In other words, the reference energy in Eq. (1) is strictly related to the geometry and orientation of the dimer with respect to the electric field.

The definition of the interaction energy with a reference energy no longer dependent on the effect of the external field on the monomers is reported here below:

$$\Delta E(R_{AB}) = E^{\mathrm{TOT}}(\vec{F}; \theta_A, \theta_B; \boldsymbol{R}_{AB}) - E^{\circ}_A(F=0) - E^{\circ}_B(F=0) \tag{2}$$

E°_A and E°_B are computed at $|F| = 0$ and refer to the corresponding equilibrium geometry.

We may thus define a "relaxation energy":

$$\Delta E_{\mathrm{REL}} = [E'_A(\vec{F}, \theta_A) + E'_B(\vec{F}, \theta_B)] - [E^{\circ}_A + E^{\circ}_B] \tag{3}$$

with

$$\Delta E_{AB}(R_{AB}) = \Delta E'_{AB}(R_{AB}) + \Delta E_{\mathrm{REL}} \tag{4}$$

ΔE_{REL} measures the energetic effect of placing the monomers at a given orientation in the electric field, accompanied by changes in the nuclear equilibrium geometry and electron distribution.

$\Delta E'_{AB}$ alone is subjected to energy decomposition and to *CP* corrections to the BSSE. This definition parallels that we have given for the case in which the reaction act occurs in the presence of an electrostatic reaction field [3]; see Ref. [3] for a discussion about the congruence with the ΔE_{DEF} term introduced by Umeyama et al. in a different context [45].

The technique for the introduction of *CP* corrections to the individual components of $\Delta E'_{AB}$ is similar to that employed for dimers without external fields (see, e.g. [46]). The *CP* corrections may be thus summarized:

$$\Delta^{\mathrm{TOT}} = \Delta^{\mathrm{TOT}}_A + \Delta^{\mathrm{TOT}}_B \tag{5}$$

$$\Delta^{\mathrm{TOT}}_M = E'_M(\vec{F}, \theta_M; \chi_M) - E^{CP}_M(\vec{F}, \theta_M; \chi_{AB}) \tag{6}$$

$$\Delta^{\mathrm{TOT}}_M = \Delta^{\mathrm{EX}}_M + \Delta^{\mathrm{CT}}_M + \Delta^{I}_M + \Delta^{II}_M + \Delta^{III}_M + \Delta^{IV}_M + \Delta^{\mathrm{RES}}_M \tag{7}$$

where $M = A$ or B.

In Eq. (7) we have supplemented the KM partition [43] with the NYFK one [47]. The correction in Eq. (5) is computed by repeating the calculation on the monomer M at the same conditions, but using the monomeric basis set χ_M or the dimeric one χ_{AB}. The partial corrections in Eq. (7) are computed as energy differences on the monomer using the χ_M basis set and enlarged basis sets of different nature (see the source papers [46, 48]). Only Δ_M^{RES} is computed as a difference between Δ^{TOT} and the other six terms in Eq. (8). In many occasions the last five terms of Eq. (7) are collected in a unique term:

$$\Delta_M^{\mathrm{MIX}} = \Delta_M^{I} + \Delta_M^{II} + \Delta_M^{III} + \Delta_M^{IV} + \Delta_M^{\mathrm{RES}} \tag{8}$$

The expression of the interaction energy, after CP correction, is given by:

$$\begin{aligned} \Delta E_{AB}^{CP} &= \Delta E_{AB}^{\prime CP} + \Delta E_{\mathrm{REL}} = \Delta E'_{AB} + \Delta^{\mathrm{TOT}} + \Delta E_{\mathrm{REL}} \\ &= ES' + PL' + EX'^{CP} + CT'^{CP} + MIX'^{CP} + \Delta E_{\mathrm{REL}} \end{aligned} \tag{9}$$

The meaning of the energy components reported in the last part of Eq. (9) may be found in preceding papers [43, 46] and in the section of this paper devoted to the analysis of the results.

3 Calculations

The molecular model is composed by two HF monomers, kept at a fixed internal geometry ($r_{\mathrm{HF}} = 0.930$ Å). The reference disposition of the two monomers in the dimer is reported in Fig. 1.

We shall refer to a restricted selection of the numerical data at our disposal. In particular we shall limit ourselves to cases in which the electric field $\vec{F}$ is directed along the z axis, i.e. colinear with the proton acceptor (PA) monomer. The field $\vec{F}$ may be positive or negative.

The distance R between the two monomers is varied, as well as the orientation θ of the proton donor (PD) monomer.

The picture of the electric field effects on $(HF)_2$ given by this selection of data is clearly incomplete, but sufficient, in our opinion, to put in evidence the effects of larger importance in solvation and in non-covalent clustering interactions.

The calculations have been performed at the SCF level with the 4-31G, 6-31G** and the 6-311++G(3d, 2p) basis sets [49].

4 The components of the dimerization energy

We shall briefly examine here the effect of the field on the separate components of ΔE for the linear dimer ($\theta = 180°$). To save space, we shall report, as general rule, numerical values for only three values of the external field: +2.0, 0.0 and -2.0×10^8 Volt/cm.

