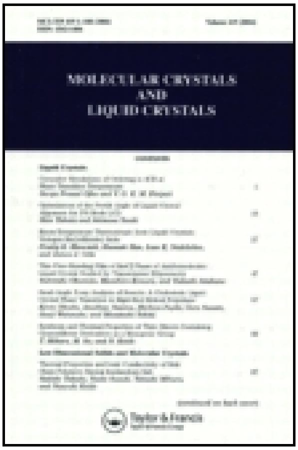

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Semiempirical Estimations for Rate of Electron Excitation Transfer and Dispersion Energy Beyond Multipole Expansion

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A new quantum-mechanical scheme is proposed for estimations of dispersion interactions and transfer matrix elements of electronic excitations. The key step in the implementation of the scheme is the use of singular value decomposition for matrices of the two-electron operator responsible for interactions between two molecules. Thus obtained decomposition contains only few leading terms having asymptotics of conventional multipole terms. It turns out that the first of these terms (quasi-monopole term), usually ignored by conventional approaches, may give a marked contribution to the transfer amplitudes. Within this technique some calculations on π-systems of aromatic molecules and fullerenes are performed.

Keywords: dispersion interaction; singular values; molecular crystals; fullerenes

INTRODUCTION

The dispersion interaction determines a great variety of physical effects in condensed media, and the energy transfer (ET) in nonpolar molecular crystals is a typical example. The vast majority of models used for describing ET and related phenomena is based on the well-known multipole expansion[1-3]. Its applicability at actual distances R between neighbor molecules (typically $R = 3.5 \div 5$ Å) is known to be questionable itself, and in addition the multipole expansion is restricted not infrequently to the dipole term only. To overcome this difficulty, the so-called non-expanded dispersion energy method was suggested (for example, see[4,5]). Though several results are known for diatomics, for large molecular systems this method becomes prohibitive[5].

The purpose of the paper is to develop a new computational scheme capable of correct semiempirical estimations of ET amplitudes and dispersion energies for complex molecules.

COMPACT REPRESENTATION OF INTERACTION MATRIX

Our approach is based on the idea that potential g^{AB} that causes dispersion forces between given molecular subunits A and B is the two-electron Coulomb operator[3,5], the matrix representation of which, generally non-Hermitian, assumes the simplest form when singular value decomposition is applied. This opens the way for complete account of dispersion interactions within any standard quantum-chemical method for excited states.

To be specific, let us introduce AO set $\{\chi_\mu^A(\vec r)\}_{1\le\mu\le N_A}$ for molecule A and AO set $\{\chi_\nu^B(\vec r)\}_{1\le\nu\le N_B}$ for molecule B. Hereafter we assume the validity of zero different overlap (ZDO) approximation[6], so overlap integrals $\langle\chi_\mu^A\,|\,\chi_\nu^B\rangle$ and related effects can be neglected. Then for the Coulomb interaction operator

$$g^{AB}\equiv g^{AB}(\vec r_1,\vec r_2)=|\vec r_1-\vec r_2|^{-1} \tag{1}$$

a finite-dimensional approximation will be used in the form

$$g^{AB}(\vec r_1,\vec r_2)=\sum_{\mu=1}^{m_A}\sum_{\nu=1}^{m_B}\gamma_{\mu\nu}\left[\chi_\mu^A(\vec r_1)\right]^2\left[\chi_\nu^B(\vec r_2)\right]^2. \tag{2}$$

Here

$$\gamma_{\mu\nu}=\left\langle\chi_\mu^A\chi_\nu^B\,\middle|\,g^{AB}\,\middle|\,\chi_\mu^A\chi_\nu^B\right\rangle \tag{3}$$

are known Coulomb two-center integrals which can be easily estimated in a number of ways, e.g. using the Ohno formula.

