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Interaction energy calculation scheme employing one-electron Hamiltonian approximation for the evaluation of short-range interactions

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A semiempirical scheme for the calculation of intermolecular energy is presented. A distinctive feature of the scheme is the employment of the one-electron Hamiltonian approximation in EHT parametrization for the calculation of exchange repulsion and charge transfer energies. Electrostatic, induction and dispersion components are calculated according to known approximate formulas containing point multipole moments and bond polarizabilities. The proposed scheme is applied to the calculation of binding energies and equilibrium geometries of various molecular dimers.

Key words: Intermolecular interactions—semiempirical methods—calculations of molecular dimers

1. Introduction

Semiempirical interaction calculations are mostly performed by perturbation methods which allow the evaluation of separate contributions to the total interaction energy ΔE (e.g. electrostatic, exchange repulsion, dispersion etc.). It is possible to estimate all the contributions to ΔE within the framework of some NDO method. But the calculations of the ΔE components via approximate formulas containing semiempirical or experimental parameters are more widely used and seem to be more effective [1–9].

In these calculations the electrostatic contribution, ES, is usually approximated by interactions of point multipole moments calculated for each of the interacting molecules semiempirically [1, 3, 9] or from *ab initio* wave functions [5, 6].

Using experimental bond polarizabilities the dispersion energy, DISP, is calculated as a sum of bond–bond interactions [1, 7, 8]. Similar approximations are used for the induction energy, IND, calculation [1, 7].

The exchange repulsion term, EX, is estimated as a sum of atom–atom or bond–bond interactions which vary exponentially with the intermolecular distance [1, 5, 10, 11]. Simplified formulas are also applicable for the charge transfer energy, CT, calculations [6, 11]. On the whole the methods for an approximate evaluation of EX and CT are less developed than those for the calculation of long-range components.

In the present paper a scheme is proposed which combines the calculation of long-range contributions by above mentioned methods [1, 7, 9] with the application of the one-electron Hamiltonian approximation in EHT parametrization to the computation of expressions for EX and CT from [10]. The scheme is applied to the calculation of dimers with binding of various physical origins. The results are compared with experimental data and *ab initio* calculations.

2. Method

2.1. Electrostatic, dispersion and induction components

Electrostatic contribution was approximated by the interaction of point monopole, dipole and quadrupole moments [9]. Point multipoles were calculated by the IEHT method [12]. The multipoles of monocentric and bicentric distributions were centered, respectively, on the atoms and on the middle of each atom pair (cf. [5]).

Dispersion energy was calculated as a sum of bond–bond interactions via a London-type formula [1, 7, 13]. Transverse and longitudinal bond polarizabilities entering this formula were taken from Le Fevre [14]. This formula contains also average excitation energies $\bar{U}$ related to ionization potentials of molecules via a coefficient d. We assumed that $\bar{U} = 2.7I$, as the value $d = 2.7$ gives satisfactory agreement between London-type and non-empirical DZ calculations [15] of the benzene dimer (usually $2 \leq d \leq 2.6$ [8, 13]).

The induction contribution was estimated according to Eq. (A15) from [7] which contains bond polarizabilities of one molecule and electric field of the other and vice versa. The electric field was calculated via the point multipoles used for the estimation of ES as in [5].

2.2. Exchange repulsion and charge transfer

The expressions for EX and CT obtained by Murrell et al. in [10] were evaluated in the one-electron Hamiltonian approximation. In this case Hamiltonians H_A and H_B of individual molecules A and B and Hamiltonian H_{AB} of the combined

AB system are expressed as

$$H_A = \sum_i^A h^A(i); \qquad H_B = \sum_j^B h^B(j);$$
$$H_{AB} = \sum_k^{AB} h^{AB}(k), \tag{1}$$

where h^A, h^B, h^{AB} are effective one-electron Hamiltonians, i, j, k denote electrons. Hamiltonians h^A and h^B satisfy equations

$$h^A\varphi_m^A = \varepsilon_m\varphi_m^A; \qquad h^B\varphi_l^B = \varepsilon_l\varphi_l^B;$$
$$\varphi_m^A = \sum_r^A a_{mr}\chi_r^A; \qquad \varphi_l^B = \sum_s^B b_{ls}\chi_s^B \tag{2}$$

where φ_m^A and φ_l^B are MOs of molecules A and B, and χ_r^A, χ_s^B are AOs of these molecules. If

$$h_{mm'}^{AB} = \int \varphi_m^A h^{AB} \varphi_{m'}^A \, d\tau = h_{mm'}^A = \varepsilon_m \delta_{mm'}$$

then the equation for EX from [10] takes form (see Appendix)

$$\mathrm{EX} = \sum_m^A \sum_l^B \left[-4h_{ml}^{AB} S_{ml} + 2(\varepsilon_m + \varepsilon_l) S_{ml}^2\right] \tag{3}$$

where

$$h_{ml}^{AB} = \int \varphi_m^A h^{AB} \varphi_l^B \, d\tau, \qquad S_{ml} = \int \varphi_m^A \varphi_l^B \, d\tau.$$

The condition $h_{mm'}^{AB} = \varepsilon_m \delta_{mm'}$ is fulfilled when, for example, isolated molecules are calculated by EHT and the approximations used in EHT are employed for the evaluation of the matrix elements of the operator h^{AB} between AO χ_r^A, $\chi_{r'}^A$, χ_s^B etc. (see Appendix).

