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Charge Transfer Interaction in the Effective Fragment Potential Method

Hui Li  
_Iowa State University_

Mark S. Gordon  
_Iowa State University, mgordon@iastate.edu_

Jan H. Jensen  
_University of Iowa_

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Charge transfer interaction in the effective fragment potential method

Hui Li and Mark S. Gordon a)
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Jan H. Jensen
Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

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An approximate formula is derived and implemented in the general effective fragment potential (EFP2) method to model the intermolecular charge transfer interaction. This formula is based on second order intermolecular perturbation theory and utilizes canonical molecular orbitals and Fock matrices obtained with preparative self-consistent field calculations. It predicts charge transfer energies that are in reasonable agreement with the reduced variational space energy decomposition analysis. The formulas for the charge transfer gradients with respect to EFP translational and rotational displacements are also derived and implemented. © 2006 American Institute of Physics. [DOI: 10.1063/1.2196884]

I. INTRODUCTION

Modeling intermolecular interactions is of high interest in many fields of theoretical and computational studies in chemistry, physics, materials, engineering, and pharmaceuticals. High-level quantum mechanical ab initio calculations are currently the only means that can, in principle, provide very accurate descriptions of intermolecular interactions. At present, however, they are not applicable to fast modeling for large systems due to their high computational costs. Therefore, developing low cost computational methods has received much attention. In general, low cost methods are based on quantum mechanics and are usually parametrized based on some combination of high-level ab initio calculations and experimental data.

Following fundamental quantum mechanical principles, the intermolecular interaction may be decomposed into electrostatic interactions, exchange-repulsion interaction (Pauli repulsion), polarization (induction) interactions, dispersion (van der Waals) interactions, and charge transfer. Each of these types of intermolecular interactions may be expressed as an infinite series expansion. Many low cost methods contain parameters for the calculations of some subset of these interactions, in which the series expansion is truncated.

The effective fragment potential (EFP) method ¹, ² has been developed over the past decade as a low cost method for modeling intermolecular interactions in combined quantum mechanical and molecular mechanical (QM/MM) studies. The original EFP method has been developed based on Hartree-Fock, ³ density functional theory, ⁴ and second order perturbation theory. ⁵ These implementations contain parameters for electrostatic, exchange-repulsion, and induction interactions, as well as higher-order terms that can be obtained from the corresponding QM calculations. This EFP1 method developed specifically for modeling water contains fitting parameters derived from QM calculations. The EFP1 method has been successfully applied in studies of many chemical systems. ⁶

In order to model intermolecular interactions for various molecules and solvents, the general EFP method ², ⁶ (EFP2) has been developed so that fitting parameters are not required. Rather, all interaction terms are derived directly from fundamental quantum mechanics and employ preparative QM calculations for isolated individual molecules. The exchange-repulsion interaction is represented as a power series expansion in the intermolecular overlap, using localized molecular orbitals (LMOs). ⁶ The induction energy is modeled with LMO polarizability tensors and the electrostatic fields via a self-consistent scheme. The dispersion interaction is modeled with LMO dynamic polarizability points obtained from time dependent Hartree-Fock calculations. ⁷ Recent applications ⁸ show that the intermolecular interactions predicted with the EFP2 method are comparable to those predicted with second order perturbation theory (MP2) calculations. The computational cost for the EFP2 calculations is many orders of magnitude lower than that for the corresponding MP2 calculations.

The intermolecular charge transfer interaction may be analyzed using many QM energy decomposition analysis algorithms, such as the Morokuma-Kitaura method, ⁹ natural bond orbital analysis (NBOA), ⁹ natural energy decomposition analysis (NEDA), ¹⁰ reduced variational space (RVS) analysis, ¹¹ and the block-localized wave function energy decomposition (BLW-ED) scheme. ¹² From the molecular orbital point of view, the charge transfer interaction is the energy lowering due to the promotion of electrons from the occupied orbitals of one molecule into the empty orbitals of another molecule. It can be significant in QM calculations for ionic or even highly polar molecular systems.

Consequently, the EFP2 method, with parameters de-
rived from QM calculations on isolated individual molecules, should exhibit similar charge transfer interactions when electrons in the occupied MOs of one molecule interact with the virtual MOs of a neighboring molecule. An approximate formula for the charge transfer interaction in the EFP method has been derived previously. Based on the previous work, a similar, more accurate approximate formula is derived in the present work using a second order perturbative treatment of the intermolecular interactions. The corresponding energy and energy gradients have been implemented in the EFP2 method. Including charge transfer interaction in the EFP2 method improves its accuracy and broadens its applicability.

The derivations of the formulas for charge transfer energy and gradients in the EFP2 method are presented in Secs. III B and III C to illustrate the accuracy and efficiency methodology in Sec. III A, numerical results are discussed in II A and II B. After a brief description of the computational methodology in Sec. III A, numerical results are discussed in Secs. III B and III C to illustrate the accuracy and efficiency of the method. A summary and conclusions are presented in Sec. IV.

II. THEORY

A. Approximate formula for charge transfer interaction

1. First order energy

The energy of a closed shell molecule \( M \) may be written as

\[
E_M = 2 \sum_i \sum_k h_{ik} S_{ik}^{-1} + 2 \sum_i \sum_{\bar{k}} S_{ik}^{-1} \sum_r \sum_s (2 \langle ik|rs \rangle - \langle ir|ks \rangle) S_{rs}^{-1} + E_{\text{nuc}}.
\]

The summantions in Eq. (1) are over occupied molecular orbitals, \( h_{ik} \) and \( 2 \langle ik|rs \rangle - \langle ir|ks \rangle \) are one- and two-electron integrals, respectively, and \( E_{\text{nuc}} \) is the nuclear repulsion energy. Here the molecular orbitals may be nonorthogonal and non-normalized, so long as they are linearly independent. If orthonormality is imposed, Eq. (1) reduces to the usual closed shell Hartree-Fock expression. According to the property of the Slater determinant wave function, any unitary transformation of the set of orthogonal occupied MOs is still a solution of the HF equations.

Using the definition

\[
S^{-1} = I - P,
\]

Eq. (1) becomes

\[
E_M = 2 \sum_i \sum_k h_{ik} (\delta_{ik} - P_{ik}^M) + \sum_i \sum_k (\delta_{ik} - P_{ik}^M) \times \sum_r \sum_s (2 \langle ik|rs \rangle - \langle ir|ks \rangle) (\delta_{rs} - P_{rs}^M) + E_{\text{nuc}}.
\]

Now, consider two interacting molecules \( A \) and \( B \). To establish a perturbative description of the intermolecular interaction, one must choose a zeroth order wave function for the system. One possibility is to choose the simple product of the self-consistent field (SCF) wave functions obtained for isolated molecules \( A \) and \( B \) (i.e., no interaction between \( A \) and \( B \)) as the zeroth order wave function for the system. Then, the corresponding zeroth order energy of the system is simply the sum of the SCF energies of isolated \( A \) and \( B \), and the first order energy of the system is the sum of the SCF energies of isolated \( A \) and isolated \( B \) plus the electrostatic interaction between \( A \) and \( B \). However, the simple product of the SCF wave functions of isolated \( A \) and \( B \) is not antisymmetric to electron exchanges; thus it is not the correct wave function for the total Hamiltonian of the system when the \( A \) and \( B \) wave functions overlap. An antisymmetrized product must be used to provide a correct description of this system of fermions. Using an antisymmetrized product wave function for \( A \) and \( B \), the zeroth order energy of the system is the sum of the SCF energies of isolated \( A \) and \( B \), while the first order energy of the system is the sum of the SCF energies of isolated \( A \) and \( B \) plus the electrostatic and exchange-repulsion interactions between \( A \) and \( B \).

