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Charge Transfer Interaction Using Quasiatomic Minimal-Basis Orbitals in the Effective Fragment Potential Method

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Abstract
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Keywords
Charge transfer, Energy transfer, Intermolecular forces, Wave functions, Basis sets

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The charge transfer (CT) interaction, the most time-consuming term in the general effective fragment potential method, is made much more computationally efficient. This is accomplished by the projection of the quasiatomic minimal-basis-set orbitals (QUAMBOs) as the atomic basis onto the self-consistent field virtual molecular orbital (MO) space to select a subspace of the full virtual space called the valence virtual space. The diagonalization of the Fock matrix in terms of QUAMBOs recovers the canonical occupied orbitals and, more importantly, gives rise to the valence virtual orbitals (VVOs). The CT energies obtained using VVOs are generally as accurate as those obtained with the full virtual space canonical MOs because the QUAMBOs span the valence part of the virtual space, which can generally be regarded as “chemically important.” The number of QUAMBOs is the same as the number of minimal-basis MOs of a molecule. Therefore, the number of VVOs is significantly smaller than the number of canonical virtual MOs, especially for large atomic basis sets. This leads to a dramatic decrease in the computational cost.

I. INTRODUCTION

Modeling intermolecular interactions accurately and efficiently has been a target of computational chemistry for decades. Intermolecular interactions play an important role in determining the structures and consequently the properties of molecular systems that have physical, chemical, and biological significance. For example, it is essentially the hydrogen-bonding pattern between the nucleotide bases that enables the correct transcription and translation processes in expressing a protein. The dispersion interaction among the stacking nucleotide bases provides a significant portion of the stabilization. Protein structures are ultimately the result of chemical and intermolecular interactions between the amino acids. High-level ab initio methods that include dynamic electron correlation can provide accurate descriptions of all of the contributions to intermolecular interactions, including Coulomb, induction/polarization, exchange repulsion, dispersion, and charge transfer interactions. Unfortunately, such correlated methods are very computationally demanding. For example, second order perturbation theory (MP2) and coupled cluster theory with single, double, and perturbative triple excitations, CCSD(T), scale as N⁵ and N⁷, respectively, where N is the number of basis functions. Consequently, such methods quickly become prohibitive for large systems, unless approximations are introduced.

Chemistry is often carried out in a solvent. A fundamental understanding of how solvent molecules interact with solutes and with each other can provide molecular-level insights about how chemical phenomena occur. In order to capture explicit solvent effects one frequently needs to include a large number of solvent molecules, more than is practicable for correlated ab initio methods. One therefore needs to develop methods that are more efficient and at the same time retain the accuracy of the correlated methods. Implicit solvent methods circumvent these scaling problems, but at the expense of omitting explicit solute-solvent interactions, such as hydrogen bonding.

The effective fragment potential (EFP) method is an explicit solvent method. The original EFP implementation, called EFPI, was designed solely for water. The components of the EFPI potential are the Coulomb interaction, the induction/polarization interaction, and a remainder term. The Coulomb interaction is modeled using the Stone distributed multipole analysis (DMA) method, expanded through octopoles, where the expansion points are the atom centers and the bond midpoints. The polarization interaction is modeled with localized molecular orbital (LMO) polarizability tensors on individual bonds and lone pairs of electrons and is iterated to self-consistency. The iterative process incorporates many-body effects into the model. The remainder term is fitted to the water dimer potential calculated either with Hartree-Fock (HF) or density functional theory (DFT, with the B3LYP functional). For EFPI/HF, the remainder term includes exchange repulsion and charge transfer. In the EFPI/DFT method the remainder term also includes some correlation effects.

The general EFP implementation, often called EFPI2, has no empirically fitted parameters and is therefore applicable to any (closed shell) molecular species. The components of the EFPI2 method are: Coulomb, induction/polarization, dispersion, exchange repulsion, and charge transfer. Each of these intermolecular interactions is derived from first principles, based on truncated expansions. The Coulomb and induction interactions are the same as in EFPI1. The exchange repulsion interaction is derived from a power expansion in the intermolecular overlap, truncated at the second order, expressed in terms of LMOs. The dispersion interaction is...
modeled with LMO dynamic (imaginary frequency) polarizability tensors obtained from time-dependent Hartree-Fock calculations. The charge transfer interaction term is obtained using a second-order perturbative treatment and is also derived based on an expansion in the intermolecular overlap, neglecting second and higher order terms. All of the required EFP2 input parameters are generated in one ab initio preparative calculation on the isolated individual molecule. There is no empirical parameterization and EFP2 can be systematically improved by including higher order terms in the expansions. In the following, EFP2 will be called, simply, EFP.