In the approximation similar to that used for the derivation of approximate formula (3) for EX the expression for CT from [10] becomes

$$\mathrm{CT} = 2x \sum_m^A \sum_{l^*}^B \frac{|h_{ml^*}^{AB} - \varepsilon_m S_{ml^*}|^2}{\varepsilon_m - \varepsilon_{l^*}} + 2x \sum_{m^*}^A \sum_l^B \frac{|h_{m^*l} - \varepsilon_l S_{m^*l}|^2}{\varepsilon_l - \varepsilon_{m^*}} \tag{4}$$

where m^* and l^* denote vacant MOs of molecules A and B, respectively. The coefficient x is less than unity because the variation calculation [16] has shown that charge transfer excited states enter the wave function expansion with lesser weight than locally excited states which lead to DISP and IND. In our calculations $x = 0.7$ (in [16] $x \approx 0.65$).

Formulas (3) and (4) for EX and CT coincide (if $x = 1$ in Eq. (4)) with the expressions for the intermolecular interaction energy obtained in the perturbation theory for EHT [17] (see also [18]).

Details of calculations of quantities entering Eqs. (3) and (4) are as follows. Molecular orbitals φ_m^A and φ_l^B and their energies ε_m and ε_l (Eq. (2)) were calculated by EHT and in so doing the matrix elements of Hamiltonians h^A and h^B between AOs were computed via the usual formula

$$h_{pp'} = K(I_p + I_{p'})S_{pp'} \tag{5}$$

where $S_{pp'}$, is the overlap integral between AOs χ_p^C and $\chi_{p'}^C$ ($p, p' = r, r'$ or s, s', $C = A$ or B); I_p is the ionization potential of AO χ_p^C and K is an adjustable coefficient.

Formula (5) was also applied to the computation of intermolecular matrix elements h_{rs}^{AB}, h_{rr}^{AB}, appearing in the calculation of h_{ml}^{AB} and $h_{mm'}^{AB}$, (Eq. (A3) in Appendix). The coefficient K was the same for the calculation of both intra- and intermolecular matrix elements. This ensures the fulfilment of the condition $h_{mm'}^{AB} = h_{mm'}^{A} = \varepsilon_m \delta_{mm'}$.

Standard Slater AOs (SL) or Slater type AOs (CS) suggested in [19] by Cusachs et al. for the correct description of the AO behaviour at large distances from the nucleus were used. Parametrizations with SL and CS AOs are designated, respectively, as SL (K) and CS (K); K is the value of the adjustable coefficient from Eq. (5).

In our calculations K was varied from 0.825 to 1; AO exponents ζ for C, N, O atoms from [19] are cited in the Appendix; ζ_{1s}^H was always 1.3.

3. Dimers of molecules with carbonyl groups

We calculated the formaldehyde dimer $(H_2CO)_2$ non-empirically in two minimal basis sets and found semiempirical parametrizations simulating non-empirical results for different basis sets. These semiempirical parametrizations were used for the calculation of polyatomic dimer $(HN(CO)_2C_6H_2(CO)_2NH)_2$ of pyromel-

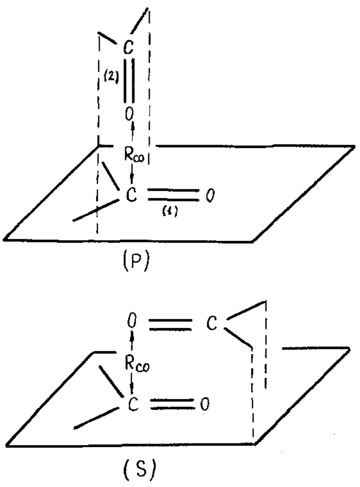


Fig. 1. The s and p configurations of a dimer $(H_2CO)_2$ (1) and (2) are numbers of the molecules

litimide (PMI) for which the interaction between carbonyl groups of different PMI molecules is substantial.

3.1. *Dimer* $(H_2CO)_2$

The calculation of $(H_2CO)_2$ was carried out for configurations *s* and *p* (Fig. 1) simulating mutual orientations of the C=O groups of adjacent PMIs in crystal domains of polyimides (see below Fig. 3).

Ab initio SCF calculation of the interaction energy, ΔE^{scf} was carried out in STG-3G and NEW minimal basis sets. The NEW basis set has been suggested in [20] for intermolecular calculations. Basis set superposition error (BSSE) was eliminated by using the counterpoise (CP) method [21]. As in some previous minimal basis set interaction calculations [13, 22] we assumed that the total interaction energy $\Delta E = \Delta E^{scf} + \mathrm{DISP}$ with DISP calculated via the London-type formula.

The results of *ab initio* calculations are compared in Table 1 with semiempirical results for CS (0.825) and SL (1) parametrizations and also for the CS^a (0.875; 1.23) parametrization in which the exponents CS and $K = 0.875$ were used and all multipoles for ES and IND calculations were multiplied by the scale factor $a = 1.23$ equal to the ratio of dipole moments of H_2CO calculated with the NEW basis set and by IEHT. (The meaning of CS (0.825) and SL (1) designations was given in Sect. 2.2).