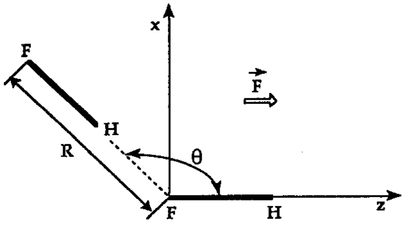

Fig. 1. Reference geometry and direction of the external field $\vec{F}$

Table 1. Values of the electrostatic contribution ES' computed at several intermolecular distances R, for three values of the external field $\vec{F}$. Values of the dipole-dipole approximation ES', at $F=0$[a]

	ES'			ES_{DD}
R	$F=+2.0$	$F=0.0$	$F=-2.0$	$F=0.0$
2.4	−17.56	−14.13	−11.29	−11.00
2.6	−12.88	−9.88	−7.20	−8.65
2.8	−9.89	−7.38	−5.03	−6.93
3.0	−7.87	−5.79	−3.79	−5.63
3.2	−6.42	−4.69	−3.01	−4.64
3.4	−5.32	−3.89	−2.47	−3.87
3.6	−4.47	−3.27	−2.07	−3.26
3.8	−3.79	−2.78	−1.76	−2.77

[a] The values refer to the 4-31G basis set. Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

4.1 Electrostatic component, ES'

The $ES'(R, \vec{F})$ contributions to ΔE, obtained with the 4-31G BS, are reported in Table 1. Positive fields correspond to more stabilizing values of the ES' component of ΔE, negative fields to less stabilizing values. For fields of small and intermediate strength $|F|$ these shifts of energy are symmetrical (to a good approximation) at every distance R: in other words the differences $ES(R, F_i) - ES(R, 0) = \Delta ES(R; F_i, 0)$ for the couples F_i and $-F_i$ are of the same magnitude. Asymmetries in the $\Delta ES(R; F_i, 0)$ values are evident in Table 1 for short distances. The origin of these asymmetries, according to the definition of the ES term, lies in the different behaviour of the monomer charge distribution under the effect of a reversal of the electric field.

It may be of some interest to check to what extent this asymmetry (or saturation effect) is reproduced by the first term of a multipole expansion of ES. The first term of this expansion, the dipole-dipole term, for $F=0$ is reported under the heading $ES_{DD}(R, 0)$ in Table 1. It turns out clear that the DD approximation is valid only at large distances and that it gives serious errors also near the equilibrium distance ($R \simeq 2.8$ Å). It is a well known fact that at short distances the multipole expansions are rather inaccurate [50] and the present test documents the numerical defects of the DD approximation in the present case. Table 2 gives us some data for our check. We report here the differences $\Delta ES(R; \pm 2.0)$ computed exactly and in the DD approximation for our three BS. The DD approximation describes the ΔES values for the $+2.0$ case better than for the -2.0 one, but a noticeable portion of the saturation is represented in any cases by the dipole term.

This analysis may be supplemented with the examination of the changes in the dipole moment of HF under the action of $\vec{F}$, reported in Fig. 2. The rate of change of μ near $F=0$ is directly related to the appreciation of the molecular polarizability given by the SCF method for our basis set (the figure also reports, for comparison, analogous values obtained with the other two basis sets); a deviation from linearity at the highest values of $|F|$ is evident, and this saturation effect is stronger for the positive values of the field.

Table 2. Comparison of the differences in the *ES'* term computed with and without an external field ($F = \pm 2.0 \times 10^8$ Volt/cm) and the corresponding differences computed in the dipole-dipole approximation[a]

		$\Delta ES'(F, 0)$		$\Delta ES'_{\mathrm{DD}}(F, 0)$	
Basis Set	*R*	$F = +2.0$	$F = -2.0$	$F = +2.0$	$F = -2.0$
4-31G	2.6	−2.52	2.35	−2.94	2.97
	3.0	−2.08	2.00	−1.91	1.93
	3.4	−1.43	1.42	−1.32	1.33
6-31G**	2.6	−3.10	2.47	−2.95	2.70
	3.0	−2.12	1.84	−1.92	1.76
	3.4	−1.46	1.30	−1.32	1.21
6-311++G(3*d*, 2*p*)	2.6	−4.04	2.74	−3.77	3.18
	3.0	−2.75	2.05	−2.45	2.03
	3.4	−1.86	1.57	−1.69	1.39

[a] Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

The change in the dipole moment of HF may be decomposed into submolecular components. In our model, the use of a fixed nuclear geometry makes this analysis easier: it is sufficient to look at the displacement of the LO charge centres. The data of interest are summarized in Table 3. The change in μ is almost completely supported by the σ_{FH} orbital: the lone pairs have a lower polarizability than the σ bonds [2, 44].

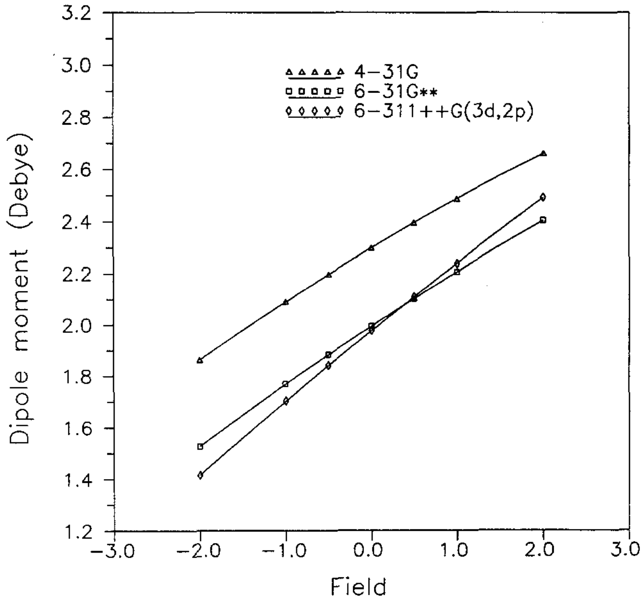

Fig. 2. Changes of the dipole moment induced by the external field $\vec{F}$ (in 10^8 Volt/cm)

Table 3. Shift in the position of the charge centres of two localized orbitals of HF. The σ HF bond, and one of three equivalent F lone pairs due to the effect of $\vec{F}$ (values in Å)

		$F = +2.0$		$F = -2.0$	
Basis set	LO	$\langle \Delta z \rangle$[a]	$\langle \Delta r \rangle$[b]	$\langle \Delta z \rangle$[a]	$\langle \Delta r \rangle$[b]
4-31G	σ_{HF}	−0.023	−0.023	0.026	0.026
	l_F	−0.006	0.001	0.006	−0.002
6-31G**	σ_{HF}	−0.021	−0.021	0.025	0.025
	l_F	−0.007	0.002	0.007	−0.001
6-311++G(3*d*, 2*p*)	σ_{HF}	−0.023	0.023	0.029	0.025
	l_F	−0.011	0.004	0.011	−0.003

