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Nonempirical Atom-Atom Potentials for Main Components of Intermolecular Interaction Energy

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Atom-atom potentials representing separate contributions to the nonempirical interaction energy have been derived in the SCF decomposition scheme corrected for basis set superposition error by the counterpoise method. The nontransferable long-range electrostatic multipole and classical induction terms have been evaluated directly from cumulative atomic multipole expansions, whereas the short-range exchange, charge-transfer, and electrostatic penetration contributions have been represented by simplified potentials of the form $(\beta + \delta R^{-1}) \exp(-\delta R)$ fitted to the corresponding *ab initio* results for 336 dimer configurations formed by HF, H₂O, NH₃, CH₄, CO, and CO₂. The dominant anisotropic character of electrostatic multipole atom-atom potentials and much more isotropic nature of the potentials representing short-range terms is illustrated in the Appendix for head-on interactions in CO...OC and HF...FH dimers.

I. INTRODUCTION

Intermolecular interactions determine most of the unique properties of condensed matter. Unfortunately, currently available theoretical techniques do not allow rigorous study of interactions between molecules much larger than the water dimer. Therefore, in recent years several attempts have been made¹⁻²⁰ to obtain an analytical representation of intermolecular forces based on first principles resembling widely used empirical potentials (Lennard-Jones, Buckingham, etc.²¹ The majority of previously reported nonempirical potentials¹⁻¹⁵ have not been corrected for the nonphysical basis set superposition error^{22,23} (BSSE), but some recent ones¹⁶⁻²⁰ have included the correction. Moreover, in the earlier investigations various components of the interaction energy differing strongly in their anisotropy, transferability, and range have been mixed together in the process of fitting to analytical potentials. Therefore, by separating different physical components of the interaction energy we ex-

pect to obtain more adequate potentials to investigate the nature of interactions in large molecular systems while using atom-atom potentials and to derive simpler theoretical models. The *ab initio* interaction energies, even when corrected for intermolecular BSSE, still display some basis set dependence^{24,25} originating from the lack of the intramolecular balance of the basis set. Therefore, besides BSSE correction, carefully balanced basis sets should be used to obtain satisfactory nonempirical results.²⁶ The aim of this work is to obtain separate nonempirical atom-atom potentials for electrostatic multipole, electrostatic penetration, exchange, short- and long-range induction components of the interaction energy and fitting corresponding *ab initio* SCF results corrected in BSSE in our decomposition scheme²⁷ for 336 model dimer configurations.

Calculations have been performed with well-balanced minimal valence (3s3p/3s) → [1s1p/1s] MODPOT basis sets²⁸ with *ab initio* effective-core model potentials known to yield interaction energies very close to results obtained in extended basis sets, but at much lower cost.²⁵ The nontransferable and strongly anisotropic electrostatic multipole contributions have been evaluated from

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the cumulative atomic multipole moments²⁹ obtained directly from the monomer wave functions.

II. COMPONENTS OF INTERMOLECULAR INTERACTION ENERGY AND THEIR SIMPLIFIED ANALYTICAL REPRESENTATION

Numerous variants of the exchange perturbation theory of intermolecular interactions have been generalized by Jeziorski and Kołos³⁰, and they seem to be at present the most complete theoretical approach for evaluation of intermolecular forces. The main components of the total two-body interaction energy ΔE are:

$$\Delta E = E_{\text{EL}}^{(1)} + E_{\text{EX}}^{(1)} + E_{\text{IND}}^{(2)} + E_{\text{DISP}}^{(2)} + \dots \quad (1)$$

where $E_{\text{EL}}^{(1)}$ is the first order electrostatic, $E_{\text{EX}}^{(1)}$, exchange, $E_{\text{IND}}^{(2)}$, second order induction, and $E_{\text{DISP}}^{(2)}$, dispersion contribution.

The advantage of the perturbation approach consists in its ability to obtain an explicit analytic formulation suitable for further approximations and to evaluate each additive term separately. However, practical use of the rigorous exchange perturbation method is limited to weak interactions and rather small systems, due to the time consuming integral transformations involved. On the other hand, approximate exchange perturbation methods appear to be quite sensitive to integral approximations.³¹

Fortunately, the first three components of (1) can also be easily estimated from decomposition of the variational ΔE_{SCF} interaction energy corrected for nonphysical BSSE.³²

$$\begin{aligned} \Delta E_{\text{SCF}} &= E_{AB} - E_{A(B)} - E_{B(A)} \\ &\approx E_{\text{EL}}^{(1)} + E_{\text{EX}}^{(1)} + E_{\text{IND,CT}}^{(R)} + E_{\text{IND,LE}}^{(R)} \quad (2) \end{aligned}$$

where E_{AB} , $E_{A(B)}$, and $E_{B(A)}$ denote the SCF total energies of interacting dimer, and isolated monomers A and B (evaluated in dimer basis set), respectively.