As follows from Table 1 regardless of basis sets or semiempirical parametrizations used the binding ($\Delta E^e < 0$) is larger in the *s*-configuration and equilibrium R^e_{co} is less in the *p*-configuration. (In the case of CS (0.825) $R^e_{co}(s) \approx R^e_{co}(p)$).

NEW^{cp} and STO-3G^{cp} calculations performed with the bases NEW and STO-3G with elimination of BSSE by CP method yielded smaller binding energy and

Table 1. Comparison of equilibrium R^e_{co} (in nm) and ΔE^e (in kJ mol^{-1}) for the *s* and *p* configurations of formaldehyde dimer

	Ab initio calculation					
	NEW^{cp} [a]		STO-3G		STO-3G^{cp}	
	s	*p*	*s*	*p*	*s*	*p*
R^e_{co}	0.323	0.312	0.295	0.278	0.315	0.300
ΔE^e	−9.4	−4.3	−11.9	−6.9	−8.9	−5.2
	Semiempirical calculation					
	CS^a (0.875; 1.23)		CS (0.825)		SL (1)	
	s	*p*	*s*	*p*	*s*	*p*
R^e_{co}	0.320	0.310	0.313	0.310	0.285	0.276
ΔE^e	−9.5	−4.1	−9.0	−3.8	−13.5	−7.1

[a] BSSE eliminated by CP method [21]

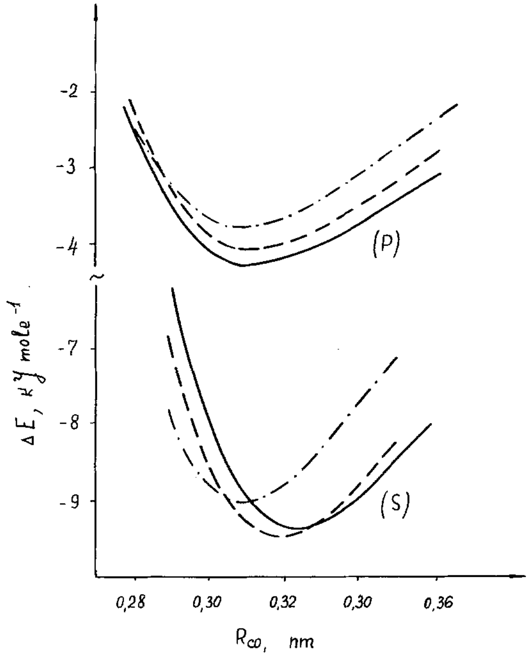


Fig. 2. ΔE as a function of R_{co} calculated by different methods for the *s* and *p* configurations of a dimer $(H_2CO)_2$: (——) a NEW$^{\mathrm{cp}}$ *ab initio* calculation, (– – –) CS$^{\mathrm{a}}$ (0.875, 1.23) semiempirical calculation, (– · – · –) CS (0.825) semiempirical calculation. The three upper curves refer to the *p* configurations, those below refer to the *s* configurations

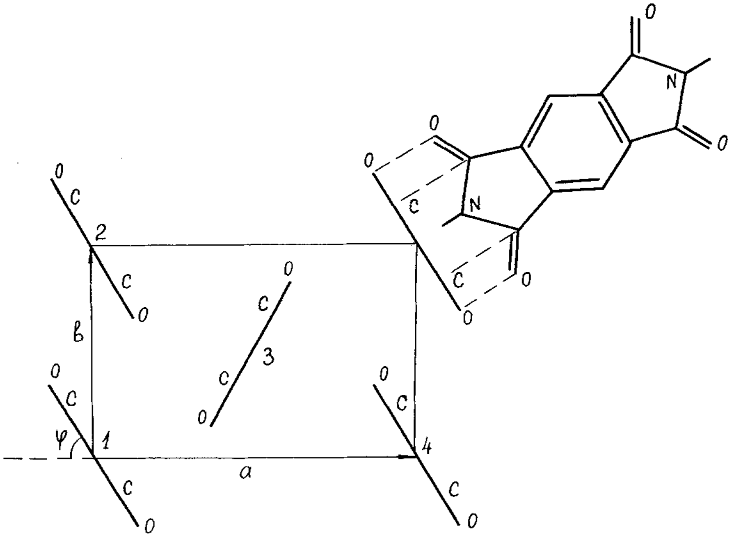


Fig. 3. The packing of pyromellitic residues in a cell of the crystalline domain of polymer PMIB. The axis of the macromolecule is perpendicular to a plane of the figure

Table 2. Calculated and experimental polyimide PMIB cell parameters

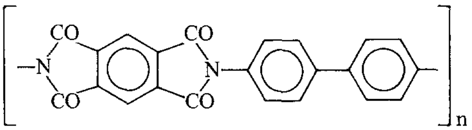
Cell parameters	Calculation CS (0.825)	SL (1)	Experiment[a]
a, nm	0.862	0.840	0.858 ± 0.005
b, nm	0.550	0.524	0.548 ± 0.005
φ, deg	56.5	55	50–60

[a] From Ref. [24]

larger equilibrium R^e_{co} than STO-3G calculation without BSSE elimination. The results for parametrizations CS (0.825) and CS[a] (0.875; 1.23) are closer to the NEW^{cp} and STO-3G^{cp} results and those for SL (1) are closer to the STO-3G results. Semiempirical calculation also describes fairly well the dependence of ΔE on R_{co} in the vicinity of energy minimum (Fig. 2).