[a] Component of the position vector along the z axis

[b] Modulus of the position vector. In both cases a negative value corresponds to a shorter distance from the fluorine atom

Another index of the polarizing effect of the field on the monomer is given by the difference between the energies of occupied and non-occupied MOs of σ symmetry. In our case (molecule and field colinear) the polarization is supported by the σ subsystem of charges, and may be viewed as a mixing of σ and σ^* orbitals. A simple numerical index is given by the difference $\Delta\varepsilon_\sigma = \varepsilon_6 - \varepsilon_3$ between the lowest unoccupied and the highest occupied orbital of σ symmetry. ε_3 is almost constant (as well as ε_2) over the whole range of $\vec{F}$, while ε_6 steadily increases with the increase of F (see Fig. 3). There is a good linear relationship between $\Delta\mu(F)$ and $\Delta\varepsilon_\sigma(F)$ over the entire range. Table 4 extends this comparison to the other two basis sets.

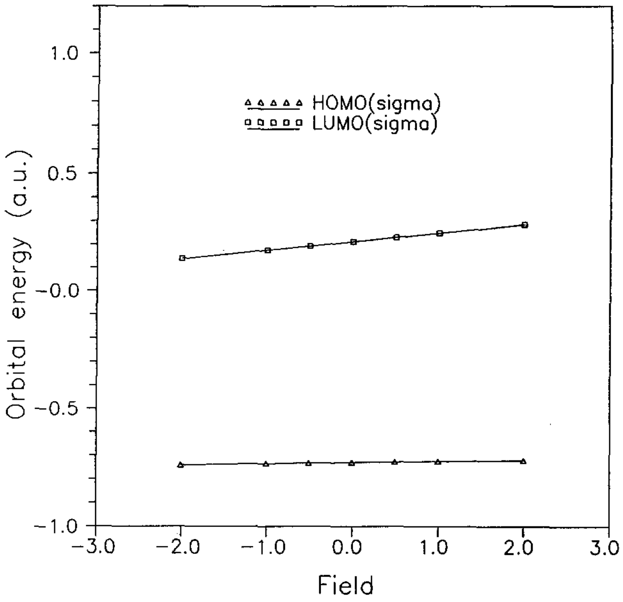

Fig. 3. Changes of the orbital energies of the ε_3 and ε_6 orbitals of HF induced by the external field $\vec{F}$. 4-31G calculations; orbital energies in atomic units (1 a.u. = 627.509 kcal/mol); electric field in 10^8 Volt/cm

Table 4. Orbital energy difference $\Delta\varepsilon_\sigma = \varepsilon_6 - \varepsilon_3$ between the lowest unoccupied and the highest occupied orbital of σ symmetry in the HF monomer, in function of the applied field $\vec{F}$ [a]

	F						
Basis Set	2.0	1.0	0.5	0.0	−0.5	−1.0	−2.0
4-31G	1.0064	0.9731	0.9568	0.9407	0.949	0.9093	0.8791
6-31G**	1.0190	0.9856	0.9694	0.9525	0.9362	0.9200	0.8883
6-311++G(3*d*, 2*p*)	0.8714	0.8472	0.8289	0.8081	0.7856	0.7619	0.7122

[a] Energies in hartrees, electric field in 10^8 Volt/cm

We may conclude that linear relationships among the quantities considered in this section, ES', μ, $\Delta\varepsilon$, etc. may be safely exploited in modelling environmental effects on the properties of a molecule and of a biomolecular system.

4.2 The polarization component PL'

In our definition of CP corrections, the polarization term PL as well as the rigid electrostatic term, ES, are not subjected to CP corrections. The practical reasons supporting this choice have been expressed in other occasions, see e.g. Ref. [50]. The choice of the reference system reported in Eq. (1) makes ES' and PL' numerically different from their counterparts, ES and PL, computed in the absence of an external field.

A set of numerical values of $PL'(R, F)$ for $F = \pm 2.0 \times 10^8$ Volt/cm are reported in Table 5. Positive values of the field correspond to more negative contributions to the binding energy, and conversely negative values of $\vec{F}$ correspond to less negative contributions to ΔE_{AB}, in agreement with intuition. The interacting monomers are in fact already polarized by the field, and what we are

Table 5. Values of the polarization contribution, PL', computed at different intermolecular distances, for three values of the external field $\vec{F}$ [a]

	PL'		
R	$F = +2.0$	$F = 0.0$	$F = -2.0$
2.4	−2.04	−1.86	−1.77
2.6	−1.10	−0.93	−0.75
2.8	−0.65	−0.54	−0.40
3.0	−0.41	−0.34	−0.25
3.2	−0.26	−0.22	−0.17
3.4	−0.18	−0.15	−0.12
3.6	−0.12	−0.11	−0.08
3.8	−0.09	−0.07	−0.06

[a] The values refer to the 4-31G basis set. Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

looking for here is an additional polarization effect due to the presence of the second monomer.

We may check to what extent this additional polarization is described by the first terms of a multipole expansion of the polarization energy. The induction term for two polarizable dipoles, with polarizability α, may be reduced in our special case (two identical colinear dipoles) to the following simple expression (see, e.g. Refs. [51] and [52])

$$E_{\text{ind}}^{\text{DD}} = -4[(\mu^*)^2\alpha]R^{-6}$$

in which the asterisk indicates that the dipole moment of the monomer feels the effect of $\vec{F}$.

The ratio of this expression, for two values of the external field, F and 0:

$$E_{\text{ind}}^{\text{DD}}(F)/E_{\text{ind}}^{\text{DD}}(0) = [\mu^*(F)/\mu^*(0)]^2$$

may be compared with the corresponding ratio:

$$PL'(F)/PL'(0)$$

The comparison is reported in Table 6. In this table we have reported the value for $PL'(F)/PL'(0)$ at $R = 3.0$ Å: the dependency on R of this ratio is in fact quite limited.