In addition, the induction components also contain remaining (R) higher-order corrections, and it is decomposed into an additive long-range classical component, $E_{\text{IND,LE}}^{(R)}$, arising from interactions of local excitations (LE) with the static charge distribution of another molecule, and a short range, $E_{\text{IND,CT}}^{(R)}$, term corresponding to interaction of ionic charge-transfer configurations (CT) with the

respective static charge distributions. Unfortunately, the second-order dispersion term is not included in the SCF approach and if calculated rigorously, the use of extended basis sets with polarization functions seems to be unavoidable.³³

The most annoying problem in rigorous calculations of interaction energy is the strong basis set dependence of the results. The basis set dependence can be reduced²⁵ by correcting the intermolecular BSSE by the Boys counterpoise method.²³ However, the counterpoise-corrected ΔE_{SCF} still displays a small basis set dependence originating mainly from the electrostatic term, $E_{\text{EL}}^{(1)}$ which could be ascribed to imbalance of the intramolecular basis.^{25, 26, 34} Reasonable values for ΔE_{SCF} can be obtained even with minimal basis sets,^{25, 26, 34, 35} provided they are properly balanced and the resulting ΔE_{SCF} is corrected for intermolecular BSSE. In this study (unless noted otherwise), a well-balanced minimal valence ($3s3p/3s$) \rightarrow [$1s1p/1s$] MODPOT basis set with *ab initio* effective-core model potentials²⁸ has been used. This basis set gives, at much lower cost, interaction energies very close to results obtained in extended 6-31G* and 6-31G** basis sets.²⁵

In general, all interaction energy components can be classified into two categories: long-range forces, i.e., electrostatic multipole, $E_{\text{EL,MTP}}^{(1)}$, classical induction, $E_{\text{IND,LE}}^{(R)}$, and dispersion, $E_{\text{DISP}}^{(2)}$, terms, and short-range forces, i.e., exchange, $E_{\text{EX}}^{(1)}$, electrostatic penetration, $E_{\text{EL,PEN}}^{(1)}$, and charge-transfer, $E_{\text{IND}}^{(R)}$, contributions.

The first-order electrostatic term is also subdivided into the long-range multipole part, $E_{\text{EL,MTP}}^{(1)}$, and short-range penetration component, $E_{\text{EL,PEN}}^{(1)}$:

$$E_{\text{EL}}^{(1)} = E_{\text{EL,MTP}}^{(1)} + E_{\text{EL,PEN}}^{(1)} \quad (3)$$

The multipole component of the electrostatic term can be easily estimated from an atomic multipole expansion.²⁹ In this study, the molecular charge distribution was divided into the most natural atomic segments represented by atomic monopoles (charges) q , dipoles $\vec{\mu}$, and quadrupoles \vec{Q} derived directly from the *ab initio* wave function²⁹:

$$\begin{aligned} E_{\text{EL,MTP}}^{(1)} &= \sum_{a \in A} \sum_{b \in B} \{ q_a q_b R_{ab}^{-1} + q_b (\vec{\mu}_a \cdot \vec{R}_{ab}) R_{ab}^{-3} \\ &\quad - q_a (\vec{\mu}_b \cdot \vec{R}_{ab}) R_{ab}^{-3} + (\vec{\mu}_a \cdot \vec{\mu}_b) R_{ab}^{-5} \} \end{aligned}$$