Assuming \( A \) and \( B \) form a supermolecule, then Eq. (3), which satisfies the antisymmetry requirements, can be adapted to calculate the total energy of \( A \) and \( B \) to the first order approximation with the full Hamiltonian of the system and the zeroth order wave functions, i.e., the SCF MOs of isolated \( A \) and \( B \). With \( i' \), \( k' \), \( r' \), and \( s' \) representing the occupied MOs of isolated \( A \) and \( B \), Eq. (3) becomes

\[
E_{AB}^{(0)} + E_{AB}^{(1)} = \langle \Psi^{(0)} | H | \Psi^{(0)} \rangle
\]

\[
= 2 \sum_{i'k'} h_{i'k'}^{AB} (\delta_{i'k'} - P_{i'k'}^{AB})
\]

\[
+ \sum_{i'k'} (\delta_{i'k'} - P_{i'k'}^{AB}) \times \sum_{r's'} (2 \langle i'k'|r's' \rangle - \langle i'k'|s'r' \rangle)
\]

\[
\times (\delta_{r's'} - P_{r's'}^{AB}) + E_{\text{nuc}},
\]

where \( E_{AB}^{(0)} \) is the zeroth energy of the system (i.e., the sum of the SCF energies of \( A \) and \( B \)), \( E_{AB}^{(1)} \) is the first order perturbation energy correction, and \( H \) is the full Hamiltonian of the system [note that it is equivalent to the Fock operator when restricted Hartree-Fock (RHF) single determinant wave func-
tions are used). In the summation occAB means the sum is taken over occupied A and occupied B orbitals. The superscript AB on the one-electron operator $h$ means that the nuclear potentials are from both molecules A and B:

$$h^{AB} = T + V^{macA} + V^{macB}. \quad (5)$$

The superscript $AB$ on $P$ means that it is associated with the inverse of the overlap matrix of the supermolecule:

$$P^{AB} = I - (S^{AB})^{-1}. \quad (6)$$

With $i, k, r, s, j, l, t$, and $w$ representing occupied MOs of $A$ and $B$, Eq. (4) may be expanded as

$$E^{(0)}_{AB} + E^{(1)}_{AB} = 2 \sum_{i,j} h^{AB}_{ij} (\delta_{ik} - P^{AB}_{ik}) - 2 \sum_{i,j} \sum_{k,l} h^{AB}_{ij} P^{AB}_{kl} - 2 \sum_{j,k} h^{AB}_{jk} P^{AB}_{kj} + 2 \sum_{j,k} h^{AB}_{jk} (\delta_{ij} - P^{AB}_{ij})$$

$$+ \sum_{j,k} (\delta_{ik} - P^{AB}_{ik}) \left( \sum_{r,s} (2\langle ik|rs \rangle - \langle ir|ks \rangle)(\delta_{rs} - P^{AB}_{rs}) - \sum_{r,s} (2\langle ik|rw \rangle - \langle ir|kw \rangle)P^{AB}_{rw} \right)$$

$$- \sum_{i,j} \sum_{k,l} P^{AB}_{il} \left( \sum_{r,s} (2\langle il|rs \rangle - \langle ir|ls \rangle)(\delta_{rs} - P^{AB}_{rs}) - \sum_{r,s} (2\langle il|rw \rangle - \langle ir|lw \rangle)P^{AB}_{rw} \right)$$

$$+ \sum_{j,k} (\delta_{ij} - P^{AB}_{ij}) \left( \sum_{l,m} (2\langle jk|lm \rangle - \langle jk|ls \rangle)(\delta_{lm} - P^{AB}_{lm}) - \sum_{l,m} (2\langle jk|rw \rangle - \langle jk|lw \rangle)P^{AB}_{rw} \right)$$

$$+ \sum_{j,k} (\delta_{ij} - P^{AB}_{ij}) \left( \sum_{l,m} (2\langle jk|lm \rangle - \langle jk|ls \rangle)(\delta_{lm} - P^{AB}_{lm}) - \sum_{l,m} (2\langle jk|rw \rangle - \langle jk|lw \rangle)P^{AB}_{rw} \right)$$

$$+ \sum_{i,j} \sum_{k,l} h^{AB}_{ij} (\delta_{ij} - P^{AB}_{ij}) = E^{mac}. \quad (7)$$

If the MOs are normalized (not necessarily orthogonal), the diagonal elements of the overlap matrix are unity. If one defines $\tilde{S}$ as the off-diagonal part of the overlap matrix,

$$\tilde{S} = S - I, \quad (8)$$

the $P$ matrix can be expanded in $\tilde{S}$ as follows:

$$P = I - S^{-1} = I - (I + \tilde{S})^{-1}$$

$$= I - (I - \tilde{S} + \tilde{S}^2 - \tilde{S}^3 + \cdots) = \tilde{S} - \tilde{S}^2 + \tilde{S}^3 - \cdots. \quad (9)$$

If the MOs within a given molecule are orthogonal to each other, then the leading term in the $P$ matrix elements whose indices are from the same molecule (either $A$ or $B$) is of the second power of $S$. For example (note that $\tilde{S}_{ik} = \tilde{S}_{ji} = \tilde{S}_{jk} = 0$ due to orthonormality), truncating the expansion after the second order term,

$$P^{AB}_{ik} = \tilde{S}_{ik} - (\tilde{S}^2)_{ik} + (\tilde{S}^3)_{ik} - \cdots \approx - \sum_{j} \tilde{S}_{ij} \tilde{S}_{ik} - \sum_{j} \tilde{S}_{ij} \tilde{S}_{jk} = - \sum_{j} S_{ij} S_{jk}. \quad (10)$$

The $P$ matrix elements with their indices from two different molecules are of the first power of $S$ (note $\tilde{S}_{ik} = \tilde{S}_{ij} = 0$ due to orthonormality),
\[ P_{ij}^{AB} = P_{ji}^{AB} = S_{ij} - (\bar{S}^2)_{ij} + (\bar{S}^3)_{ij} - \cdots \]
\[ = \bar{S}_{ij} - \sum_k S_{i\bar{k}} S_{\bar{k}j} - \sum_l \bar{S}_{i\bar{k}} \bar{S}_{\bar{k}j} = S_{ij}. \quad (11) \]

Based on Eqs. (7), (10), and (11), Jensen and Gordon\(^6\) derived an approximate formula, which is accurate to \( \bar{S}^2 \) in the expansion of \( P \), for the intermolecular exchange-repulsion energy.

The present study aims at the simplest formula for the second order perturbation energies; thus only the terms on the order of the first power of \( S \) are retained. Neglecting the second and higher powers of \( S \) in the expansion of \( P \) (i.e., \( P_{ikr}^{AB} P_{jrt}^{AB} P_{rs}^{AB} P_{tw}^{AB} = 0 \)), Eq. (7) becomes