There is a large variation in the $[\mu^*(F)/\mu^*(0)]^2$ function over the range of $\vec{F}$ values, which reflects the effect of the external field on the monomer's charge distribution. This variation is fairly well respected by the $[PL'(F)/PL'(0)]$ function, with deviations of not negligible extent only at the two extrema, $F = +2.0$ and -2.0×10^8 Volt/cm (respectively 12% and 15% for the 4-31G basis set).

The 6-31G** and 6-311++G(3*d*, 2*p*) calculations lead to similar conclusions: for external fields of strength comparable to those found in solution or in molecular aggregations, the non-linear term in the polarization energy plays a minor role, and it seems safe to elaborate numerical models based on the linear first order description.

Table 6. Comparison of $PL'(\vec{F})/PL'(0)$ with $(\mu^*(\vec{F})/\mu^*(0))^2$

		F^{a}						
Basis Set		2.0	1.0	0.5	0.0	−0.5	−1.0	−2.0
4-31G	$PL'(\vec{F})/PL'(0)$	1.18	1.10	1.05	1.00	0.95	0.89	0.76
	$(\mu^*(\vec{F})/\mu^*(0))^2$	1.34	1.17	1.09	1.00	0.91	0.83	0.66
6-31G**	$PL'(\vec{F})/PL'(0)$	1.32	1.16	1.08	1.00	0.92	0.84	0.68
	$(\mu^*(\vec{F})/\mu^*(0))^2$	1.45	1.22	1.10	1.00	0.89	0.79	0.59
6-311++G(3*d*, 2*p*)	$PL'(\vec{F})/PL'(0)$	1.48	1.21	1.09	1.00	0.81	0.81	0.69
	$(\mu^*(\vec{F})/\mu^*(0))^2$	1.59	1.28	1.14	1.00	0.87	0.74	0.51

[a] Electric field in 10^8 Volt/cm

Table 7. Values of the repulsion-exchange contribution EX'^{CP}, computed at different intermolecular distances, for three values of the external field $\vec{F}$ [a]

	EX'^{CP}		
R	$F=+2.0$	$F=0.0$	$F=-2.0$
2.4	13.80	16.14	19.77
2.6	5.59	6.73	8.58
2.8	2.24	2.79	3.72
3.0	0.87	1.14	1.60
3.2	0.33	0.45	0.68
3.4	0.12	0.18	0.28
3.6	0.04	0.07	0.11
3.8	0.01	0.03	0.04

[a] The values refer to the 4-31G basis set. Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

4.3 The exchange-repulsion contribution EX'^{CP}

The repulsive contribution deriving from the exchange terms of the interaction energy is responsible to a good extent for the value assumed by the intermonomer distance at equilibrium.

The effect of fields of intensity $\pm 2.0 \times 10^8$ Volt/cm on EX'^{CP} at different distances are shown in Table 7. This contribution is more repulsive (positive) for negative values of the external field.

For the interpretation we may resort again to the examination of the effects of $\vec{F}$ on the charge distribution of the monomers. The data about the effects of $\vec{F}$ on the electron distribution reported on occasion of the discussion of the ES' term, show that there is a remarkable difference in the charge shifts of the σ bond LO and of the F lone pair LOs. The same set of data may be used here to put in evidence some quantitative relationships. Figure 4 depicts the spatial relationships between the LOs of the two monomers which are of interest here.

The change of the $D_{\sigma l}$ distances in function of $\vec{F}$ is reported in Fig. 5. The relationship is linear (in both basis sets). Also the relationship between the overlap $S_{\sigma l} = \langle \sigma_{\mathrm{FH}}(\mathrm{PD}) \mid l_F(\mathrm{PA}) \rangle$ and $\vec{F}$ is linear (see Fig. 6).

The distance $D_{\sigma l}$ and the overlap $S_{\sigma l}$ have a linear relationship with EX'^{CP}: see Fig. 7.

The data displayed in Figs. 5–7 refer to $R = 2.8$ Å, but analogous values are found for other distances. Small deviations are present only at $R = 2.4$ Å.

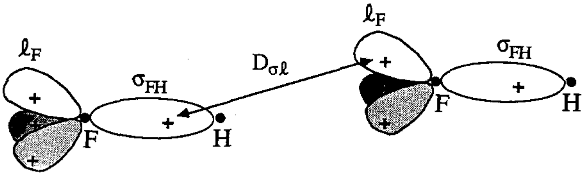

Fig. 4. Definition of the distance $D_{\sigma l}$ between the electronic charge centres of the bonding σ LO of the Proton Donor and one of the F lone pairs of the Proton Acceptor monomer

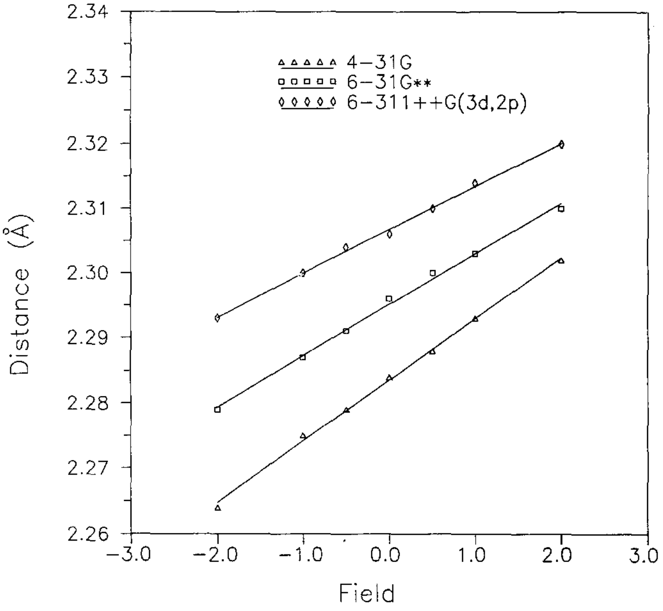

Fig. 5. Correlation between the values of $D_{\sigma l}$ and of $\vec{F}$. Regression coefficients: 4-31G $r = 1.000$; 6-31G** $r = 0.997$; 6-311++G(3d, 2p) $r = 0.992$. $R = 2.8$ Å