$$\begin{aligned}
& + 3(\vec{\mu}_a \cdot \vec{R}_{ab})(\vec{\mu}_b \cdot \vec{R}_{ab})R_{ab}^{-5} \\
& + q_b(\vec{R}_{ab} \cdot \vec{Q}_a \cdot \vec{R}_{ab})R_{ab}^{-5} + q_a(\vec{R}_{ab} \cdot \vec{Q}_b \cdot \vec{R}_{ab}) \\
& \quad \cdot R_{ab}^{-5} + 2(\vec{\mu}_b \cdot \vec{Q}_a \cdot \vec{R}_{ab})R_{ab}^{-5} \\
& - [5(\vec{\mu}_b \cdot \vec{R}_{ab})(\vec{R}_{ab} \cdot \vec{Q}_a \cdot \vec{R}_{ab})]R_{ab}^{-7} \\
& \quad - 2(\vec{\mu}_a \cdot \vec{Q}_b \cdot \vec{R}_{ab})R_{ab}^{-5} \\
& + [5(\vec{\mu}_a \cdot \vec{R}_{ab})(\vec{R}_{ab} \cdot \vec{Q}_b \cdot \vec{R}_{ab})]R_{ab}^{-7} \quad (4)
\end{aligned}$$

It has to be noted, however, that the corresponding *molecular* multipole expansion fails to converge at short and intermediate distances,³⁶ and only by dividing the molecular charge distribution into smaller segments can one obtain reasonable results at distances of chemical interest. For molecules with zero atomic charges ($q_i = 0$) the multipole expansion (4) was terminated at R_{ab}^{-4} term (dipole-quadrupole) and for the remaining cases at R_{ab}^{-3} term (dipole-dipole and monopole-quadrupole). Use of such atomic multipole expansions permits the proper representation of the strongly anisotropic electrostatic multipole term at the atomic level.³⁷

The remaining short-range, $E_{\text{EL, PEN}}^{(1)}$, $E_{\text{EX}}^{(1)}$, and $E_{\text{IND, CT}}^{(R)}$ terms are much less anisotropic at the atomic level (see Appendix) and can be satisfactorily represented by an isotropic potential:

$$E = \sum_{a \in A} \sum_{b \in B} (\beta_{ab} + \gamma_{ab} R_{ab}^{-1}) \exp(-\delta_{ab} R_{ab}) \quad (5)$$

This form reflects the analytical character of short-range terms due to the presence of charge overlap contributions appearing explicitly in exchange perturbation formulation of the terms (for example, see refs. 31 and 37 and references quoted therein). The parameters β , γ , and δ have been fitted for each short-range term and contact type separately to reproduce the corresponding *ab initio* components of interaction energy.

Recently, Singh and Kollman³⁸ fitted *ab initio* charge-transfer energies (not corrected for BSSE) in $(\text{H}_2\text{O})_2$ by anisotropic *one-center* potential functions. Our *multicenter* isotropic potential function⁵ should be capable of accounting for at least part of the angular dependence of charge-transfer interactions. In fact Singh and Kollman³⁸ admit that their charge-transfer component has surprisingly small angular dependence. In addition, the anisotropy of charge-transfer term uncor-

rected for BSSE could originate from the stronger angular dependence of nonphysical basis set superposition error (BSSE) [compare Fig. 1(b) and Table II in ref. 27]. Additional support for the use of isotropic atom-atom representation of charge-transfer interactions is presented in Appendix.

The classical long-range induction term, $E_{\text{IND, LE}}^{(R)}$, has been approximated as:

$$E_{\text{IND, LE}}^{(R)} = -1/2 \left[\sum_{a \in A} \alpha_a (\vec{E}_a^{B \rightarrow A})^2 + \sum_{b \in B} \alpha_b (\vec{E}_b^{A \rightarrow B})^2 \right] \quad (6)$$

where α_a and α_b represent atomic polarizabilities approximating the nonempirical $E_{\text{IND, LE}}^{(R)}$ values in the least squares sense according to eq. (6). Because of the appearance of the infinite sum over excited states in the perturbation expression for this term,^{31,37} the use of extended basis sets is unavoidable.^{33,39} Therefore, the nonempirical $E_{\text{IND, LE}}^{(R)}$ values evaluated in minimal valence MODPOT basis set will be underestimated, as will the α 's. Fortunately, this term is the least important among all terms considered in this study, so the use of incomplete basis sets will not seriously affect the final results. $\vec{E}_a^{B \rightarrow A}$ and $\vec{E}_b^{A \rightarrow B}$ represent electric field vectors which have been estimated in this work from cumulative atomic multipoles²⁹:

$$\begin{aligned}
\vec{E}_b^{A \rightarrow B} = \sum_{a \in A} [q_a \vec{R}_{ab} R_{ab}^{-3} - \vec{\mu}_a R_{ab}^{-3} \\
+ 3(\vec{\mu}_a \vec{R}_{ab}) \vec{R}_{ab} R_{ab}^{-5} - 2(\vec{Q}_a \vec{R}_{ab}) R_{ab}^{-5} \\
+ 5\vec{R}_{ab}(\vec{R}_{ab} \cdot \vec{Q}_a \cdot \vec{R}_{ab}) R_{ab}^{-7}] \quad (7)
\end{aligned}$$