3.2. *Interaction between* PMI *molecules in a crystalline cell of polyimide*

Crystalline domains of polyimide which we denote by PMIB are characterized by a rectangular cell (Fig. 3). We calculated the cell parameters, *a*, *b* and φ,



taking into account only the interactions between PMI residues since the influence of diphenyl residues on the formation of crystalline domains is much less important [23, 24]. Since the interaction between PMI$_1$ and PMI$_4$ (Fig. 3) is small only interactions of PMI$_1$ with PMI$_2$ and PMI$_3$ were considered.

The computation was carried out in parametrizations CS (0.825) and SL (1). The equilibrium *a*, *b* and φ for these parametrizations are compared in Table 2 with their experimental values [24]. Both parametrizations yield equilibrium φ close to experimental data [24], but only the parametrization CS (0.825) gives *a* and *b* in agreement with their experimental values since parametrization SL (1) underestimates these quantities.

The results of polyimide crystalline cell calculations suggest that parametrization CS (0.825) is more suitable for intermolecular calculations than parametrization SL (1).

4. Electron donor–acceptor complexes

4.1. *Tetracyanoethylene–aromatic donor complexes*

Benzene, naphthalene, *p*-xylene and durene were chosen as aromatic donors. The calculation was carried out for energetically favorable stacking configurations in which planes of molecules are parallel and the center of TCNE is just above that of the benzene ring. The interplane distance and the angle of rotation about the axis connecting the centers of TCNE and phenyl ring was varied. The calculation was carried out in CS (0.825) and SL (1) parametrizations.

The calculated equilibrium R^e and ΔE^e and the experimental enthalpies ΔH of the complexes under investigation are listed in Table 3. Parametrization CS (0.825) yields for *p*-xylene and durene ΔE^e close to gas phase enthalpies; parametrization SL (1) overestimates the stabilization of these complexes. It may be noted that the calculated results reproduce the tendency of the ΔH variation of these complexes in solution.

Parametrization SL (1) yields shorter equilibrium distances than parametrization CS (0.825). (In a mixed crystal containing alternate layers of TCNE and naphthalene the distance between the layers is 0.34 nm [26]).

Table 3. Calculated intermolecular distances R^e and binding energies ΔE^e, experimental enthalpies ΔH for complexes TCNE and aromatic donors (R^e in nm, ΔE^e, ΔH in kJ mol^{-1})

	CS (0.825)[a]		SL (1)[a]		Gas phase[b]	Solution[b]
Donor	R^e	ΔE^e	R^e	ΔE^e	ΔH	ΔH^c
Benzene	0.354	−28.7	0.324	−42.8	—	−13.2
Naphthalene	0.350	−34.5	0.320	−52.7	—	−18.2
p-Xylene	0.347	−35.4	0.320	−51.3	−33.9	−14.1
Durene	0.347	−41.6	0.318	−59.2	−45.2	−21.2

[a] Ionization potentials in DISP calculation were equal to 11.62 eV for TCNE (MNDO estimation) and 9.25, 8.44 and 8.02 eV for benzene, *p*-xylene and durene, respectively (experimental data). Assumed for naphthalene the value $I = 9.25$ eV was higher than experimental one to compensate for larger polarizability of $C_{ar}—C_{ar}$ bond in naphthalene as compared with benzene.

[b] Experimental ΔHs are listed in Ref. [25].

[c] These values of ΔH correspond to identical experimental conditions

Table 4. Energy components (in kJ mol^{-1}) for tetracyanoethylene–benzene and carbonyl cyanide–benzene π-complexes

Complex	Method	*R*, nm	EX	CT	IND	ES	DISP[c]	ΔE
$TCNE\cdots C_6H_6$	CS (0.825)	0.35	23.1	−5.0	−2.1	−8.1	−36.6	−28.7
$TCNE\cdots C_6H_6$	SL (1)	0.32	35.3	−8.4	−3.1	−10.0	−56.4	−42.6
$(CN)_2CO\cdots C_6H_6$	STO-3G[a]	0.32	12.5	−3.1	−0.4	−6.2	−6.6[d]	−3.8
$(CN)_2CO\cdots C_6H_6$	SL (1)	0.32	21.2	−4.6	−1.4	−5.5	−38.6	−29.0
$(CN)_2CO\cdots C_6H_6$	SL (0.825)	0.32	13.5	−3.1	−1.4	−5.5	−38.6	−35.1
$(CN)_2CO\cdots C_6H_6$	CNDO/2[b]	0.32	8.7	−3.5	−0.8	−2.3	−8.2	−5.5

[a] *Ab initio* STO-3G calculation [27].

[b] CNDO/2 calculation [28] of energy components from [10].