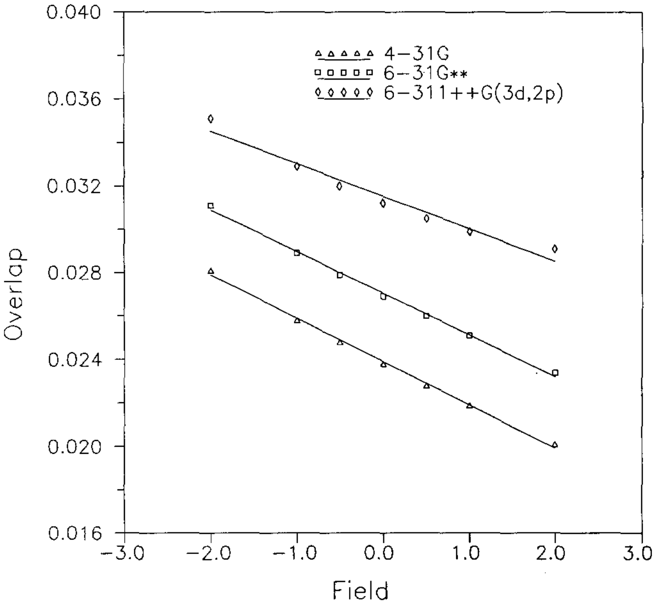

Fig. 6. Correlation between the values of $S_{\sigma l}$ and of $\vec{F}$. Regression coefficients: 4-31G $r = 0.999$; 6-31G** $r = 0.999$; 6-311++G(3d, 2p) $r = 0.980$

The formal relationship between *EX* and the charge overlap has been presented on different occasions, see e.g. van Duijneveldt [53], Daudey et al. [54]. What we have presented here is a numerical example of the use of these simple concepts with the additional suggestion of using $D_{\sigma l}$, or $S_{\sigma l}$, as a measure of the total charge overlap between the two monomers. To summarize, in this case again simple models based on the change of the overlap, or of the distance

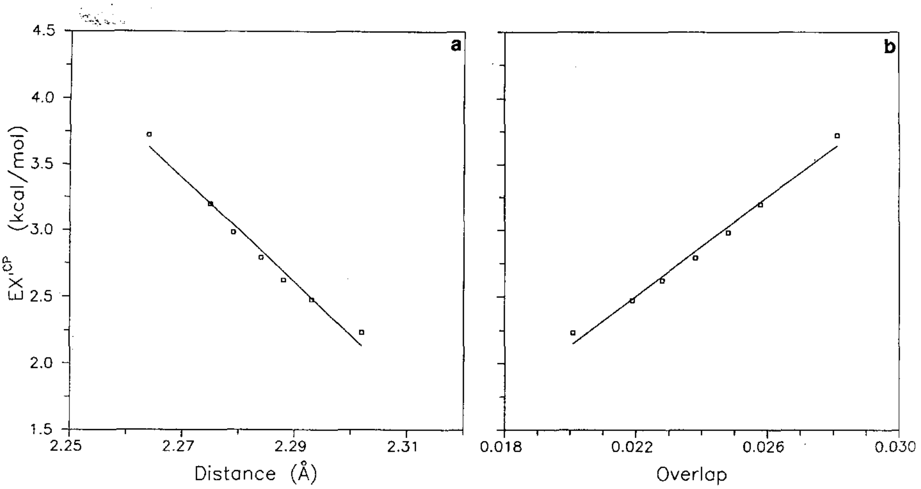

Fig. 7. Correlation between EX'^{CP} and: (a) $D_{\sigma l}$; (b) $S_{\sigma l}$. 4-31G calculations. Regression coefficients: (a) $r = 0.991$; (b) $r = 0.996$

between appropriate charge centres, may be used to model repulsion interactions and the changes produced by the environment.

4.4 The charge-transfer component CT'^{CP}

The values of CT'^{CP} at different distances for three values of F, $+2.0$, 0.0, -2.0×10^8 Volt/cm, are reported in Table 8.

Positive values of the field produce higher charge transfer contributions. The influence of $\vec{F}$ on the charge transfer process may be related to the change of the HOMO(σ)–LUMO gap in the proton acceptor–proton donor couple of molecules ($\Delta\varepsilon_{63} = \varepsilon_6(PD) - \varepsilon_3(PA)$).

Table 8. Values of the charge-transfer contribution CT'^{CP}, computed at different intermolecular distances, for three values of the external field $\vec{F}$ [a]

	CT'^{CP}		
R	$F = +2.0$	$F = 0.0$	$F = -2.0$
2.4	−5.35	−4.19	−4.07
2.6	−3.73	−2.56	−2.15
2.8	−2.66	−1.67	−1.25
3.0	−1.79	−1.06	−0.74
3.2	−1.15	−0.65	−0.42
3.4	−0.71	−0.38	−0.23
3.6	−0.42	−0.21	−0.12
3.8	−0.24	−0.11	−0.06

[a] The values refer to the 4-31G basis set. Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