Finally, all the above-mentioned terms can be supplemented by the second-order dispersion contribution $E_{\text{DISP}}^{(2)}$ (not included in the SCF approach) estimated from the atom-atom expression:

$$E_{\text{DISP}}^{(2)} = - \sum_{a \in A} \sum_{b \in B} \sqrt{C_{aa} C_{bb}} R_{ab}^{-6} \quad (8)$$

where C_{aa} and C_{bb} parameters were fitted^{25,40} to reproduce the best nonempirical dispersion energy values for nitrogen heterocycles,⁴⁰ water,³² and hydrogen fluoride dimers.⁴¹ The recent study of Szczesniak and Scheiner⁴² has demonstrated that expression (8) can describe properly the functional dependence of dispersion energy on both the distance and angular features of hydrogen bonded complexes. This conclusion is also supported by

the earlier work of Prisette and Kochanski.⁴³ The set of C_{aa} coefficients used in our study (Table I) seems to agree even better with MP2 results.⁴⁴

III. RESULTS AND DISCUSSION

Determining the approximate atom-atom potentials is certainly not a trivial problem^{10, 12, 13, 19, 45} and there is no established general procedure. Results presented in Appendix clearly indicate that the electrostatic multipole term, $E_{\text{EL}, \text{MTP}}^{(1)}$, is the predominant anisotropic contribution at the atom-atom level. Therefore, by separating $E_{\text{EL}, \text{MTP}}^{(1)}$ from the remaining, more isotropic terms, we hope to reduce to some degree the complexity of this problem encountered in previous studies.^{1–20} The nonlinear exponential character of the short-range potentials makes the direct fitting of all potentials at the same time an impossible task⁴⁶ for most heteronuclear systems. It is especially difficult to obtain pairwise additive potentials for atoms usually screened by other atoms. To overcome this, the following iterative procedure was devised to obtain all pairwise additive atom-atom potentials. A group of 48 molecular complexes of HF, H₂O, NH₃, CH₄, CO, and CO₂ was selected to represent 15 atom-atom contact types (H-H, H-C, H-N, H-O, H-F, C-C, C-N, C-O, C-F, N-N, N-O, N-F, O-O, O-N, F-F). For each complex, we evaluated from energy-partitioned SCF calculations corrected for BSSE all interaction energy components E ; ($E_{\text{EL}, \text{MTP}}^{(1)}$, $E_{\text{EL}, \text{PEN}}^{(1)}$, $E_{\text{EX}}^{(1)}$, $E_{\text{IND}, \text{LE}}^{(R)}$, $E_{\text{IND}, \text{CT}}^{(R)}$) for at least seven different intermolecular distances covering the range characteristic for a given contact in molecular crystals ($R_{\text{min}} \leq R \leq R_{\text{max}}$). Based on the observation¹³ that short-range interaction energy terms are essentially dominated by contributions arising from the shortest contacts, the full set of atom-atom contacts (X)

has been divided into two subsets: the shortest (S) and the remaining (X/S) contacts. In the fitting process, the following expression was minimized

$$S(\beta_a^j, \gamma_a^j, \delta_a^j) = \sum_{G_a} \left[E_i - \sum_{\substack{n \in a \\ a \in S}} (\beta_a^j + \gamma_a^j R_{an}^{-1}) \cdot \exp(-\delta_a^j R_{an}) - \sum_{b \in X/S} \sum_{m \in b} (\beta_b^{j-1} + \gamma_b^{j-1} R_{bm}) \cdot \exp(-\delta_b^{j-1} R_{bm}) \right]^2 \quad (9)$$