Applying the singular value decomposition to $\gamma = \|\gamma_{\mu\nu}\|$ one may write $\gamma = U\Gamma V^{+}$, where Γ is a diagonal matrix of corresponding singular values and U, V are accompanying unitary matrices[7]. Therefore, instead of (2) one gets the following bilinear representation

$$g^{AB} = \sum_{l=0}^{r-1} \Gamma_l U_l(\vec{r}_1) V_l(\vec{r}_2) \qquad (4)$$

with $U_l(\vec{r})$, $V_l(\vec{r})$ being the special-purpose one-electron functions

$$U_l(\vec{r}) = \sum_{\mu=1}^{M_A} \left[\chi_\mu^A(\vec{r})\right]^2 U_{\mu l} \qquad (5)$$

$$V_l(\vec{r}) = \sum_{\nu=1}^{M_B} \left[\chi_\nu^B(\vec{r})\right]^2 V_{\nu l} \qquad (6)$$

localized on A and B respectively. In a similar fashion a more general case without invoking ZDO can be treated. In so doing a counterpart of (4) is expressed via new functions that can be presented as a simple modification of $U_l(\vec{r})$, $V_l(\vec{r})$ to nonempirical approaches.

It is important that in practical calculations the number r of non-zero singular values can be replaced with some other actual number of significant values Γ_l. For instance, one may discard all the terms with $\Gamma_r \leq 10^{-4}$ a.u. in (4) (Γ_l are assumed to be arranged in decreasing order). Usually this is sufficient for obtaining good estimations of effects quadratic in g^{AB} and, in addition, considerably reduces computational efforts.

The individual contributions into decomposition (4) reveal a certain correspondence with appropriate terms of the multipole series. In particular, the first singular value Γ_0 varies asymptotically as R^{-1}; accordingly the first term in (4) will be referred to as quasi-monopole term. Similarly, asymptotics of the next 2 or 3 terms (depending on symmetry) coincides with that of dipole terms of the multipole expansion. Nevertheless, at short and intermediate distances R the individual terms in (4) effectively incorporate intermolecular interactions in a more complicated way.

A rapid decrease of Γ_l values with the increase of l can be demonstrated, for example, for interactions of two C_{60} molecules at two distances R = 3.5 Å and R = 7.0 Å (see table 1).

TABLE 1. Singular values Γ_l of the interaction matrix for C_{60} (in a.u.)

l	0	1	2	3	4	5	6	7	8
(3.5 Å)	3.275	0.155	0.155	0.155	0.015	0.015	0.014	0.014	0.014
(7.0 Å)	2.390	0.058	0.057	0.057	0.003	0.003	0.003	0.002	0.002

A similar behaviour is also characteristic for stacking typical aromatic systems .

ENERGY TRANSFER AMPLITUDES

The ET probability is determined first of all by the squared amplitude T^2 of transition $\left| A^* B^0 \right\rangle \rightarrow \left| A^0 B^* \right\rangle$ representing an exchange of excitation between two molecules under study. Here $\left| A^0 \right\rangle$ and $\left| A^* \right\rangle$ are designations for the ground state and excited state of A respectively. Neglecting the electron exchange, the amplitude expression may be cast in the form

$$T = N_A N_B \left\langle A^0 B^* \left| g^{AB} \right| A^* B^0 \right\rangle \equiv N_A N_B \left\langle A^0 B^0 \left| g^{AB} \right| A^* B^* \right\rangle \quad (7)$$

where N_A and N_B denote numbers of electrons in A and B respectively. With g^{AB} in the form (4) it gives the working formula

$$T = \sum_{l=0}^{r-1} T_l, \qquad T_l = \Gamma_l Q_l^{(A)} R_l^{(B)} \quad (8)$$

where the quantities

$$Q_l^{(A)} = N_A \left\langle A^0 \left| U_l \right| A^* \right\rangle, \qquad R_l^{(B)} = N_B \left\langle B^0 \left| V_l \right| B^* \right\rangle \quad (9)$$

are calculated using the above introduced operators (5), (6) and the density matrix formalism[6].

In calculating π-systems of aromatic molecules, the so-called CIS model (interaction of singly excited configurations) for $\left| A^{*} \right\rangle$ and $\left| B^{*} \right\rangle$ is used. Rather representative are results of ET calculations for $\pi\pi^{*}$-excitation ${}^{1}A_{1g} \rightarrow {}^{1}B_{2u}$ in tetracene crystals. For two nearest translationally non-equivalent molecules the first eight contributions T_l ($l = 0 \div 7$) to the overall value of $|T|$ = 595 cm^{-1} are as follows (all values are in cm^{-1}):

$$\{T_l\} = \{366,\ 112,\ 251,\ -2,\ -95,\ 6,\ -16,\ -26\}.$$

From these data it can be inferred that this quasi-monopole contribution (the first term T_0 in the above array) is the main contribution to T and thereby the summary rate of ET can not be correctly described by the conventional dipole model. Qualitatively similar results are observed for the transition ${}^{1}A_{1g} \rightarrow {}^{1}T_{1u}$ in solid C$_{60}$, for which the estimation $|T|$ = 334 cm^{-1} is obtained.