\[
E_{AB}^{(0)} + E_{AB}^{(1)} = 2 \sum_{i} \sum_{k} h_{ik}^{AB} \delta_{ik} - 2 \sum_{i} \sum_{j} h_{ij}^{AB} S_{ij} - 2 \sum_{j} \sum_{k} h_{jk}^{AB} S_{jk} + 2 \sum_{i} \sum_{j} h_{ij}^{AB} \delta_{ij} + \sum_{i} \sum_{k} \sum_{r} \sum_{s} (2 \langle ik | rs \rangle - \langle ir | ks \rangle) \delta_{rs} - \sum_{r} \sum_{w} (2 \langle ik | rw \rangle - \langle ir | kw \rangle) S_{rw} \]
\[ + \sum_{i} \sum_{k} \sum_{r} \sum_{s} (2 \langle ik | tw \rangle - \langle ir | kw \rangle) \delta_{tw} - \sum_{i} \sum_{j} (2 \langle ik | ts \rangle - \langle ir | ks \rangle) S_{ts} \]
\[ - \sum_{i} \sum_{k} \sum_{r} \sum_{s} (2 \langle il | rs \rangle - \langle ir | ls \rangle) \delta_{rs} + \sum_{t} \sum_{w} (2 \langle il | tw \rangle - \langle it | lw \rangle) \delta_{tw} \]
\[ - \sum_{j} \sum_{k} \sum_{r} \sum_{s} (2 \langle jk | rs \rangle - \langle jr | ks \rangle) \delta_{rs} + \sum_{t} \sum_{w} (2 \langle jk | tw \rangle - \langle jt | lw \rangle) \delta_{tw} \]
\[ + \sum_{j} \sum_{k} \sum_{r} \sum_{s} (2 \langle jl | rs \rangle - \langle jr | ls \rangle) \delta_{rs} + \sum_{t} \sum_{w} (2 \langle jl | tw \rangle - \langle jx | lw \rangle) S_{tw} \]
\[ + \sum_{j} \sum_{k} \sum_{r} \sum_{s} (2 \langle jl | tw \rangle - \langle jx | lw \rangle) \delta_{tw} - \sum_{i} \sum_{j} (2 \langle jl | ts \rangle - \langle jl | ts \rangle) S_{tx} \]
\[ + E^{\text{nuc}}. \quad (12) \]

**2. Charge transfer interaction**

Now, consider the second order energy of the system when the interaction between \( A \) and \( B \) is included as a perturbation. The interaction between \( A \) and \( B \) includes nuclear repulsion, electronic repulsion, and nucleus-electron attraction. In this work, the averaged electrostatic interaction between \( A \) and \( B \) is taken to be the perturbation. This assumes that molecule \( A \) experiences the electrostatic field created by a second molecule \( B \), which can be obtained from the electron density obtained from a SCF calculation and the nuclear charges and positions. Under the electrostatic perturbation, the occupied MOs of \( A \) may mix with the virtual MOs of \( A \), resulting in changes in the electron density and energy lowering. This is sometimes referred to as the induction energy. The occupied MOs of \( A \) may also mix with the virtual MOs of \( B \), leading to further energy lowering, provided that mixing the virtual MOs of \( A \) is insufficient to reach the variational limit. This insufficiency arises due to the use of incomplete atomic basis sets and may be especially apparent for ionic molecules. The energy lowering due to mixing the occupied MOs of one molecule with the virtual MOs of another molecule is referred to as the charge transfer energy.

In general, the second order total energy of a system may be obtained by averaging the full Hamiltonian of the system over the zeroth order and the first order wave functions:

\[
E_{AB}^{(0)} + E_{AB}^{(1)} + E_{AB}^{(2)} = \langle \Psi^{(0)} | H | \Psi^{(1)} \rangle. \quad (13) \]

So, the second order perturbation energy is

\[
E_{AB}^{(2)} = \langle \Psi^{(0)} | H | \Psi^{(1)} \rangle - \langle \Psi^{(0)} | H | \Psi^{(0)} \rangle. \quad (14) \]

In Eq. (12) the average value of the Hamiltonian over the unperturbed zeroth order wave function [i.e., the second term in Eq. (14)] is calculated. Similarly, the average value of the Hamiltonian over the zeroth and first order wave functions [i.e., the first term in Eq. (14)] can be obtained by substituting one set of \( \psi_l \) with \( \psi_l^{(1)} \) in Eq. (12). Perturbed by the electrostatic field of \( B \), an unperturbed occupied MO of \( A \), \( \psi_i^0 \), mixes with the virtual MOs of \( B \), \( \psi_l^B \), to form the first order perturbed MO, \( \psi_i^{(1)} \).
\[ \psi_i^{(1)} = \psi_i^{\text{vir}} + \sum_n U_{in} \psi_n^{\text{occ}} \]  

(15)

where \( U_{in} \) is the mixing coefficient. It is very important to note that two sets of MOs are present in Eq. (12) (in the \( \text{bra} \) and \( \text{ket} \)) and one set must remain as an unperturbed zeroth order wave function. For convenience, \( \psi_i^A \) and \( \psi_i^B \) are selected to be substituted with \( \psi_i^{A(1)} \) and \( \psi_i^{B(1)} \), respectively.

When \( \psi_i^1 \) in the first term in Eq. (12) is substituted with \( \psi_i^{A(1)} \), the corresponding energy change is

\[ E_{1\text{st}}^{(2)} = 2 \sum_i \sum_k \left[ h_{ik}^{AB} \delta_{ik} + \sum_n U_{in} h_{in}^{AB} \right] \delta_{ik} - 2 \sum_k h_{ik}^{AB} \delta_{ik} \]

\[ = 2 \sum_i \sum_k \sum_n U_{in} h_{ik}^{AB} \delta_{ik} = 2 \sum_i \sum_k U_{in} h_{ik}^{AB} \]  

(16)

Similarly, the energy change associated with the second term in Eq. (12) is

\[ E_{2\text{nd}}^{(2)} = -2 \sum_i \sum_n U_{in} \sum_{ij} h_{ij}^{AB} S_{ij}. \]  

(17)

Although the third term in Eq. (12) contains MOs of \( A \), \( \psi_i^A \), these MOs are from the zeroth order wave function and are therefore not subject to substitution. So, the energy change associated with the third term is zero. As stated above, only \( \psi_i^A \) and \( \psi_i^B \) are selected to be substituted with \( \psi_i^{A(1)} \) and \( \psi_i^{B(1)} \). The fourth term in Eq. (12) contains only the MOs of \( B \) and therefore also has zero contribution to the energy change, since only the perturbation of \( A \) due to \( B \) is considered here.

The energy change due to the fifth term in Eq. (12) can be derived in the same manner as for terms 1 and 2:

\[ E_{5\text{th}}^{(2)} = 2 \sum_i \sum_n U_{in} \sum_{kk} (2\langle n|kk\rangle - \langle nk|ik\rangle) \]

\[ -2 \sum_i \sum_n U_{in} \sum_{kj} (2\langle n|kj\rangle - \langle nk|ij\rangle) S_{kj} \]

\[ - \sum_k \sum_j \sum_n U_{in} (2\langle kk|nj\rangle - \langle kn|kj\rangle) S_{kj} \]

\[ + \sum_j \sum_n U_{in} (2\langle jj|ij\rangle - \langle nj|ij\rangle). \]  

(18)

When \( i \neq k \) the second term in Eq. (18) involves four different MOs and the integrals are relatively small and negligible. The largest contribution to this term occurs for \( i = k \):

\[ -2 \sum_i \sum_n U_{in} (2\langle ni|ji\rangle - \langle ni|ij\rangle) S_{ij} \]

\[ = -2 \sum_i \sum_n U_{in} (ni|ij) S_{ij} \]  

(19)

Compared to the fourth term in Eq. (18), the quantity in Eq. (19) is still relatively small because \( i \) and \( j \) are two occupied MOs from different molecules:

\[ |\langle ni|jj\rangle| \ll |\langle ni|ij\rangle|, \]

\[ |S_{ij}| \ll 1. \]  

(20)

So, the second term in Eq. (18) can be neglected, and this equation can be simplified to

\[ E_{5\text{th}}^{(2)} = 2 \sum_i \sum_n U_{in} \sum_{kk} (2\langle n|kk\rangle - \langle nk|ik\rangle) \]

\[ - \sum_k \sum_j \sum_n U_{in} (2\langle kk|nj\rangle - \langle kn|kj\rangle) S_{kj} \]

\[ + \sum_j \sum_n U_{in} (2\langle jj|ij\rangle - \langle nj|ij\rangle). \]  

(21)