employing the nonlinear least squares procedure of Golub and Pereyra.⁴⁷ G_a indicates complexes where the shortest contacts belong to type a (altogether 15 types have been considered); n and m denote contacts of the same type within the given subset. However, the long-range contacts of type a may belong to the X/S subset. Index j stands for the iteration number. In the first iteration, the last term of (9) is assumed to be zero ($\beta_b^0, \gamma_b^0, \delta_b^0 = 0$). This iterative cycle was repeated until the parameters β^j , γ^j , and δ^j had converged. The final values of β , γ , and δ have been presented in Table II for the exchange, $E_{\text{EX}}^{(1)}$, electrostatic penetration, $E_{\text{EL}, \text{PEN}}^{(1)}$, and short-range induction, $E_{\text{IND}, \text{CT}}^{(R)}$. For $R > R_{\text{max}}$, we assume that all short-range components vanish. Table I contains α values reproducing the long-range induction term, $E_{\text{IND}, \text{LE}}^{(R)}$, and C_{aa} coefficients used for estimating dispersion energy, $E_{\text{DISP}}^{(2)}$.^{25, 39} The absolute difference between the approximate and *ab initio* interaction energy components is on the average:

- 0.659 kcal/mol for exchange term, $E_{\text{EX}}^{(1)}$
- 0.076 kcal/mol for short-range induction term, $E_{\text{IND}, \text{CT}}^{(R)}$
- 0.231 kcal/mol for electrostatic penetration term, $E_{\text{EL}, \text{PEN}}^{(1)}$ and
- 0.144 kcal/mol for long-range induction term, $E_{\text{IND}, \text{LE}}^{(R)}$

Table I. α_i and C_{aa} coefficients reproducing $E_{\text{IND}, \text{LE}}^{(R)}$ and $E_{\text{DISP}}^{(2)}$, respectively (in atomic units).

Element	H	C	N	O	F
α_i	0.804	4.894	0.792	0.456	0.770
C_{aa}	1.958 ^a	47.134 ^a	24.31 ^a	11.316 ^b	4.425 ^c

^aTaken from ref. 40.

^bFitted to data from ref. 32.

^cFitted to data from ref. 41.

Table II. Nonempirical atom-atom potentials for $E_{\text{EX}}^{(1)}$, $E_{\text{EL, PEN}}^{(1)}$, and $E_{\text{IND, CT}}^{(R)}$ interactions fitting *ab-initio* results for 336 dimers ($R_{\text{min}} < R < R_{\text{max}}$). (All quantities in atomic units).

Contact	R_{min}	R_{max}	Exchange Term $E_{\text{EX}}^{(1)}$			Electrostatic Penetration Term $E_{\text{EL, PEN}}^{(1)}$			Short-Range Induction Term $E_{\text{IND, CT}}^{(R)}$		
			β	γ	δ	β	γ	δ	β	γ	δ
HH	3.50	6.40	4299.5	-18384.0	3.1398	0	-0.03032	0.57865	-2.3884	7.5162	2.0879
HC	2.84	4.99	0	11.843	1.5754	-17.069	43.219	1.9217	0	0	0
HN	2.55	5.53	0	17.027	1.7424	-87.614	192.86	2.4856	-4.6548	6.8843	1.8354
HO	2.38	4.77	20.127	-21.154	2.1116	-188.62	405.48	2.9791	-4.6177	6.7247	1.9576
HF	2.59	4.48	3.8649	4.6540	1.9257	0.29078	-1.1549	1.0224	-3.8597	5.1638	2.0442
CC	4.91	8.70	0	1215.2	2.1072	0	-41.124	1.6068	0	0	0
CN	4.91	6.80	2276.3	-6719.1	2.2585	0	-54.439	1.5024	0	-5.9028	1.2845
CO	4.91	8.88	0	29.542	1.5976	11.118	-65.903	1.4982	0	-2.6963	1.4329
CF	4.91	6.80	-39.567	288.83	1.6437	0	-267.02	2.1240	-32.939	115.68	1.8272
NN	5.00	7.44	-39.515	307.60	1.4736	0	0.11073	0.49445	0	0	0
NO	4.82	6.00	3720.8	-1156.6	2.4137	277.13	-1332.9	2.0082	0	0	0
NF	2.55	6.18	-40.441	281.78	1.6195	2011.6	-10376.	2.7266	0	0	0
OO	4.68	8.50	-53.847	367.11	1.6494	6829.7	-31680.	2.6689	0	0	0
OF	4.11	6.01	-26.958	164.79	1.5353	919.92	-4524.0	2.6438	0	0	0
FF	4.32	6.20	-95.337	593.02	1.9708	0	-1028.6	2.9525	0	0	0