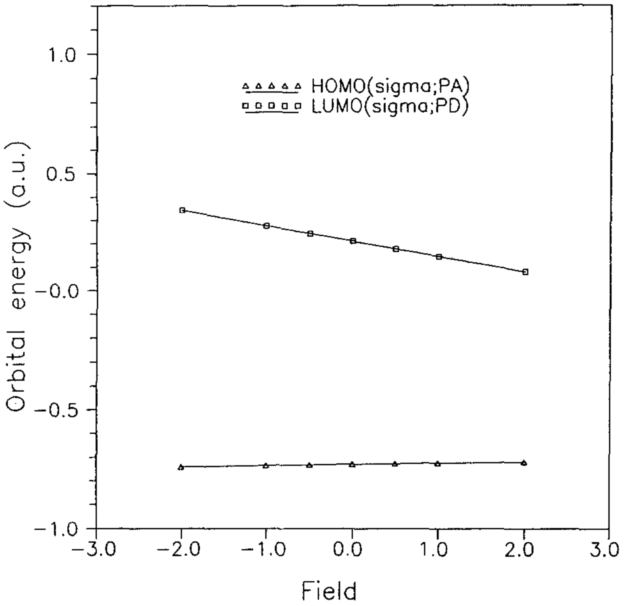

Fig. 8. Changes of the $\varepsilon_3(PA)$ and of the $\varepsilon_6(PD)$ orbital energies induced by the external field. 4-31G calculations at $R = 2.8$ Å. Orbital energies in atomic units; electric field in 10^8 Volt/cm

The trend of these changes is reported in Fig. 8. The effect of the field on the orbital energy of the occupied (PA) orbital is relatively small, as we have remarked above, but the shift of the virtual PD orbital is remarkable, and almost linear with the field. Remark that the trend of the $\varepsilon_6(PD)$ shift presented in Fig. 8 is the opposite of the ε_6 shift of the monomer displayed in Fig. 3. This apparent contradiction may be easily resolved if one considers that we are here considering the energy of a charged subunit (the electrons described by the MO in question) localized over a molecule different from that of the reference unit, the proton acceptor monomer. The system may be assimilated to a couple of electrons put in two separate boxes of given length d, subjected to a constant field $\vec{F}$ and placed at a fixed distance R (see e.g. Ref. [55]).

The data reported in Fig. 8 fit quite well the first order description of this model. The functional dependences of $\varepsilon_n(R, d)$ upon the two parameters, $\vec{F}$ and R, are linear with regression coefficients $r > 0.9999$. Table 9 extends this comparison to the two other basis sets.

A direct linear relationship between $CT(R, F)$ and $[\Delta\varepsilon_{63}(R, F)]^{-1}$ implies that in the perturbation theory expression of the CT energy contribution (see e.g. [43, 56, 57]) the double sums over occupied and virtual orbitals may be reduced to a single term, and that for this term only the changes in the denominator are important. The relationship between $CT(R, F)$ and $[\Delta\varepsilon_{63}(R, F)]^{-1}$ is represented by a linear expression with a regression coefficient $r = 0.985$, where the deviations – which are symmetric – are evident only at the extreme values of F: $\pm 2.0 \times 10^8$ Volt/cm.

More complex expressions, involving changes in the numerator (overlap, two electron matrix elements [57, 58]) do not improve the correlation.

Table 9. Orbital energy difference $\Delta\varepsilon_{63} = \varepsilon_6(PD) - \varepsilon_3(PA)$ between the lowest unoccupied orbital of the proton donor and the highest occupied orbital of the proton acceptor (σ symmetry), in function of the applied field $\vec{F}$ [a]

	F						
Basis Set	2.0	1.0	0.5	0.0	−0.5	−1.0	−2.0
4-31G	0.801	0.870	0.905	0.941	0.976	1.012	1.085
6-31G**	0.813	0.822	0.918	0.952	0.988	1.023	1.094
6-311++G(3*d*, 2*p*)	0.666	0.744	0.777	0.808	0.837	0.865	0.918

[a] Energies in hartrees, electric field in 10^8 Volt/cm

4.5 The mixing contribution MIX'

The MIX'^{CP} values are comparable, but of opposite sign with respect to the corresponding PL' values, over the whole range of F values (compare Tables 10 and 5). For other conformations and other basis sets the compensation between PL' and MIX'^{CP} values is looser, and we do not assign a physical meaning to the numerical correlation found in the present case.

MIX'^{CP} may be divided into several contributions: E_I, E_{II}, E_{III} and E_{IV} (see Sect. 2 and Refs. [47, 48]). These contributions have been interpreted as mixing between CT and PL terms. We do not present an analysis of their dependence on the external field F, because it would burden the presentation with details of scarce importance, because the single contributions are quite small.

Table 10. Values of the polarization-charge transfer coupling and of the residual term MIX'^{CP}, computed at several intermolecular distances R, for three values of the external field $\vec{F}$ [a]

	MIX'^{CP}		
R	$F = +2.0$	$F = 0.0$	$F = -2.0$
2.4	1.50	1.24	1.15
2.6	1.21	0.82	0.73
2.8	0.96	0.62	0.50
3.0	0.68	0.43	0.33
3.2	0.44	0.27	0.20
3.4	0.27	0.16	0.11
3.6	0.16	0.08	0.06
3.8	0.09	0.04	0.03

[a] The values refer to the 4-31G basis set. Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

4.6 *Non-linear geometries*

The detailed analysis done for the linear dimer ($\theta = 180°$) seems to us sufficient to show that it is possible to get a rationale of the effects of an external field on the dimerization energy based on simple concepts. We have repeated the calculations, and the analyses, for a set of θ values, from $\theta = 180°$ to $\theta = 90°$. The conclusions are similar, but the exposition would be a little longer, because for non-linear geometries one has to separate the perpendicular and the parallel component of $\vec{F}$. A specimen of analysis at $\theta \neq 180°$ has been reported in Refs. [44] and [59]. The results make stronger our feeling that interpretation and modelization of electric field effects may be easily performed using simple concepts and easy-to-compute quantities.

We have also performed a more limited number of calculations over non-linear dimers with $\vec{F}$ colinear with the proton donor monomer, and the results again confirm our conclusions.