[c] $I_{(CN)_2CO}$ used in DISP calculation was 12.9 eV (MNDO calculation). For I_{TCNE} and $I_{C_6H_6}$ see Table 3.

[d] STO-3G perturbation calculation [27]

Calculations of TCNE–C_6H_6 complex in both parametrizations show (Table 4) that at the equilibrium distances (0.35 and 0.32 nm for CS (0.825) and SL (1), respectively) the main contribution to the binding energy is provided by the dispersion interaction and attraction due to electrostatic and charge transfer interactions is less important. Similar relations between the components of ΔE exists for the other complexes investigated.

4.2. Energy components of carbonyl cyanide–benzene π-complex

For stacking configuration of a similar π-complex $(CN)_2CO\cdots C_6H_6$ there is an *ab initio* STO-3G calculation [27]. As calculations of $(H_2CO)_2$ showed that STO-3G results were simulated by semiempirical SL parametrizations in Table 4 the ΔE components for $(CN)_2CO\cdots C_6H_6$ complex from [27] are compared with components for parametrizations SL (1) and SL (0.825). In addition Table 4 includes semiempirical results from [28] where the calculation of all ΔE components from [10] has been carried out in CNDO/2 approximation using Mulliken's formula for the evaluation of integrals containing intermolecular overlap.

As follows from Table 4, the values of EX and CT, particularly for parametrization SL (0.825), are fairly close to the STO-3G data. The same can be said about ES. The data from [28] are somewhat lower in absolute value.

There is a marked difference in dispersion energies. (Differences in IND are less important). But it is known (see e.g. [2]) that dispersion energy calculations in minimal basis sets such as [27, 28] significantly underestimate this contribution. The dominant role of DISP in the stabilization of this complex has been shown in [13].

4.3. Energy components of carbonyl cyanide–water $n\pi$-complex

Ab initio ΔE components for $n\pi$-complex $(CN)_2CO\cdots H_2O$ [27, 29] at the equilibrium geometry are listed in Table 5. *Ab initio* data clearly indicate that in this

Table 5. Comparison of energy components (in kJ mol^{-1}) for carbonyl cyanide–water $n\pi$-complex at $R = 0.27$ cm[a]

Method	EX	CT	IND	ES	DISP	ΔE
4-31G[b]	18.4	−7.5	−4.2	−40.6	−4.6[b]	−38.5
STO-3G[c]	8.4	−4.6	−0.8	−17.6	−1.6[b]	−16.6
CS (0.825)	23.6	−7.9	−3.8	−18.8	−14.5[d]	−21.2
SL (0.875)	9.2	−4.0	−3.8	−18.8	−14.5	−31.9

[a] R is the distance between the oxygen atom in the water molecule and the carbonyl cyanide plane [29]; $R = 0.27$ nm is equilibrium distance for STO-3G and 4-31G calculations [27, 29].

[b] Results from [27].

[c] Results from [29].

[d] I_{H_2O} in DISP calculation was 12.62 ev (experiment). For $I_{(CN)_2CO}$ see Table 4

$n\pi$-complex the main contribution to the stabilization energy is provided by the electrostatic rather than by dispersion attraction.

The same conclusion can be drawn from semiempirical calculation (Table 5). It follows from the comparison of *ab initio* and semiempirical results that semiempirical ES is close to the STO-3G value (basis 4-31G usually overestimates electrostatic interaction [27, 30]). The values of EX and CT in parametrizations CS (0.825) and SL (0.875) are close to those for 4-31G and STO-3G basis sets, respectively.

The largest differences are obtained for the dispersion energies. As in the case of the STO-3G basis, the 4-31G calculation results in underestimating the dispersion attraction if compared with semiempirical DISP values.

5. Benzene–benzene and ethylene–ethylene interactions

5.1. Benzene crystal cell

The calculation of interactions in crystalline benzene was carried in CS (0.825) parametrizations for benzene crystal structure from [31, 32]. The pair-wise interactions of the first neighbors yield the packing energy per molecule $E_{\text{pack}} = -34.2$ kJ mol^{-1}. The main attractive contribution comes from dispersion interaction equal to -63.4 kJ mol^{-1} ($\text{DISP}^{\text{nemp}}_{\text{at–at}}$ calculated via non-empirical atom–atom potentials from [15] is -62.8 kJ mol^{-1}). ES and IND contributions are small (-3 and -0.8 kJ mol^{-1}, respectively). This agrees with the previous inferences [32, 33] that the influence of electrostatic interactions on benzene crystal packing is negligible. Short-range repulsion EX + CT = 33 kJ mol^{-1}.

It has been shown [32] that dispersion attraction between all distant molecules amounts to approximately 20% of the dispersion attraction between the first neighbors. The addition of 20% of the first neighbors DISP to E_{pack} rises $-E_{\text{pack}}$ to 46.9 kJ mol^{-1} which is very close to the experimental value 47.7 kJ mol^{-1} [33].