The energy change due to the sixth term of Eq. (12) is

\[ E_{6\text{th}}^{(2)} = - \sum_i \sum_n U_{in} \sum_{ij} S_{ij} \sum_k (2\langle n|kk\rangle - \langle nk|kj\rangle) \]

\[ - \sum_k \sum_j \sum_n U_{in} (2\langle kl|ni\rangle - \langle kn|li\rangle) \]

\[ - \sum_i \sum_j \sum_n U_{in} (2\langle nj|ll\rangle - \langle nl|jl\rangle) \]  

(22)

Similarly, the second term of Eq. (22) is relatively small and can be neglected:

\[ E_{6\text{th}}^{(2)} = - \sum_i \sum_n U_{in} \sum_{ij} S_{ij} \sum_k (2\langle n|kk\rangle - \langle nk|kj\rangle) \]

\[ - \sum_k \sum_j \sum_n U_{in} (2\langle kl|ni\rangle - \langle kn|li\rangle) \]

\[ - \sum_i \sum_j \sum_n U_{in} (2\langle nj|ll\rangle - \langle nl|jl\rangle) \]  

(23)

The energy change due to the seventh term of Eq. (12) is

\[ E_{7\text{th}}^{(2)} = - \sum_j \sum_k \sum_i U_{in} (2\langle jk|ni\rangle - \langle jn|ki\rangle) \]  

(24)

This term is relatively small and can be neglected. The energy change due to the eighth term of Eq. (12) is

\[ E_{8\text{th}}^{(2)} = \sum_j \sum_i \sum_n U_{in} (2\langle jj|ni\rangle - \langle jn|ji\rangle) \]

\[ - \sum_j \sum_i \sum_n U_{in} (2\langle ll|nj\rangle - \langle ln|jj\rangle) S_{ij}. \]  

(25)

Combining Eqs. (16), (17), (21), (23), and (25), the total energy change, i.e., the charge transfer energy for molecule \( A \), is
The one-electron operator $h^{AB}$ is the sum of the kinetic energy operator and the nuclear potential operators of $A$ and $B$ [cf. Eq. (5)], so Eq. (26) becomes

$$CT^{A(B)} = 2 \sum_{i} \sum_{n} U_{in}(T_{nj} + V_{nuc}^{in} + V_{nuc}^{nj}) - 2 \sum_{i} \sum_{n} U_{in} \sum_{j} \left( T_{nj} + V_{nuc}^{nj} + V_{nuc}^{nj} \right) S_{ij}^{AB}$$

$$- \sum_{i} \sum_{n} U_{in} \sum_{j} \left( 2(\langle k|k \rangle - \langle ik|nk \rangle) \right) S_{ij}^{AB} + 2 \sum_{i} \sum_{n} U_{in} \sum_{j} \left( 2(\langle in|jj \rangle) \right) S_{ij}^{AB}$$

(27)

In the second term of Eq. (28),

$$T_{nj} + V_{nuc}^{nj} + \sum_{l} \left( 2(\langle n|ll \rangle - \langle nl|jl \rangle) \right) = F_{nj}^{B} = 0.$$  

(29)

In the first term of Eq. (28),

$$T_{in} + V_{nuc}^{in} + \sum_{k} \left( 2(\langle in|kk \rangle - \langle ik|nk \rangle) \right) = F_{in}^{A}.$$  

(30)

Since orbital $\phi_{B}^{B}$ is a virtual MO of molecule $B$ and has no relation to $A$, $F_{in}^{A}$ is not necessarily zero. In the limit of a complete linearly independent basis set on $A$, in which case $\phi_{B}^{B}$ can be expressed as a linear combination of all MOs of $A$, and if it is assumed that $\phi_{B}^{B}$ is orthogonal to the occupied MOs of $A$, it would then follow that $F_{in}^{A} = 0$.

Then, Eq. (28) becomes

$$CT^{A(B)} = 2 \sum_{i} \sum_{n} U_{in} \left[ V_{nuc}^{in} + \sum_{j} \left( 2(\langle in|jj \rangle - \langle ij|nj \rangle) \right) \right]$$

$$- \sum_{i} \sum_{n} U_{in} \sum_{j} \left[ V_{nuc}^{nj} + \sum_{k} \left( 2(\langle nk|kk \rangle) \right) \right] S_{ij}.$$  

(32)

Of course, practical basis sets are never complete, so this approximation must be carefully evaluated. In the following discussion, $\phi_{B}^{B}$ is assumed to be orthogonal to both the occupied and virtual MOs of $A$. The impact of this approximation is discussed below.

Two additional approximations may be used to further simplify Eq. (32). The first one is to neglect the exchange integrals $(ij|nj)$ and $(nk|jk)$, which are difficult to compute, and represent the electrostatic potentials of the molecules with multipole expansion points:

$$V_{nuc}^{in} + \sum_{j} \left( 2(\langle in|jj \rangle - \langle ij|nj \rangle) \right)$$

$$= V_{nuc}^{in} + \sum_{j} \left( 2(\langle in|jj \rangle) \right) = V_{nuc}^{in}.$$  

(33)

$$V_{nuc}^{nj} + \sum_{k} \left( 2(\langle nk|kk \rangle - \langle nk|jk \rangle) \right)$$

$$= V_{nuc}^{nj} + \sum_{k} \left( 2(\langle nk|kk \rangle) \right) = V_{nuc}^{nj}.$$  

(34)

The superscripts EFA and EFB on $V$ in Eqs. (33) and (34) represent the EFP multipole potentials of molecules $A$ and $B$, respectively. In the EFP method, molecular electrostatic potentials are expanded up to octupoles at the atoms and bond midpoints using the distributed multipole analysis of Stone and Alderton. However, a truncation at the quadrupole is used in this study for the charge transfer interactions after...
tests with the octupoles. No significant differences were found when octupoles were included. In general, octupoles in the EFP method have very small contribution to the total electrostatic interaction.

Though the approximations are similar in Eqs. (33) and (34), the accuracies might be very different from each other. In Eq. (33) $\psi^A_i$ and $\psi^B_n$ are occupied orbitals of $A$ and virtual orbitals of $B$, respectively. In Eq. (34) $\psi^B_i$ and $\psi^A_n$ are occupied and virtual orbitals of the same molecule $B$.

The other possible approximation is to form the Fock matrix elements and approximate them as zero so only the kinetic energy terms are kept:

$$\begin{align*}
\Sigma^{\text{occB}}_m &= \sum_j (2\langle i|j\rangle - \langle ij|nj\rangle)|T_{mn}| = T_{mn} \approx -T_{mn}, \\
\Sigma^{\text{occA}}_n &= \sum_j (2\langle n|k\rangle - \langle nk|jk\rangle)|T_{mj}| = T_{nj} \approx -T_{nj}.
\end{align*}$$

Similarly, the accuracies of Eqs. (35) and (36) might be very different from each other.

It is difficult to judge the accuracies of the above four approximations without numerical values. The accuracies may depend on basis sets, electronic structures of the molecules, relative geometries of the molecules, and the shapes (localized or canonical) of the molecular orbitals. Numerical tests (see Appendix) using canonical MOs show that the combined use of Eqs. (33) and (36) is the best of the four possible combinations. So finally Eq. (32) is approximated as

$$C^A(B) = 2\sum_i \sum_n U_{in} \left( V_{in}^{\text{EFB}} + \sum_j T_{nj}^S \right).$$

### 3. Mixing coefficients

In general, the first order perturbed ground state wave function can be formed with the zeroth order ground state wave function and the excited state wave functions. In SCF molecular orbital theory, the first order occupied MOs can be obtained by mixing the zeroth order occupied MOs and virtual MOs. When orthonormal canonical MOs are used, the mixing coefficient $U_{in}$ for orbitals $\psi^A_n$ and $\psi^A_m$ (both from molecule $A$) is

$$U_{in} = \frac{\langle \psi^A_m | V | \psi^A_n \rangle}{\varepsilon^A_m - \varepsilon^A_n} = \frac{\langle \psi^A_m | V | \psi^A_n \rangle}{F^A_{nn} - F^A_{nm}},$$

where $V$ is the perturbation potential and $\varepsilon^A_n$ and $\varepsilon^A_m$ are the orbital energies, i.e., the diagonal elements $F^A_{nn}$ and $F^A_{nm}$ of the Fock matrix in the canonical MO basis in the SCF calculation for $A$.