The charge transfer (CT) interaction may be defined as the energy stabilization due to the mixing of the occupied orbitals of one molecule with the virtual orbitals of another molecule. The CT interaction can be important in ionic and polar molecular systems such as water. Previously the CT energy and gradient between two EFP fragments were derived and implemented using a perturbative approach with self-consistent field (SCF) canonical molecular orbitals (CMOs) (both occupied and virtual orbitals). The CT interaction is the most time-consuming part of an EFP calculation, mainly due to the large number of canonical virtual orbitals when reliable basis sets are used. The goal of the present work is to present a new implementation that decreases the number of virtual orbitals used in the calculation, while retaining the accuracy of the original method. This goal is accomplished by making use of the quasiatomic minimal-basis-set orbitals (QUAMBOs), a localized orbital-based method developed by Ruedenberg and co-workers. QUAMBOs may be thought of as the virtual orbital complement of the valence occupied space of a molecule. They therefore provide a natural set of virtual orbitals with which to determine the majority of the charge transfer interaction energy.

The reduced variational space (RVS) method is an energy decomposition analysis algorithm proposed by Stevens and Fink which is closely related to the commonly used Kitaura-Morokuma (KM) energy decomposition analysis (EDA). Both analyses partition the interaction energy, at the Hartree-Fock level of theory, into electrostatic/Coulomb, polarization, exchange, and charge transfer components. It has been demonstrated that the RVS interaction energy components are better behaved than their counterparts in the KM analysis when the orbital interactions are strong. This is because the corresponding wave function from which the RVS component energies are obtained is antisymmetrized. Since the EFP-EFP CT formula is also derived using the antisymmetrized wave function as the zeroth order wave function, the numerical results from EFP and RVS are comparable. RVS CT results serve as benchmark numbers in this study.

This paper is organized as follows. The derivation of the EFP charge transfer energy and gradients has been described in a previous paper in detail and is only briefly summarized here in Sec. II A. The formulation of QUAMBOs is also detailed in another paper and is only briefly described in Sec. II B. The computational methodology used in this study is summarized in Sec. III A. Numerical results are discussed in Sec. III B. Conclusions are drawn in Sec. IV.

II. THEORY

A. EFP2 charge transfer interaction

The detailed derivation of the EFP-EFP charge transfer energy and gradient was presented in a previous paper using a second-order perturbative treatment with CMOs. The key steps and important approximations in the derivation are summarized here.

The starting point is the expression for the energy of a closed-shell molecule M with nonorthogonal molecular orbitals:

\[ E_M = 2 \sum_{i} \sum_{k} h_{ik} S^{-1}_{ik} + \sum_{i} \sum_{k} S^{-1}_{ik} \sum_{r} \sum_{s} (2 \langle ik | rs \rangle - \langle ik | ks \rangle S^{-1}_{rs} + E_{nuc}, \] (1)

where \( i, k, r, \) and \( s \) are the occupied orbitals of molecule \( M \) (thus, the upper limit \( \text{occ}M \) in the summations). \( h_{ik} \) is a one-electron integral, \( 2 \langle ik | rs \rangle - \langle ik | ks \rangle \) are the two-electron integrals, \( S \) is the matrix of overlap integrals, and \( E_{nuc} \) is the nuclear repulsion energy. The molecular orbitals can be nonorthogonal and non-normalized but they are linearly independent. Next, using the definition

\[ S^{-1} = I - P \] (2)

and substituting Eq. (2) into Eq. (1), one obtains

\[ E_M = 2 \sum_{i} \sum_{k} h_{ik} (\delta_{ik} - P_{ik}^{M}) \]

\[ + \sum_{i} \sum_{k} (\delta_{ik} - P_{ik}^{M}) \times \sum_{r} \sum_{s} (2 \langle ik | rs \rangle - \langle ik | ks \rangle (\delta_{rs} - P_{rs}^{M}) + E_{nuc}, \] (3)

Now, to approach the intermolecular interaction in a perturbative manner, suppose two weakly interacting molecules A and B form a supermolecule; then the zeroth-order wave function, \( \Psi^{(0)} \), for the supermolecule is the antisymmetrized product wave function formed from wave functions that describe A and B.