NON-EXPANDED DISPERSION ENERGY

For two molecular systems, A and B, the second-order dispersion energy E_{AB}^{disp} is determined by the common expression

$$E_{AB}^{disp} = -\sum_{a}\sum_{b}(\lambda_a + \lambda_b)^{-1}|T_{ab}|^2 \tag{10}$$

where λ_a and λ_b are excitation energies for A and B respectively, and the amplitudes

$$T_{ab} = N_A N_B \left\langle A^0 B^0 \left| g^{AB} \right| A_a^{*} B_b^{*} \right\rangle \tag{11}$$

generalize the ET amplitudes (7).

Within our approach the problem of calculating (11), (12) is easily resolved by applying the compact bilinear representation (4) along with the moment theory methods for obtaining perturbation corrections[8]. Furthermore, we can naturally decompose the overall quantity E_{AB}^{disp} into 'quasi-multipole' contributions as follows

$$E_{AB}^{disp} = \sum_{l,l'=0}^{r-1} E_{ll'} \tag{12}$$

where

$$E_{ll'} = -\left\langle A^0B^0 \left| U_l W_l (\Omega_A + \Omega_B)^{-1} U_{l'} W_{l'} \right| A^0 B^0 \right\rangle \tag{13}$$

with Ω_A, Ω_B being excitation operators for A and B. The asymptotic behaviour of these contributions is similar to that of the conventional expansion of E_{AB}^{disp}. Even at short distances only a few numbers of quantities $E_{ll'}$ contribute to E_{AB}^{disp}. In the case of the nearest molecules A and B in a pentacene crystal this feature can be demonstrated by the following values of the diagonal contributions E_{ll} ($l = 0 \div 7$) (all values are in kJ/mol):

$$\{E_{ll}\} = \{-0.14,\ -2.02,\ -1.05,\ -0.88,\ -0.29,\ -0.13,\ 0.56,\ -0.02\}$$

with the summary value –5.1 to be compared with the 'exact' value $E_{AB}^{disp} = -5.2$ involving all 253 quantities (13). On the other hand, 'dipole' contributions give underestimated value –3.07. In table 2 some additional results for linear polyacenes and fullerenes are presented (HF is the abbreviation for the Hartree-Fock perturbation theory used for constructing Ω_A and Ω_B).

TABLE 2. Total dispersion π-energy (in kJ/mol) for stacking at the interplane distance R = 3.5 Å.

Method	$C_{10}H_8$	$C_{14}H_{10}$	$C_{18}H_{12}$	$C_{22}H_{14}$	C_{60}	C_{70}	C_{80}
CIS	–4.5	–7.4	–10.9	–14.3	–6.7	–7.3	–7.9
HF	–3.3	–5.4	–7.4	–9.8	–4.6	–4.9	–5.3

Judging from the previous calculations on dipole polarizabilities[9], the HF model seems to be a more appropriate for quantum-chemical estimations of E_{AB}^{disp}, so the HF results from table 2 are more reliable. An interesting peculiarity of the values given in table 2 is that dispersion energies computed for fullerenes (60 and more carbon atoms) are relatively small in comparison with that for polyacenes (less than 25 carbon atoms). Note that proceeding from values of London constant C_6 (that is from the dipole contribution) one may arrive at the incorrect conclusion.

CONCLUSIONS

In this paper, it is shown how the interaction matrix that arises when calculating dispersion effects can be advantageously decomposed. The ease with which the interaction can be handled by (4) is quite evident for semiempirical models implemented here. The efficacy of the approach is also supported by our preliminary non-empirical computations for CH_4 in the Huzinaga-Dunning-type basis set. In this case 324×324 matrix of Coulomb interaction operator (1) can be accurately represented by just 21 terms of decomposition (4). This is the encouraging result from the calculation for if this holds generally it will essentially simplify *ab initio* calculations of dispersion effects including triplet excitation transfer and related phenomena.

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