These more or less transferable potentials may constitute the initial guess for finding a more refined set of potentials for a particular class of more complex molecular crystals, where solving the entire problem would otherwise be impossible. Such a case has been described in our preliminary study of CH_3NO_2 crystal packing.⁴⁸ Another possibility to improve the quality of the atom-atom potentials is to include the atomic charge as a variable. Exchange repulsion increases with the number of electrons. This effect could be especially important for hydrogen, because even a small change of the atomic charge would be relatively larger as compared with heavier elements. Indeed, the charge dependence of exchange interactions for $X - \text{H} \dots Y$ hydrogen-bonded contacts was found in our preliminary study (in 4-31G basis set) to be of the form:

$$E_{\text{H} \dots Y} = (60.75 - 81q_{\text{H}}) / (3.5q_{\text{H}} - 0.5Z_Y) \exp(-0.54Z_Y R_{\text{HY}}) \quad (10)$$

where Z_Y denotes the atomic number of Y atoms.

The nonempirical atom-atom potentials have proved to be a useful tool in studying the nature of intermolecular interactions in crystals⁴⁹ and the catalytic activity of molecular environment for most chemical reactions.⁵⁰ Ensuring the best possible description of the most active electrostatic multipole term and representing other interaction energy components at a nonempirical level could overcome

the shortcomings⁵¹ of some recently proposed models.^{1-3, 52}

In order to enable wide applications of our potentials we completed recently the library of cumulative atomic multipoles for nucleic acid bases.⁵³ Similar library is currently prepared for aminoacids also.⁵⁴

APPENDIX

Anisotropy of Nonempirical Atom-Atom Potentials

All the main interaction energy contributions described in previous sections have been calculated for 11 separations $R_{\text{XX}} (2.5 \text{ \AA} \leq R_{\text{XX}} \leq 3.5 \text{ \AA})$ for each different orientation $\alpha = \angle Y - X - X \cdot (90^\circ \leq \alpha \leq 180^\circ)$ of $\text{CO} \dots \text{OC}$ and $\text{HF} \dots \text{FH}$ dimer ($X = \text{F, O}$ and $Y = \text{H, C}$) in the minimal yet well-balanced all valence ($3s3p/3s \rightarrow [1s1p/1s]$ MODPOT basis set²⁸ where the inner shell electrons are represented by *ab initio* effective core model potentials. According to our recent study,²⁵ this basis set yields a satisfactory description of intermolecular interactions

$$Y-X \dots \dots X-Y$$

Next, each interaction energy component E has been fitted numerically by least squares to the expression

$$E = a(\alpha) R_{\text{XX}}^{-12} \quad (11)$$

for every orientation α , separately. Only the shortest intermolecular contact $X - X$ has been considered here, as it yields the predominant contribution to the overall interaction energy^{55,56} (in particular for α values close to 180°). The remaining $X - Y$ and $Y - Y$ interactions may become nonnegligible for smaller α values. The very simple formula (11) should describe properly the strongly repulsive dimer configurations considered in this study, although it is not the best analytic representation for all components of (1). This way we will have a chance to compare on an equal footing the anisotropy of all interaction energy components represented at the atomic level by $a(\alpha)$. The angular dependence of constant a directly related to anisotropy of atom-atom potentials is represented in Figure 1 (CO dimer) and Figure 2 (HF dimer).

In Table III the nonlinear correlation coefficients have been presented for various interaction energy components of (CO)₂ dimer fitted by aR^{-12} expression. It is evident that at least short-range exchange and charge-transfer interactions are well represented by aR^{-12} potential function and the fitting errors do not overshadow their isotropic nature. Slightly poorer correlation is observed for electrostatic penetration term due to higher

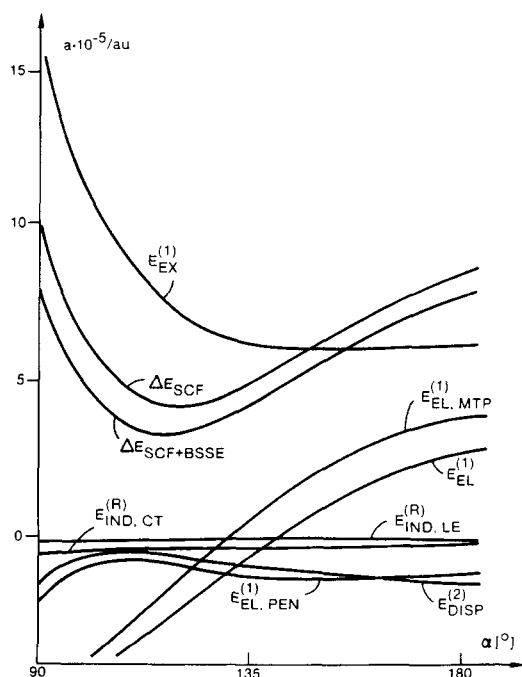


Figure 1. The nature of anisotropy of O-O interactions in CO...OC dimer represented by α dependence of a coefficients for main ΔE components (1).