Let \( H \) be the full Hamiltonian, including the perturbation. Then the zeroth + first order energy is

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

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

\[ + \sum_{i} \sum_{k} (\delta_{ik} - P_{ik}^{AB}) \sum_{r} \sum_{s} (2 \langle ik | rs \rangle - \langle ik | ks \rangle (\delta_{rs} - P_{rs}^{AB}) + E_{nuc}, \] (4)

where the indices \( i, k, r, \) and \( s \) represent the occupied molecular orbitals (MOs) of isolated A and B.

\( E_{AB}^{(0)} \) and \( E_{AB}^{(1)} \) are the zeroth- and first-order energies of the system. \( h_{AB}^{AB} \) includes the electron kinetic energy plus the electron-nuclear attraction from both molecules:

\[ h_{AB}^{AB} = T + V_{nuc}^A + V_{nuc}^B. \] (5)
The superscript AB on P means that the overlap matrix used to define the P matrix is the overlap matrix of the supermolecule AB. If the orbitals are normalized, the diagonal elements of the overlap matrix are unity and one can separate the off-diagonal part of the matrix:

$$\tilde{S} = S - I. \quad (6)$$

Then, the P matrix can be expanded in terms of $\tilde{S}$:

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

$$= I - (I - \tilde{S} + \tilde{S}^2 - \tilde{S}^3 + \ldots) = S - \tilde{S}^2 + \tilde{S}^3 - \ldots. \quad (7)$$

For those off-diagonal elements in which both orbitals belong to the same molecule, the leading term in the expansion is the quadratic power of $S$ because the orbitals within the same molecule are orthogonal. Suppose both $i$ and $k$ are MOs on atom A,

$$p_{ik}^{AB} = \sum_{r}^{occA} \tilde{S}_{ir} \tilde{S}_{rk} - \sum_{j}^{occB} \tilde{S}_{ij} \tilde{S}_{jk}$$

$$= -\sum_{j}^{occB} \tilde{S}_{ij} \tilde{S}_{jk} = -\sum_{j}^{occB} (S_{ij} - I_{ij})(S_{jk} - I_{jk})$$

$$= -\sum_{j}^{occB} S_{ij} S_{jk}. \quad (8)$$

If the two indices are from different molecules, the leading term of P contains the first power of S.

$$p_{ij}^{AB} = \tilde{S}_{ij} - (\tilde{S}^2)_{ij} + (\tilde{S}^3)_{ij} - \ldots$$

$$\approx \tilde{S}_{ij} - \sum_{k}^{occA} \sum_{l}^{occB} S_{ik} S_{lj}$$

$$= \tilde{S}_{ij} = (S_{ij} - I_{ij}) = S_{ij}. \quad (9)$$

The original EFP charge transfer formula resulted from truncating the 2nd and higher order powers of S in the expansion of P.

Now, let $i, j, k, r, t, s$ be the occupied MOs of A and $j, l, t, w$ be the occupied MOs of B. Substituting Eqs. (8) and (9) into Eq. (4) gives

$$E_{AB}^{(0)} + E_{AB}^{(1)} \approx 2 \sum_{i}^{occA} \sum_{k}^{occA} h_{ik}^{AB} \delta_{ik} - 2 \sum_{i}^{occA} \sum_{j}^{occB} h_{ij}^{AB} S_{ij} - 2 \sum_{j}^{occB} \sum_{k}^{occA} h_{jk}^{AB} S_{jk} + 2 \sum_{j}^{occB} \sum_{l}^{occB} h_{jl}^{AB} S_{jl}$$

$$+ \sum_{i}^{occA} \sum_{k}^{occA} \sum_{r}^{occA} \sum_{s}^{occA} (2 \langle ik | rs \rangle - \langle ir | ks \rangle) \delta_{rs} + \sum_{i}^{occA} \sum_{k}^{occA} \sum_{r}^{occA} \sum_{w}^{occA} (2 \langle ik | tw \rangle - \langle it | kw \rangle) \delta_{tw}$$