The mixing coefficient $U_{in}$ in Eq. (15) can be calculated approximately with a similar equation (note $\psi^B_n$ is a virtual orbital of molecule $B$):

$$U_{in} = \frac{\langle \psi^B_n | V_{\text{EFB}} | \psi^B_m \rangle}{\varepsilon^B_n - \varepsilon^B_m} = \frac{\langle \psi^B_n | V_{\text{EFB}} | \psi^B_m \rangle}{F^B_{nn} - F^B_{nm}}.\quad (39)$$

$V_{\text{EFB}}$ is the multipole potential of molecule $B$ at the electronic coordinates, $\varepsilon^B_n$ is the orbital energy of $\psi^B_n$ (i.e., the diagonal Fock matrix element $F^B_{nn}$ determined by the SCF calculation for isolated $B$), $\psi^B_n$ is the orbital energy of $\psi^B_n$ when it is assumed to be an orthonormal canonical virtual MO of molecule $A$ (note that only canonical orbitals have meaningful orbital energies), and can be written as a Fock matrix element $F^A_{nn}$:

$$F^A_{nn} = T_{nn} + V_{\text{EFB}}^{\text{A}} + \sum_i (2\langle in|ii\rangle - \langle ni|ni\rangle) = T_{nn} + V_{\text{EFB}}^{\text{A}} - \sum_i \langle ni|ni\rangle. \quad (40)$$

It is important to note that this $F^A_{nn}$ is unrelated to $F^B_{nn}$, which is the orbital energy of $\psi^B_n$ determined by the SCF calculation for isolated $B$.

Since $\psi^A_i$ and $\psi^B_i$ are from $A$ and $B$, respectively, and are made orthonormal to each other [cf. Eq. (43)], the exchange term in Eq. (40) is relatively small and can be neglected. Furthermore, for the sake of having the simplest formula (especially in the gradient expression), $F_{nn}$ is replaced with $T_{nn}$:

$$F^A_{nn} = T_{nn} + V_{\text{EFB}}^{\text{A}}, \quad (41a)$$

$$F^A_{nn} = T_{nn}. \quad (41b)$$

So Eq. (39) becomes

$$U_{in} = \frac{V_{\text{EFB}}^{\text{A}}}{F^A_{nn} - T_{nn}}. \quad (42)$$

Numerical tests show that the difference between the charge transfer energies [cf. Eqs. (44) and (45)] obtained by using Eqs. (41a) and (41b) to calculate the mixing coefficients is very small. For example, the charge transfer energies obtained with Eqs. (41a) and (41b) are $-0.7525$ and $-0.7563$ kcal/mol, respectively, for a pair of water molecules [with the 6-31+ +G(d,p) basis set], and are $-6.0589$ and $-6.0894$ kcal/mol, respectively, for a pair of ammonium and nitrate ions [with the 6-31+ +G(df,p) basis set].

In the derivation of Eqs. (15)–(25), as well as of Eqs. (31) and (42), $\psi^B_n$ is assumed to be orthonormal to the occupied MOs of $A$ and $B$. Otherwise there would be very many terms containing the nonzero overlap integrals between $\psi^B_n$ and the other MOs of $A$ and $B$. Furthermore, since the excitation from the occupied MOs of $A$ to the virtual MOs of $A$ is considered separately as induction energy, $\psi^B_n$ must be orthogonal to all the virtual MOs of $A$.

The orthonormality of $\psi^B_n$ to the occupied MOs of $B$ is already satisfied because they are the occupied and virtual orbitals of the same molecule. However, the orthonormality of $\psi^B_n$ to all the MOs of $A$ is not generally satisfied and must be enforced. The following approximate orthonormalization procedure is used for $\psi^B_n$:

$$\psi^B_n = \frac{1}{\sqrt{1 - \sum_m S_{nm}^A \psi^A_m}} \left( \psi^B_n - \sum_m S_{nm}^A \psi^A_m \right). \quad (43)$$

Combining Eqs. (37) and (42) and replacing $\psi^B_n$ with $\psi^B_n$ as in Eq. (43), we have
proving the accuracy; very complicated gradient formula which requires significantly more computing time; and (c) whether or not the orthonormalized orbital \( \psi_B^{n+} \) is used to calculate the kinetic energy in Eq. (42), Eq. (44) gives zero charge transfer energy when a complete basis set is used for \( A \) (one of the main purposes of the enforced orthonormalization).

### 4. Multimolecule system

For a system that consists of more than two molecules \((A, B, C, D, \ldots)\), the total charge transfer energy of \( A \) is taken as the sum of the independent pairwise terms:

\[
\text{CT}^{A(B)} = \text{CT}^{A(B)} + \text{CT}^{A(C)} + \text{CT}^{A(D)} + \cdots .
\]

The total charge transfer energy of the system is the sum of the charge transfer energy of each fragment. Defined in this way, the charge transfer energy for a collection of molecular fragments is strictly pairwise additive. Many-body effects in the EFP method arise only from the self-consistent polarization (induction) term.

### B. The charge transfer forces and torques

#### 1. General expressions for the derivatives

In the EFP method, the internal geometry of each molecular fragment is frozen, with three independent degrees of translational freedom and three independent degrees of rotational freedom about its center of mass. Since the charge transfer interactions in this model are pairwise additive, the translational and rotational gradients of the charge transfer energy are also pairwise additive.

As described above, the charge transfer energy for a pair of molecules, \( A \) and \( B \), is the sum of the change in the charge transfer energy of \( A \) induced by \( B \) [\( \text{CT}^{A(B)} \)] and the charge transfer energy of \( B \) induced by \( A \) [\( \text{CT}^{B(A)} \)]. When \( B \) is fixed and \( A \) translates and rotates, both \( \text{CT}^{A(B)} \) and \( \text{CT}^{B(A)} \) are subject to change, creating forces and torques on \( A \).

Based on Eqs. (44) and (45), the forces and torques that \( B \) exerts on \( A \) are the (negative) first derivatives of \( \text{CT}^{A(B)} + \text{CT}^{B(A)} \) with respect to the translation or rotation coordinate \( q_A \) of \( A \):
The following derivatives with respect to the translational or rotational coordinate \( q_A \) of \( A \) are required to evaluate Eq. (48):

\[
\begin{align*}
\frac{\partial V_{jm}^{\text{EFA}}}{\partial q_A} & = \sum_v c_{uv} \sum_u c_{au} (\frac{\partial V_{jm}^{\text{EFA}}}{\partial q_A}) \\
\frac{\partial T_{mn}}{\partial q_A} & = \sum_v c_{uv} \sum_u c_{au} (\frac{\partial T_{mn}}{\partial q_A}) \\
\frac{\partial S_{nm}}{\partial q_A} & = \sum_v c_{uv} \sum_u c_{au} (\frac{\partial S_{nm}}{\partial q_A}) \\
\end{align*}
\tag{49}
\]

These derivatives of the MO integrals can be obtained from the derivatives of the corresponding AO integrals and the derivatives of the MO coefficients. For example,

\[
\frac{\partial V_{jm}^{\text{EFA}}}{\partial q_A} = \sum_v c_{uv} \sum_u c_{au} (\frac{\partial V_{jm}^{\text{EFA}}}{\partial q_A}) + \sum_v c_{uv} \sum_u c_{au} (\frac{\partial c_{au}}{\partial q_A}) V_{jm}^{\text{EFA}} + \sum_v c_{uv} \sum_u c_{au} (\frac{\partial V_{jm}^{\text{EFA}}}{\partial q_A}) V_{jm}^{\text{EFA}}.
\tag{50}
\]

Here, \( c \) represents the MO coefficients, while \( u \) and \( v \) represent the AOs of molecules \( A \) and \( B \), respectively.