5 Effect of the external field on the *CP* corrections

We report in Table 11 the values of the *CP* correction Δ^{TOT} and of its components for three values of $\vec{F}(+2.0, 0.0, -2.0 \times 10^8$ Volt/cm) at a fixed distance: $R = 2.80$ Å. The values of the table refer to two conformations $\theta = 180°$ and $\theta = 110°$ (4-31G calculations). The corrections are higher for the bent conformation (especially those belonging to the monomer A, the proton acceptor) and increase for the positive values of $\vec{F}$.

In both conformations the changes in the corrections are of opposite sign for the A (proton acceptor) and B (proton donor) monomers.

A positive field $\vec{F}$ shifts the electrons of A towards the space occupied by the molecule B (and by the ghost orbitals belonging to B): the *CP* correction is thus

Table 11. Values of the *CP* correction to the energy, and of its components, computed for three values of the external field $\vec{F}$ and two values of the angle θ, at $R = 2.80$ Å [a]

	$\theta = 180°$			$\theta = 110°$		
	$F = +2.0$	$F = 0.0$	$F = -2.0$	$F = +2.0$	$F = 0.0$	$F = -2.0$
Δ^{TOT}	2.01	1.24	0.94	2.50	2.06	1.79
Δ^{EX}	0.18	0.14	0.13	0.22	0.20	0.19
Δ^{CT}	0.80	0.45	0.30	0.94	0.76	0.65
Δ^{MIX}	1.04	0.65	0.51	1.35	1.10	0.95
Δ_A^{TOT}	1.66	0.85	0.43	2.12	1.65	1.31
Δ_A^{EX}	0.11	0.07	0.05	0.15	0.13	0.11
Δ_A^{CT}	0.70	0.34	0.15	0.84	0.65	0.52
Δ_A^{MIX}	0.85	0.44	0.22	1.13	0.87	0.68
Δ_B^{TOT}	0.35	0.38	0.52	0.39	0.47	0.48
Δ_B^{EX}	0.07	0.07	0.08	0.08	0.07	0.08
Δ_B^{CT}	0.09	0.11	0.15	0.10	0.11	0.13
Δ_B^{MIX}	0.18	0.21	0.28	0.22	0.23	0.27

[a] The values refer to the 4-31G basis set. Values in kcal/mol. A is the proton acceptor (PA) monomer

higher. The opposite holds for the monomer B. A reversal of the sign of $\vec{F}$, also reverses the changes in the *CP* corrections. The general trend agrees with the results obtained by Loushin and Dykstra by applying thier polarization counterpoise correction (PCC) [32, 60]. This procedure introduces *CP* corrections to ΔE_{AB} in the usual way, but starting from monomers which feel, at each $\boldsymbol{R}_{AB}$, the field created by the partner. This static electric field (SEF) is not uniform, and in actual calculations may be replaced with the field originated by a set of charges and multipoles, as detailed in Refs. [32, 60]. The motivations supporting the PCC method may be found in the already quoted references; they are different from those giving origin to this study. It rests that for the $(HF)_2$ case, also used by Dykstra and coworkers as a test case, the SEF used in PCC calculations is not far, for a selected range of θ angles, from a uniform $\vec{F}$ of appropriate strength. The numerical results of Ref. [60] are qualitatively reproduced by our calculations.

6 Effect of the external field on the equilibrium geometry of the dimer

We have to consider here the combination of two effects, the first of physical origin, the inclusion in the model of an external field $\vec{F}$, the second of computational origin, the inclusion of *CP* corrections.

The equilibrium distance R and the equilibrium interaction energies without and with *CP* corrections are reported for a set of seven values of $\vec{F}$, in Table 12. The effect of $\vec{F}$ on the geometry is a little larger when appreciated using *CP* values; the effect of the *CP* correction on R is relatively more important at negative than at positive fields.

The percent change of the equilibrium energy deriving from the introduction of the *CP* corrections is almost constant for all the values of the field, in the case of 4-31G and 6-31G** calculations: the relatively smaller corrections to 6-311++G(3*d*, 2*p*) stabilization energies depend on the intensity and direction of the field.

On the whole, the effect of *CP* corrections appear to be little dependent on the value of the applied field, mainly when it stabilizes the dimer (i.e. positive values of $\vec{F}$).

Non-covalent interactions have in general local character [61] which is exploited in molecular modelling studies. It is gratifying to remark that *CP* corrections are not strongly influenced by external fields (i.e. by non local components of the system).

The external field has, on the contrary, a remarkable effect on the equilibrium angle. We investigated the dependence of the equilibrium angle only for positive values of $\vec{F}$, because negative values correspond to unstable bent conformations. The field necessary to get a linear equilibrium conformation is $F_z = 0.21 \times 10^8$ Volt/cm according to 4-31G calculations and 0.38×10^8 Volt/cm according to 6-31G** calculations.

To complete the picture we report in Table 13 some numerical values concerning ΔE_{REL} (see Eq. (3)). These data refer again to the colinear ($\theta = 180°$) model. Each value is twice as much as the relaxation energy of the monomer. We have not considered in this paper the changes in the internal geometry of the monomer, and the effect is thus related to the electronic contribution alone. The asymmetry between positive and negative values of F we have signalled several times in Sect. 4, is here well evident. In our model ΔE_{REL} simply measures a shift

Table 12. Values of the equilibrium distance without and with *CP* corrections, and the corresponding interaction energies, computed for several values of the external field[a]