5.2. Stacking and perpendicular configurations of benzene and ethylene dimers

Benzene dimer stacking configuration (I) has D_{6h} symmetry; perpendicular one (II) is derived from the stacking configuration by 90° rotation of one of the molecules about C_2 axis passing through hexagon apexes. Calculation in CS (0.825) parametrization yielded for respective equilibrium distances of configurations I and II the following energy contributions (in kJ mol^{-1}): ΔE^e (I) = -11, ES (I) = 2.2, DISP (I) = -21, ($\text{DISP}^{\text{nemp}}_{\text{at–at}}$ (I) = -20.4); ΔE^e (II) = -6.8; ES (II) = -0.8; DISP (II) = -9.2, ($\text{DISP}^{\text{nemp}}_{\text{at–at}}$ (II) = -9.7).

Thus these results show that stacking configuration is more preferable and the main contribution to the stabilization of both configurations comes from dispersion attraction which is larger in stacking configuration.

Calculations [4, 34] have also indicated that the stacking configuration is more favorable but some other computations [35, 36] have yielded an opposite result. The difference in the energies of the two configurations is small (in our case ΔE

(II) $-\Delta E$ (I) ≈ 1 kcal mol^{-1}) and it seems that such subtle effects are beyond the scope of semiempirical methods.

We calculated semiempirically (CS (0.825)) and non-empirically (NEW^{cp}) the stacking and perpendicular configurations of ethylene dimer (configurations I and III from [37]). CS (0.825) calculation yielded in this case in contrast to benzene dimer that dispersion attractions at respective equilibrium distances of configurations I and III are approximately equal and perpendicular configuration III is slightly more preferable (in kJ mol^{-1}): DISP (I) $\approx$ DISP (III) $= -3.8$; ES (I) $= 1.4$; ES (III) $= 0.3$; ΔE^e (I) $= -1.6$; ΔE^e (III) $= -2.2$.

NEW^{cp} calculation also yielded that perpendicular configuration is preferable (ΔE^e (III) $= -4.2$ and ΔE^e (I) $= -1.6$ kJ mol^{-1}). DZ calculation [37] has indicated that perpendicular configuration III is more favorable than configuration I.

6. Hydrogen bonded dimers

6.1. Water dimer

The calculation of the linear water dimer in parametrizations CS (0.825) and CS (0.875) yielded equilibrium distances R^e_{00} between the oxygen atoms 0.287 and 0.295 nm and binding energies of -25.1 and -23.1 kJ mol^{-1}, respectively. The rigorous variation-perturbation calculation [38] has led to $R^e_{00} = 0.286$ nm and $\Delta E^e = -24.3$ kJ mol^{-1} and extensive SCF CI computation [39] has yielded $\Delta E = -21.7$ kJ mol^{-1}.

The ΔE components of the linear and the bifurcated dimers $(H_2O)_2$ computed for $R_{00} = 0.3$ nm by different methods are presented in Table 6. The semiempirical energy components are close to non-empirical components; the largest deviation is observed for the charge-transfer component in the bifurcated configuration. Other recent studies of the charge-transfer term based on Murrell's formalism [6] yielded -4.6 and -1.6 kJ mol^{-1} for the linear and bifurcated dimer, respectively.

Table 6. Comparison of energy components (in kJ mol^{-1}) for linear and bifurcated water dimers at $R_{00} = 0.3$ nm

Configuration	Method	EX	CT	IND	ES	DISP	ΔE	$\Delta E - \mathrm{DISP}^e$
Linear	extended basis[a]	20.5	-6.8^c		-29.8	-6.4	-22.5	-16.1
Linear	4-31G[b]	15.5	-7.1^d	-2.5	-36.4	—	—	-30.5
Linear	CS (0.875)	15.8	-8.1	-2.1	-22.6	-5.8	-22.8	-17.0
Bifurcated	4-31G[b]	7.1	-4.6^d	-1.3	-28.0	—	—	-26.8
Bifurcated	CS (0.875)	5.1	-1.1	-2.1	-18.6	-6.2	-22.9	-16.7

[a] Extended basis variation perturbation calculation [38].

[b] 4-31G calculation [30].

[c] IND from [38] contains CT.

[d] Equal to the sum CT + MIX from [30].

[e] Hartree–Fock limit for $\Delta E^{scf} = -16.32 \pm 1.05$ kJ mol^{-1} [40].

It is essential that semiempirical results suggest that in water binding is mainly electrostatic in origin, and dispersion attraction and charge transfer are less significant. These conclusions agree with the *ab initio* results.

Although semiempirical calculation correctly follows that trends of 4-31G calculation such as a decrease in absolute value of EX, CT and ES for the bifurcated dimer in comparison with these components for the linear dimer it does not reproduce the 4-31G result that the binding energy of the linear dimer is larger than that of the bifurcated dimer (Table 6).

6.2. *Formic acid dimer*

The $(HCOOH)_2$ dimer is an example of a system rather strongly bounded by two hydrogen bonds. According to calculation in parametrization CS (0.875) for the dimer geometry D from [41], the binding energy of $(HCOOH)_2$ is -47.7 kJ mol^{-1} and the equilibrium distance R^e_{00} between the oxygen atoms is 0.285 nm. From comparison with experimental $\Delta E = -66.9 \pm 6.3$ kJ mol^{-1} and $R^e_{00} = 0.27$ nm [42] it follows that semiempirical calculation underestimates the stabilization energy of this dimer.