In \textit{ab initio} and EFP calculations, the orientations of all AOs are fixed. Therefore, the rotational derivatives of the AO integrals with respect to the AO centers (i.e., nuclear centers) are always zero. In EFP calculations, the MOs for an EFP are frozen to its internal coordinates and translate and rotate as the EFP translates and rotates.

### 2. Forces

When an EFP translates, the AO centers (i.e., nuclear centers) and MOs translate, while the MO coefficients are constants. As a consequence, the translational derivatives of the MO integrals can be obtained from the translational derivatives of the AO integrals. For example, the derivative of the integral \( V_{jm}^{\text{EFA}} \) with respect to the translational motion of molecule \( A \) (molecule \( B \) is fixed) in the \( x \) direction \((\chi_A)\) is

\[
\frac{\partial V_{jm}^{\text{EFA}}}{\partial \chi_A} = \sum_v c_{uv} \sum_u c_{au} (\frac{\partial V_{jm}^{\text{EFA}}}{\partial \chi_A}).
\tag{51}
\]

The overall translation of \( A \) in the \( x \) direction \((\chi_A)\) can be decomposed into the individual atomic translations in \( A(x) \):

\[
\frac{\partial V_{jm}^{\text{EFA}}}{\partial \chi_A} = \sum_v c_{uv} \sum_u c_{au} (\frac{\partial V_{jm}^{\text{EFA}}}{\partial \chi_A}).
\tag{51}
\]
3. Torques

When a molecule rotates about its center of mass, the AO or nuclear centers translate (unless an AO center is the center of mass), and the MO coefficients change. The rotational derivatives of the MO integrals can be evaluated with the translational derivatives of AO integrals and rotational derivatives of MO coefficients. For example, the derivative of the integral \( V_{in}^{\text{EFB}} \) with respect to the rotational motion in the \( y \)-\( z \) plane (denoted as \( \theta_{ya} \)) about the atomic centers plus individual atomic translations in the \( y \)-\( z \) plane multiplied by the distances between the atomic centers \((x_a, y_a, z_a)\) and the center of mass \((x^A_{\text{com}}, y^A_{\text{com}}, z^A_{\text{com}})\):

\[
\partial \phi_a / \partial \theta_{ya} = \sum_a \left[ \partial \phi_a / \partial x_a + \partial \phi_a / \partial z_a \right] (y_a - y^A_{\text{com}}) - \left( \partial \phi_a / \partial y_a \right) (z_a - z^A_{\text{com}}). \tag{58}
\]

Thus Eq. (57) becomes

\[
\partial V_{in}^{\text{EFB}} / \partial \theta_{ya} = \sum_v c_{uv} \sum_a c_{au} \sum_a \left[ + \left( \partial \phi_a / \partial \theta_{ya} \right) \right] V_{uv}^{\text{EFB}} |\psi_v\rangle + \left( \partial \psi_a / \partial \theta_{ya} \right) (y_a - y^A_{\text{com}}) - \left( \partial \psi_a / \partial y_a \right) (z_a - z^A_{\text{com}}) + \sum_v c_{uv} \sum_a \left[ + \partial c_{au} / \partial \theta_{ya} + \partial c_{au} / \partial \psi_a \right] \times (y_a - y^A_{\text{com}}) - \left( \partial c_{au} / \partial y_a \right) (z_a - z^A_{\text{com}}) V_{uv}^{\text{EFB}}. \tag{59}
\]

The rotational derivatives of AOs and translational derivatives of MO coefficients are always zero:

\[
\partial \phi_a / \partial \theta_{ya} = 0,
\]

\[
\partial \phi_a / \partial y_a = 0.
\]

So Eq. (59) simplifies to

\[
\partial V_{in}^{\text{EFB}} / \partial \theta_{ya} = B \sum_v c_{uv} \sum_a c_{au} \sum_a \left[ + \left( \partial \psi_a / \partial \theta_{ya} \right) \right] V_{uv}^{\text{EFB}} |\psi_v\rangle + \left( \partial \psi_a / \partial \theta_{ya} \right) (y_a - y^A_{\text{com}}) - \left( \partial \psi_a / \partial y_a \right) (z_a - z^A_{\text{com}}) + \sum_v c_{uv} \sum_a \left[ + \partial c_{au} / \partial \theta_{ya} + \partial c_{au} / \partial \psi_a \right] \times (y_a - y^A_{\text{com}}) - \left( \partial c_{au} / \partial y_a \right) (z_a - z^A_{\text{com}}) \tag{61}
\]

Similarly,

\[
\partial V_{in}^{\text{EFB}} / \partial \theta_{ya} = B \sum_v c_{uv} \sum_a c_{au} \sum_a \left[ + \left( \partial \psi_a / \partial \theta_{ya} \right) \right] V_{uv}^{\text{EFB}} |\psi_v\rangle + \left( \partial \psi_a / \partial \theta_{ya} \right) (y_a - y^A_{\text{com}}) - \left( \partial \psi_a / \partial y_a \right) (z_a - z^A_{\text{com}}) + \sum_v c_{uv} \sum_a \left[ + \partial c_{au} / \partial \theta_{ya} + \partial c_{au} / \partial \psi_a \right] \times (y_a - y^A_{\text{com}}) - \left( \partial c_{au} / \partial y_a \right) (z_a - z^A_{\text{com}}) \tag{62}
\]

Direct evaluation of \( \partial V_{in}^{\text{EFB}} / \partial \theta_{ya} \) is relatively difficult because the rotational derivative of the multipoles of \( A \), \( \partial V_{in}^{\text{EFB}} / \partial \theta_{ya} \), is required:

\[
\partial V_{in}^{\text{EFB}} / \partial \theta_{ya} = B \sum_v c_{uv} \sum_a (\partial c_{au} / \partial \theta_{ya}) V_{uv}^{\text{EFB}} |\psi_v\rangle + \sum_v c_{uv} \sum_a \left[ + \partial c_{au} / \partial \theta_{ya} + \partial c_{au} / \partial \psi_a \right] \times (y_a - y^A_{\text{com}}) - \left( \partial c_{au} / \partial y_a \right) (z_a - z^A_{\text{com}}) \tag{63}
\]

Since [cf. Eq. (58) for \( \partial \phi_a / \partial \theta_{ya} \)]

\[
\partial \phi_a / \partial \theta_{ya} = - \partial \phi_a / \partial \theta_{ya} - \left( \partial \phi_a / \partial \theta_{ya} \right) (y_a - y^A_{\text{com}}) - \left( \partial \phi_a / \partial y_a \right) (z_a - z^A_{\text{com}})
\]

one has

\[
\partial \phi_a / \partial \theta_{ya} = - \partial \phi_a / \partial \theta_{ya} - \left( \partial \phi_a / \partial \theta_{ya} \right) (y_a - y^A_{\text{com}}) - \left( \partial \phi_a / \partial y_a \right) (z_a - z^A_{\text{com}})
\]
\[
\frac{\partial E^\text{EFA}}{\partial \theta} = \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial \psi_i}{\partial \theta} \right) \left( \frac{\partial \psi_j}{\partial \theta} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial \psi_i}{\partial \theta} \right) \left( \frac{\partial \psi_j}{\partial \theta} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial \psi_i}{\partial \theta} \right) \left( \frac{\partial \psi_j}{\partial \theta} \right)
\]

Similarly,

\[
\frac{\partial V^\text{EFA}}{\partial \theta} = \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial \psi_i}{\partial \theta} \right) \left( \frac{\partial \psi_j}{\partial \theta} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial \psi_i}{\partial \theta} \right) \left( \frac{\partial \psi_j}{\partial \theta} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{\partial \psi_i}{\partial \theta} \right) \left( \frac{\partial \psi_j}{\partial \theta} \right)
\]

The rotational derivatives of the overlap and kinetic energy integrals can be obtained in similar manner.