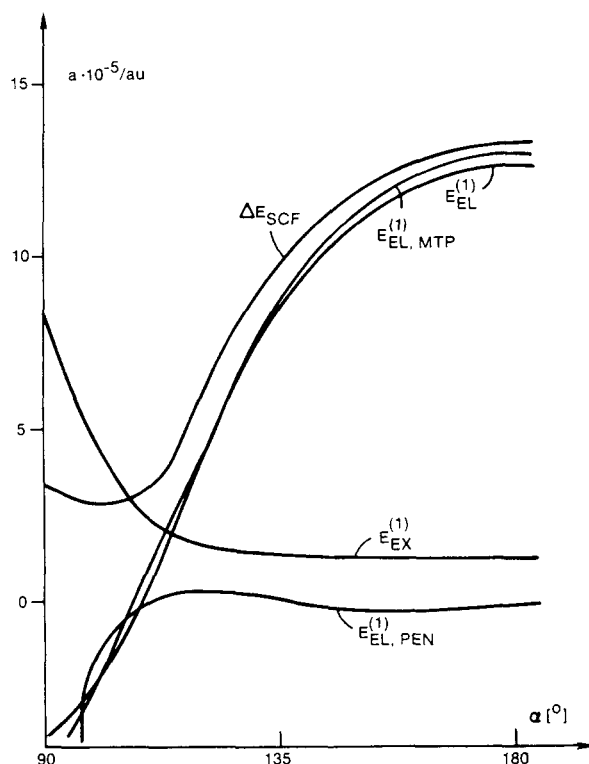


Figure 2. The nature of anisotropy of F-F interactions in HF...FH dimer represented by α dependence of a coefficients for main ΔE components (1). Terms not included here are close to 0.

Table III. Nonlinear correlation coefficients for aR^{-12} potential fitting various interaction energy components for CO₂ (See Figure 1)

Term	$\alpha = 135^\circ$	$\alpha = 180^\circ$
$E_{EL,MTP}^{(1)}$	0.952	0.905
$E_{EL,PEN}^{(1)}$	0.989	0.976
$E_{EL}^{(1)}$	0.992	0.876
$E_{EX}^{(1)}$	0.999	0.999
$E_{IND,LE}^{(R)}$	0.962	0.953
$E_{IND,CT}^{(R)}$	0.998	0.991
ΔE_{SCF}	0.998	0.979
$E_{DISP}^{(2)}$	0.958	0.944

multipole terms truncated in electrostatic multipole expansion and thus present in $E_{EL,PEN}^{(1)}$. The worst correlation is observed for electrostatic multipole term, long-range induction and dispersion terms.

As we see from Figures 1 and 2, the strong anisotropy of the overall potential originated almost entirely from the electrostatic multipole contribution, $E_{EL,MTP}^{(1)}$. The remaining terms seem to be much less anisotropic (α dependent), at least for $135^\circ \leq \alpha \leq 180^\circ$, where $X - Y$ and $Y - Y$ interactions are negligible. This supports the use of isotropic atom-atom potentials (at least for exchange

and charge-transfer interactions) and indicates the need to include anisotropic atom-atom potentials for electrostatic multipole term. With the exception of ref. 6 and this study all previously published nonempirical potentials include only isotropic atom-atom term. Analogous pure electrostatic multipole approach has been successfully applied in predicting the angular shape of van der Waals dimers.^{52,57,58}

In conclusion we would like to make reservation that the findings derived in this study may be limited. Recent study of Böhm et al.⁵⁹ indicates that the use of anisotropic potentials apparently allows one to obtain better representation of repulsive interactions of CH₃Cl, CH₂Cl₂, and CO₂ although it is not necessary for CH₄, CH₃F, CHF₃, and CH₃CN. However, this may result from representing strongly anisotropic electrostatic interactions by isotropic atomic charge-atomic charge term only.

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