At $R_{00} = 0.27$ nm our calculation yields (in kJ mol^{-1}) $\Delta E = -41.0$; $\mathrm{ES} = -62.6$; $\mathrm{DISP} = -25.1$ and $\mathrm{EX+CT} = 60.8$. DZ results [42] for the same R_{00} are (in kJ mol^{-1}): $\Delta E = -59.4$; $\mathrm{ES} = -103.6$; $\mathrm{DISP} = -28.0$ and $\mathrm{EX+CT} = 99.8$. It is evident that in comparison with DZ values our data underestimate electrostatic attraction and short-range repulsion. One of the reasons for the underestimation of ES is the absence in multipole expansion of ES of penetration effects which are substantial for $(HCOOH)_2$ at $R_{00} = 0.27$ nm [42].

7. Accuracy of semiempirical calculation of the energy components

The criteria for the accuracy of semiempirical calculation of separate energy components are mainly the *ab initio* results. Since there is a dependence of *ab initio* results on the basis set, only the extended basis set calculations can serve as a rigorous criteria. However, the comparison of semiempirical and nonempirical data calculated with restricted basis sets may also be helpful if the dependence of *ab initio* results on the basis set is kept in mind.

The minimal and split valence basis sets substantially underestimate the dispersion term [2, 13, 27] but it seems DZ basis sets lead in some cases to more satisfactory results [43]. We found that the London-type DISP computation with $d = 2.7$ in the relation $U = dI$ reproduced fairly well the DZ calculation of DISP for dimers $(C_6H_6)_2$, $(HCOOH)_2$ and also the extended basis set DISP calculation for $(H_2O)_2$ (Table 6).

Semiempirical induction energies exceed those for STO-3G basis but are close to the value yielded by other bases. The role of IND component was insignificant in the dimers considered.

Table 7. Comparison of exchange repulsion and charge transfer (in kJ mol^{-1}) calculated non-empirically and semiempirically for some dimers

	$(CN)_2CO\cdots C_6H_6$				$(HCOOH)_2$			
			R (nm)				R (nm)	
	Method	0.30	0.32	0.36	Method	0.25	0.27	0.30
EX	STO-3G[a]	28.7	12.5	2.1	split val.[b]	259	120	36.2
	SL (0.825)	29.0	13.5	2.7	CS (0.875)	246	118	36.9
CT	STO-3G[a]	−13.6	−6.5	−0.6	split val.[b]	−91.0	−56.0	−27.4
	SL (0.825)	−16.2	−7.9	−0.8	CS (0.875)	−98.0	−57.4	−22.1

[a] STO-3G calculation data from [27].

[b] Split valence basis set calculation data from [42]

There is a complicated dependence of ES upon the basis set (e.g. [44]). Thus, for the linear water dimer at $R_{OO} = 0.3$ nm STO-3G, 4-31G, 6-31G** and very extended basis sets yield −17.6, −37.2, −31.2 and −29.8 kJ mol^{-1} respectively [30, 38]. It is evident that STO-3G basis underestimates and 4-31G basis overestimates ES. Semiempirical calculation lead for $(H_2O)_2$ dimer at $R_{OO} = 0.3$ nm to ES $= -22.6$ kJ mol^{-1}. This result is in accordance with the conclusion drawn from the computations of other dimers (Tables 4 and 5) that semiempirical ES calculation using IEHT multipoles usually yield ES close to STO-3G, i.e. somewhat underestimates ES. It seems that accuracy of ES calculation can be improved appreciably if *ab initio* point multipoles were employed [5, 37].

Tables 4, 5 and 6 show that parametrizations CS and SL yield EX and CT close to STO-3G and 4-31G basis set data, respectively. The increase of the coefficient K in Eq. (5) tends to increase overall repulsion EX + CT (Table 4). As follows from Table 7 semiempirical EX and CT can correctly reproduce the trend of *ab initio* calculations in the region of equilibrium R. The results for parametrizations CS seem to be more realistic, although it can be suggested that they underestimate EX + CT if compared with DZ and extended basis sets results as was shown for dimers $(H_2O)_2$ and $(HCOOH)_2$.

It has been suggested in [5] that the repulsive term may account effectively for penetration effects not considered in the multipole expansion of ES. In our case the same applies to the sum EX + CT.

If $x = 1$ in Eq. (4) then EX + CT is close to the EHT supermolecule interaction energy (ΔE(EHT)) and this may serve as an explanation why ΔE (EHT) has been used rather successfully [45, 46] for the calculation of the short-range repulsion.

8. Discussion

The proposed scheme differs from others mainly in the use of the EHT Hamiltonian for the evaluation of Murrell's formulas for EX and CT. The calculation of other components is influenced by different authors. Although the suggested procedure is less accurate than some other schemes (Refs. [5, 6], see also review [47]) it seems simpler and possibly more rapid.

The adjustable parameters make the scheme relatively flexible. The parametrizations CS yield results close to experimental data. The parametrizations SL simulate STO-3G calculations which tend to overestimate intermolecular attraction.