4. Derivatives of MO coefficients

Since the AOs are grouped as shells (s, p, d, f, and g), the rotational derivatives of the MO coefficients are simply the intrashell linear combination of the MO coefficients. Table I presents the rotational derivatives of the MO coefficients for s-, p-, d-, f-, and g-type Cartesian Gaussian functions. For example, the derivative of the MO coefficient for the yyy component of an f-type AO with respect to the rotation about the z axis is simply a linear combination of the MO coefficients for the yyy and zyy components of the same AO:

\[
\frac{\partial c_{yy}^f}{\partial \theta} = -3c_{yy}^g + 2c_{zz}^f
\]

III. NUMERICAL RESULTS AND DISCUSSION

A. Computational methodology

All calculations were performed with the quantum chemistry program GAMESS. Codes for the calculation of the charge transfer energy and derivatives have been implemented. At present, the charge transfer interaction has been implemented for the EFP-EFP calculations only. These codes are available in GAMESS.

Various basis sets [6-31G(d), 6-31+G(d,p), 6-31+ +G(d,p), 6-311+ +G(d,p), aug-cc-pvDZ, and aug-cc-pVTZ] were used to perform the closed-shell SCF and corresponding EFP calculations. The molecular geometries were first optimized at the RHF/6-31+ +G(d,p) level of theory, in molecular pairs, and then used to construct EFPs with various basis sets. In the EFP calculations the internal geometries of the molecules are frozen. The relative positions of the molecules can be optimized.

The reduced variational space (RVS) analysis was carried out to derive the charge transfer and other interactions for the molecular pairs and compared to that obtained with the EFP calculations. The RVS analysis produces charge transfer energies that are sensitive to basis sets. The EFP charge transfer formulas derived above are analogous (with approximations) to the RVS analysis, and the numerical results from EFP and RVS are comparable.

B. Accuracy

The charge transfer energies obtained with the RVS analysis and the EFP method for six pairs of molecules (Fig. 1).

<table>
<thead>
<tr>
<th>AO Components</th>
<th>( \frac{\partial \theta_a}{\partial \theta} )</th>
<th>( \frac{\partial \theta_b}{\partial \theta} )</th>
<th>( \frac{\partial \theta_c}{\partial \theta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>p</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
<tr>
<td>d</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
<tr>
<td>f</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
<tr>
<td>g</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AO Components</th>
<th>( \frac{\partial \theta_a}{\partial \theta} )</th>
<th>( \frac{\partial \theta_b}{\partial \theta} )</th>
<th>( \frac{\partial \theta_c}{\partial \theta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>p</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
<tr>
<td>d</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
<tr>
<td>f</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
<tr>
<td>g</td>
<td>( \delta )</td>
<td>( \delta )</td>
<td>( \delta )</td>
</tr>
</tbody>
</table>

This table presents the results of the EFP analysis for six pairs of molecules, with a focus on the accuracy of the calculated charge transfer energies.
are presented in Table II. These systems are selected to represent the charge transfer interactions among cation, anion, and neutral molecules. The geometries of these molecular pairs were optimized at the RHF/6-31+G(d,p) level of theory. Using the optimized geometries, RVS calculations were performed with various basis sets and the charge transfer energies were obtained. The individual molecules were used for the preparative RHF with various basis set calculations that generated the EFP parameters. Then the EFPs were used to calculate the intermolecular interactions in the same geometries (both the internal and relative geometries).

The predicted charge transfer interaction is basis set dependent for both the RVS analysis and EFP. Not surprisingly, diffuse functions are important, especially when anions are involved. When diffuse functions are added to heavy atoms C, N, and O, the EFP predictions are much closer to the RVS ones. The charge transfer energy predicted using larger 6-31G-based basis sets, once diffuse functions have been added, does not vary much relative to the 6-31+G(d,p) basis. The aug-cc-pvDZ basis set does not appear to be consistently useful, and the aug-cc-pVTZ basis set will generally be too large. Based on these observations, it is recommended that EFPs be generated with the 6-31+G(d,p) or the 6-311+G(df,p) basis set. The latter basis set is particularly useful for the ion pairs.

The asymptotic behavior of the charge transfer interactions is shown in Fig. 2. The charge transfer interaction is <1 kcal/mol for molecules separated by more than 1.5 Å from their equilibrium geometries. The EFP charge transfer energy curves are in good agreement with those produced using the RVS analysis. For ionic molecules, the EFP charge transfer energies are ~3 kcal/mol smaller in magnitude than the RVS ones when the molecules are pulled apart from their equilibrium positions and are ~3 kcal/mol smaller when the molecules are pushed toward each other. Therefore, the EFP

**TABLE II. Charge transfer energy (kcal/mol) calculated with RVS analysis and EFP.**

<table>
<thead>
<tr>
<th>Basis set</th>
<th>1,2,3-triazolium nitrate</th>
<th>Ammonium nitrate</th>
<th>Ammonia nitrate</th>
<th>Ammonium water</th>
<th>Water-water</th>
<th>Methanol water</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G(d)</td>
<td>RVS −8.26</td>
<td>−9.88</td>
<td>−1.26</td>
<td>−3.09</td>
<td>−1.09</td>
<td>−1.12</td>
</tr>
<tr>
<td></td>
<td>EFP −2.52</td>
<td>−2.85</td>
<td>+0.05</td>
<td>−1.53</td>
<td>−0.45</td>
<td>−0.47</td>
</tr>
<tr>
<td>6-31+G(d,p)</td>
<td>RVS −6.81</td>
<td>−7.88</td>
<td>−0.51</td>
<td>−2.33</td>
<td>−0.55</td>
<td>−0.53</td>
</tr>
<tr>
<td></td>
<td>EFP −4.16</td>
<td>−5.00</td>
<td>−0.25</td>
<td>−2.72</td>
<td>−0.86</td>
<td>−0.91</td>
</tr>
<tr>
<td>6-31+G(d,p)</td>
<td>RVS −6.80</td>
<td>−7.90</td>
<td>−0.53</td>
<td>−2.19</td>
<td>−0.49</td>
<td>−0.46</td>
</tr>
<tr>
<td></td>
<td>EFP −4.08</td>
<td>−5.53</td>
<td>−0.27</td>
<td>−2.65</td>
<td>−0.76</td>
<td>−0.86</td>
</tr>
<tr>
<td>6-31++G(d,p)</td>
<td>RVS −6.76</td>
<td>−7.84</td>
<td>−0.52</td>
<td>−2.13</td>
<td>−0.47</td>
<td>−0.43</td>
</tr>
<tr>
<td></td>
<td>EFP −4.44</td>
<td>−6.09</td>
<td>−0.35</td>
<td>−2.82</td>
<td>−0.79</td>
<td>−0.91</td>
</tr>
<tr>
<td>6-311++G(d,p)</td>
<td>RVS −7.13</td>
<td>−8.27</td>
<td>−0.53</td>
<td>−2.35</td>
<td>−0.53</td>
<td>−0.50</td>
</tr>
<tr>
<td></td>
<td>EFP −6.34</td>
<td>−7.12</td>
<td>−0.37</td>
<td>−3.17</td>
<td>−0.83</td>
<td>−0.96</td>
</tr>
<tr>
<td>aug-cc-pvDZ</td>
<td>RVS −6.02</td>
<td>−7.16</td>
<td>−0.54</td>
<td>−2.86</td>
<td>−0.74</td>
<td>−0.75</td>
</tr>
<tr>
<td></td>
<td>EFP −2.98</td>
<td>−1.45</td>
<td>−0.22</td>
<td>−0.74</td>
<td>−0.43</td>
<td>−0.43</td>
</tr>
<tr>
<td>aug-cc-pvTZ</td>
<td>RVS −0.23</td>
<td>−6.66</td>
<td>−0.42</td>
<td>−2.53</td>
<td>−0.63</td>
<td>−0.62</td>
</tr>
<tr>
<td></td>
<td>EFP −4.82</td>
<td>−4.41</td>
<td>−0.57</td>
<td>−1.61</td>
<td>−0.49</td>
<td>−0.40</td>
</tr>
</tbody>
</table>