4-31G				
F	R_{eq}	R_{eq}^{CP}	$\Delta E'(R_{eq})$	$\Delta E'^{CP}(R_{eq}^{CP})$
2.0	2.55	2.58	−13.25	−10.92
1.0	2.62	2.65	−10.16	−8.41
0.5	2.66	2.70	−8.79	−7.27
0.0	2.70	2.77	−7.53	−6.20
−0.5	2.76	2.80	−6.38	−5.23
−1.0	2.81	2.87	−5.34	−4.34
−2.0	2.93	3.02	−3.58	−2.85
6-31G**				
F	R_{eq}	R_{eq}^{CP}	$\Delta E'(R_{eq})$	$\Delta E'^{CP}(R_{eq}^{CP})$
2.0	2.62	2.65	−10.08	−8.24
1.0	2.72	2.76	−7.18	−5.93
0.5	2.77	2.82	−5.95	−4.94
0.0	2.83	2.88	−4.86	−4.06
−0.5	2.91	2.95	−3.91	−3.28
−1.0	2.98	3.03	−3.09	−2.60
−2.0	3.17	3.22	−1.80	−1.49
6-311++G(3*d*, 2*p*)				
F	R_{eq}	R_{eq}^{CP}	$\Delta E'(R_{eq})$	$\Delta E'^{CP}(R_{eq}^{CP})$
2.0	2.64	2.65	−8.42	−7.91
1.0	2.76	2.78	−5.70	−5.30
0.5	2.83	2.85	−4.60	−4.23
0.0	2.90	2.92	−3.66	−3.32
−0.5	2.99	3.03	−2.86	−2.55
−1.0	3.08	3.14	−2.20	−1.91
−2.0	3.30	3.42	−1.19	−0.96

[a] Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

in the reference energy and does not deserve further comments: it will be sufficient to remark that it is little dependent on the basis set. There are other possible models in which quantities similar to ΔE_{REL} play a specific role: should this be the case, an interpretation of ΔE_{REL} could be given, without much difficulty.

7 Conclusions

We have reported and analyzed a set of numerical data regarding the interaction energy ΔE_{AB} in a H-bonded dimer, subjected to a uniform static electric field.

Table 13. Values of Δ_{REL} computed for several values of the external field[a]

F	4-31G	6-31G**	6-311++G(3d, 2p)
2.0	−47.72	−42.31	−42.96
1.0	−22.99	−20.18	−20.18
0.5	−11.27	−9.83	−9.83
0.0	0.00	0.00	0.00
−0.5	10.79	9.31	9.17
−1.0	21.03	18.09	17.68
−2.0	40.09	33.93	32.67

[a] Energies in kcal/mol, electric field in 10^8 Volt/cm

The attention has been focussed on the components of ΔE_{AB}, on the *CP* corrections to the BSS error, and on the suggestions these analyses offer to a better modelling of the components of the interaction in non-covalently bonded molecular systems, and of the solvent effect in the case of polar solvents. Though addressed to computations performed with a basis set of small size, the analyses reported here have shown their validity when applied to large basis set calculations. To document more explicitly the effects of $\vec{F}$ on the decomposition of ΔE at different distances, we present in Table 14 a synopsis of Tables 1, 5, 7, 8, 10 referred to the 6-311++G(3d, 2p) basis set.

The paper documents the "analytic stage" of a research program addressed to understand molecular interactions and to model them for more extensive calculations. The "analytic stage" has not been limited to the cases reported here, and it has been followed by a partial use in models applied to other problems. The conclusions have thus a support stronger than that shown here.

The main conclusion of the analysis is that for all the domains of the field strengths examined here, the effects are well represented by their first order approximations. This means that in most cases the effect of a SEF on the energy components is linear, though in principle these effects are not linear; of course in some cases the first order description is not linear in the parameter adopted for its modelling. The parameters we have considered are of very simple nature, some of current use in other models (charges, local dipoles, first order polarizabilities, etc.), others of direct intuitive meaning as the distance between the charge centres of two local electron distributions, or the spatial shift of a charge distribution.

The correlations are of good quality and, as already said, some of the indexes have been already employed in other types of SEF for the interpretation as well as for the prediction of external field effects.

Every interpretation is related to a model: in our case the model has the semiclassical description of the interactions at the submolecular level [44, 59] as a basic component. The success of an interpretation strengthens the confidence in the model, and in some cases also enlarges the limits of validity of the model itself.

The study reported here seems to give positive contributions to both aspects: increase in the confidence and enlargement of the range of validity.

The use of an external field with fixed shape makes possible systematic surveys, that are not so easy and not so clear when limited to fields deriving from specific molecular cases; the range of $\vec{F}$ values we have spanned is larger than

Table 14. Decomposition of $\Delta E'$ at different distances R, for three values of the external field $\vec{F}$, computed with the 6-311++G(3*d*, 2*p*) basis set[a]

	$F = +2.0$	$F = 0.0$	$F = -2.0$
R		ES'	
2.6	−10.60	−6.56	−3.82
3.0	−6.64	−3.89	−1.84
3.4	−4.52	−2.64	−1.17
R		PL'	
2.6	−2.74	−2.17	−2.25
3.0	−0.84	−0.57	−0.40
3.4	−0.32	−0.21	−0.12
R		EX'^{CP}	
2.6	6.62	7.28	9.06
3.0	1.20	1.33	1.83
3.4	0.21	0.24	0.38
R		CT'^{CP}	
2.6	−2.87	−2.17	−2.11
3.0	−0.75	−0.41	−0.34
3.4	−0.29	−0.14	−0.11
R		MIX'^{CP}	
2.6	1.71	1.63	2.27
3.0	0.34	0.24	0.27
3.4	0.12	0.07	0.06

[a] Energies in kcal/mol, distances in Å, electric field in 10^8 Volt/cm

that related to fields of molecular origin present in most applications of actual chemical interest. Three areas of applications are particularly promising: interactions in solution, molecular aggregation problems, and chemical substitution effects.

Each area will exploit in a distinct manner the relationships suggested by this study: *solvation*, the description of solute-solvent interaction via the use of solvent reaction fields derived from continuum effective molecular Hamiltonians (see e.g. Refs. [3, 62]); *molecular clustering*, via the use of effective two-body interaction potentials modulated by external fields; *chemical substitution effects*, via the introduction of the "substituent field" [1, 44, 59] in the evaluation of weak molecular interactions.

In all cases the application will represent refinement of a first-order approximation for which there are already available working computational models. It rests to the researcher to judge what chemical problems require a more refined modelling.

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