The proposed procedure may be recommended for the analysis of the interaction between large organic molecules when the application of more rigorous methods is difficult and atom–atom potentials are not plausible enough. In particular, this scheme can be used to compare the relative stability of complexes formed by molecules with varying degrees of difference in chemical structure. The calculations of the interaction between various aromatic diamines and dianhydrides in the initial stage of acylation reaction [48] and between different residues of polyimide PMIB [23] may serve as examples of the possible use of the scheme (PMIB was considered briefly in Sect. 3.2).

The proposed procedure must be applied judiciously to ionic dimers, to strongly binded EDA or hydrogen bonded complexes with equilibrium R^e less than $0.25-0.28$ nm, and also to the study of subtle effects, e.g. the calculation of the relative preference of dimer configurations with close energy values.

Appendix: Derivation of the expression for exchange repulsion in the one-electron Hamiltonian approximation

In one-electron Hamiltonian approximation interaction potential operator $V = H_{AB} - H_A - H_B$ can be written as a sum of one-electron operators h^{AB}, h^A, h^B (see Eq. (1)). For this form of the operator V the expression for EX from [1, 10] (Eq. (2.169) in [1] or Eq. (25) in [10]) takes the form

$$\begin{aligned}\mathrm{EX} = {} & -2\sum_m^A \sum_l^B (2h_{ml}^{AB} - h_{ml}^{A} - h_{ml}^{B}) S_{ml} \\ & +2\sum_m^A \sum_{m'}^A \sum_l^B \sum_{l'}^B (h_{mm'}^{AB} + h_{ll'}^{AB} - h_{mm'}^{A} - h_{ll'}^{B}) S_{ml} S_{m'l'}\end{aligned} \tag{A1}$$

if only pair permutations are taken into account. According to Eq. (2)

$$\begin{aligned} & h_{ml}^{A} = \varepsilon_m S_{ml}; \qquad h_{ml}^{B} = \varepsilon_l S_{ml}; \\ & h_{mm'}^{A} = \varepsilon_m \delta_{mm'}; \qquad h_{ll'}^{B} = \varepsilon_l \delta_{ll'}. \end{aligned} \tag{A2}$$

Matrix elements of the operator h^{AB} can be written as

$$h_{ml}^{AB} = \sum_r^A \sum_s^B a_{mr} b_{ls} h_{rs}^{AB}; \qquad h_{mm'}^{AB} = \sum_r^A \sum_{r'}^A a_{mr} a_{m'r'} h_{rr'}^{AB} \tag{A3}$$

if the expansion (2) of φ_m^A and φ_l^B into AOs is used ($h_{rs}^{AB} = \int \chi_r^A h^{AB} \chi_s^B \, d\tau$; $h_{rr'}^{AB} = \int \chi_r^A h^{AB} \chi_{r'}^A \, d\tau$). MOs of isolated molecules were obtained by EHT. Since in EHT $h_{rr'}^{A} = C_{rr'} S_{rr'}$ ($C_{rr'}$ is a parameter, r, r' label AOs of molecule A) it was also assumed that

$$h_{rs}^{AB} = C_{rs}^{AB} S_{rs}; \qquad h_{rr'}^{AB} = C_{rr'}^{AB} S_{rr'}; \qquad h_{ss'}^{AB} = C_{ss'} S_{ss'} \tag{A4}$$

where s, s' label AOs of molecule B.

The parameter $C_{rr'}$ in $h^A_{rr'}$ of EHT does depend only on the type of AOs r and r'. This EHT assumption may be considered justifiable if charge distribution in a molecule is close to uniform distribution [49]. We assumed that this condition may be regarded as fulfilled not only for isolated molecules A and B but also for AB composite system the field of which is presented by the operator h^{AB}. (Possible exceptions might be interactions of ions, mutual polarization of markedly polar molecules etc.). This means that C^{AB}_{rs} and $C^{AB}_{rr'}$ in Eq. (A4) depend only on r, s, or r, r', i.e.

$$C^{AB}_{rs} = C_{rs}; \qquad C^{AB}_{rr'} = C_{rr'}.$$

Now for the matrix elements of operators h^{AB}, h^A, h^B between AOs the same approximation may be used (e.g. Eq. (5) with equal K) and in that case $h^{AB}_{rr'} = h^A_{rr'}$, $h^{AB}_{ss'} = h^B_{ss'}$, $h^{AB}_{mm'} = h^A_{mm'}$, $h^{AB}_{ll'} = h^B_{ll'}$ and taking into account Eq. (A2) formula (3) for EX is derived from Eq. (A1).

It should be noted that for the matrix element h^A_{rs} of the operator h^A between AOs χ^A_r and χ^B_s belonging to different molecules the above mentioned condition of uniform field is not fulfilled which means that $h^A_{rs} \neq h^{AB}_{rs}$ and $h^A_{ml} \neq h^{AB}_{ml}$.

The exponents from [19] used in this paper in parametrizations CS are as follows: $\zeta^C_{2s} = 1.6$, $\zeta^C_{2p} = 1.43$, $\zeta^N_{2s} = 1.9$, $\zeta^N_{2p} = 1.69$, $\zeta^0_{2s} = 2.2$, $\zeta^0_{2p} = 1.95$.

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