**FIG. 1. Structures of six pairs of molecules.**

**FIG. 2. Asymptotic behavior of the charge transfer interactions. The 6-31++G(d,p) basis set is used for 1,2,3-triazolium nitrate and water pair; the 6-31+G(d,p) basis set is used for ammonium nitrate.
charge transfer interactions are more repulsive than the RVS ones in the whole range of interacting distances for ionic molecules.

Table III presents the interaction energies for one, two, and four pairs of various molecules (Fig. 3) calculated with EFP, RVS, and RHF methods. In these calculations, the relative geometries of the molecules have been optimized either with the RHF or the EFP method, so the molecular interactions are fully exhibited for comparisons. The EFP total interactions are simply the sum of the EFP electrostatic (without charge penetration corrections), exchange-repulsion, induction, and charge transfer contributions. The RVS total interactions are those without basis set superposition errors (BSSE) and are simply the sum of the RVS electrostatic, exchange-repulsion, induction, and charge transfer contributions. The RHF total interactions are obtained by taking the differences between the RHF energies of the monomers and the super molecules and contain the BSSE. The individual interaction energies are not available from RHF calculations.

The total interaction energies obtained with the EFP, RVS, and RHF methods are in very good agreement. For example, for four pairs of 1,2,3-triazolium nitrate, EFP, RVS, and RHF predict total interaction energies of −504.7, −495.5, and −501.3 kcal/mol, respectively. For the same system, EFP and RVS predict charge transfer energies of −24.7 and −18.0 kcal/mol, respectively. In general, the EFP predictions of the total interaction energy are closer to the RHF results than to the RVS results when more than one pair of molecules is considered. Compared to the results of the RVS analysis, the magnitudes of the electrostatic, exchange-repulsion, induction (polarization), and charge transfer energies predicted by EFP are, respectively, under-, under-, over-, and underestimated. However, the total interaction energies obtained from EFP and RVS calculations are in very good agreement due to the cancellation of the individual differences. The underestimation of the electrostatic interaction is largely due to the lack of charge penetration correction. The underestimation of the exchange repulsion is presumably due to the pairwise or partial antisymmetrization and orthonormalization of the super molecular wave function. The differ-

![Fig. 3. Structures of two and four pairs of water, ammonium nitrate, and 1,2,3-triazolium nitrate molecules.](image-url)
ences in the induction and charge transfer energies are caused by higher-order or cross terms (such as exchange induction) in the perturbative treatment and the approximations in the EFP formulas. It is interesting to note that for four pairs (eight in number) of water molecules, the charge transfer energy is about −5 kcal/mol, a relatively significant contribution.

C. Efficiency

The computing timings for interaction energy calculations with RHF, EFP (no CT), and EFP (with CT) methods are presented in Table IV. The calculations were performed on a personal computer (PC) with an Athlon XP 3000+ CPU running at 2166 MHz. The RHF timings are for the molecular pair calculations since the timings for the individual molecules are relatively small. It is obvious that the EFP calculations with charge transfer terms are 20–30 times slower than those without them (the exchange-repulsion terms are the major timing contributors in the EFP calculations without charge transfer terms). The time required for charge transfer gradient calculations are approximately two times longer than the corresponding single point charge transfer energy calculations, having achieved the limit of the scale for gradient calculations in ab initio methods. Thus including the charge transfer term in the EFP calculations is much more expensive than not including it. For neutral molecules, the charge transfer interaction is relatively small; thus the expensive charge transfer term may often be neglected. For ionic systems, however, the charge transfer term is highly recommended in order to produce quality EFP potentials.

IV. CONCLUSION

An approximate formula for intermolecular charge transfer interactions has been developed and implemented by substituting one set of zeroth order MOs with first order MOs in the first order energy expression for two interacting molecules. Implemented in the EFP2 method, this formula gives charge transfer energies that are in reasonable agreement with the values from the reduced variational space (RVS) analysis. The charge transfer gradients with respect to EFP translational and rotational coordinates have also been derived and implemented; thus efficient geometry optimization and molecular dynamics simulations are possible. With the charge transfer term, the agreement between the EFP2 and RHF predicted molecular interactions is significantly improved for ionic systems. Currently the charge transfer term is implemented only for EFP-EFP interactions. Future studies will focus on deriving and implementing the charge transfer for QM-EFP interactions.

ACKNOWLEDGMENT

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APPENDIX

Using Eqs. (33)–(36) leads to four possible formulas for charge transfer energy of A [cf. Eq. (44)]:

\[ \text{CT}^{A(B)} = 2 \sum_i \sum_n \frac{1}{1 - \sum_m (S_{nm})^2} \left( V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} \right) \left[ V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} - \sum_j \left( V_{EFA}^{in} - \sum_m S_{nm} V_{EFA}^{in} \right) \right], \quad (A1) \]

\[ \text{CT}^{A(B)} = 2 \sum_i \sum_n \frac{1}{1 - \sum_m (S_{nm})^2} \left( V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} \right) \left[ V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} - \sum_j \left( V_{EFA}^{in} - \sum_m S_{nm} V_{EFA}^{in} \right) \right], \quad (A2) \]

\[ \text{CT}^{A(B)} = 2 \sum_i \sum_n \frac{1}{1 - \sum_m (S_{nm})^2} \left( V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} \right) \left[ V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} - \sum_j \left( V_{EFA}^{in} - \sum_m S_{nm} V_{EFA}^{in} \right) \right], \quad (A3) \]

\[ \text{CT}^{A(B)} = 2 \sum_i \sum_n \frac{1}{1 - \sum_m (S_{nm})^2} \left( V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} \right) \left[ V_{EFP}^{in} - \sum_m S_{nm} V_{EFP}^{in} + \sum_j \left( V_{EFA}^{in} - \sum_m S_{nm} V_{EFA}^{in} \right) \right], \quad (A4) \]
There are four analogous formulas [not shown, cf. Eq. (45)] for the charge transfer energy of $B$. Using these formulas, the charge transfer interactions for the six pairs of molecules (cf. Table II and Fig. 1) are listed in Table V.

Clearly, Eq. (A1) tends to underestimate the magnitude of the charge transfer energy and is therefore not a good choice. Equations (A2) and (A3) can produce very good results for some basis sets such as 6-31++G($d,p$) and aug-cc-pvDZ but erroneous (positive values) results for other basis sets. Equation (A4) always gives negative charge transfer energy values, which compare well to the RVS results, for all the molecular pairs and basis sets, and are less sensitive to basis set changes. It is difficult to make a preference among Eqs. (A2)–(A4). Equation (A4) is selected as the “best” overall compromise formula based on the consideration that a good formula should be general and insensitive to basis set changes.

Equation (A4) is Eq. (44), which is based on Eq. (37).