$$- \sum_{i}^{occA} \sum_{k}^{occA} \sum_{r}^{occA} \sum_{w}^{occA} (2 \langle ik | rw \rangle - \langle ir | kw \rangle) S_{rw} - \sum_{i}^{occA} \sum_{k}^{occA} \sum_{s}^{occA} (2 \langle ik | ts \rangle - \langle it | ks \rangle) S_{xs}$$

$$+ \sum_{j}^{occB} \sum_{l}^{occB} \sum_{r}^{occB} \sum_{s}^{occB} (2 \langle jl | rs \rangle - \langle jr | ls \rangle) \delta_{rs} + \sum_{j}^{occB} \sum_{l}^{occB} \sum_{r}^{occB} \sum_{w}^{occB} (2 \langle jl | tw \rangle - \langle jl | lw \rangle) \delta_{tw}$$

$$- \sum_{j}^{occB} \sum_{l}^{occB} \sum_{r}^{occB} \sum_{w}^{occB} (2 \langle jl | rw \rangle - \langle jr | lw \rangle) S_{rw} - \sum_{j}^{occB} \sum_{l}^{occB} \sum_{s}^{occB} (2 \langle jl | ts \rangle - \langle jl | ls \rangle) S_{xs}$$

$$- \sum_{j}^{occB} \sum_{k}^{occB} \sum_{r}^{occB} \sum_{s}^{occB} (2 \langle jk | rs \rangle - \langle jr | ks \rangle) \delta_{rs} + \sum_{j}^{occB} \sum_{k}^{occB} \sum_{r}^{occB} \sum_{w}^{occB} (2 \langle jk | tw \rangle - \langle jl | kw \rangle) \delta_{tw}$$

$$- \sum_{j}^{occB} \sum_{k}^{occB} \sum_{r}^{occB} \sum_{s}^{occB} (2 \langle jk | rw \rangle - \langle jr | kw \rangle) S_{rw} - \sum_{j}^{occB} \sum_{k}^{occB} \sum_{s}^{occB} (2 \langle jk | ts \rangle - \langle jl | ks \rangle) S_{xs}$$

$$E_{\text{Enuc}}. \quad (10)$$
Let \( \Psi^{(1)} = \Psi^{(0)} + \Psi' \) where \( \Psi' \) is the first order correction to the zeroth order wavefunction \( \Psi^{(0)} \).

The second order perturbation energy is then obtained as
\[
E^{(2)}_{\text{AB}} = \langle \Psi^{(0)} | H | \Psi^{(1)} \rangle - \langle \Psi^{(0)} | H | \Psi^{(0)} \rangle. \tag{11}
\]

By definition, the energy lowering when the occupied MOs of A mix with the virtual MOs of B is referred to as the charge transfer energy of A due to B. The first-order perturbed wavefunction of one molecule is obtained by mixing in the virtual MOs of the other molecule. For example, the first-order perturbed MO \( i \) on molecule A is
\[
\Psi_i^{(1)} = \Psi_i^{(0)} + \sum_n U_{in} \Psi_n^{(0)}, \tag{12}
\]
where \( U \) is the mixing coefficient matrix.

Substituting Eq. (12) into Eq. (10) and collecting the energy changes due to the mixing from virtual orbitals of B, one obtains the charge transfer energy of A due to B. Note that if both the bra and ket wavefunctions are from molecule A, only one of them is perturbed (e.g., see Eq. (11)). In this paper, \( \Psi_{i}^{(0)} \) and \( \Psi_{r}^{(0)} \) are conveniently chosen to be perturbed to \( \Psi_{i}^{(1)} \) and \( \Psi_{r}^{(1)} \). \( \Psi_{i}^{(0)} \) and \( \Psi_{r}^{(0)} \) are unperturbed.

Combining the contributions to the energy change from each term in Eq. (10) and splitting the one-electron operator \( h_{\text{AB}} \) into the kinetic energy operator and the nuclear attraction operators from A and B, the CT energy of molecule A due to the presence of B is
\[
\text{CT}^{(A|B)} = 2 \sum_i \sum_{n} U_{in} \left[ T_{in} + V_{\text{in}}^{\text{nuc}A} + \sum_k (2 \langle in| kk \rangle - \langle ik| nk \rangle) + V_{\text{in}}^{\text{nuc}B} + \sum_j (2 \langle in| jj \rangle - \langle ij| nj \rangle) \right]
\]
\[
-2 \sum_i \sum_n U_{in} \sum_j \left[ T_{nj} + V_{nj}^{\text{nuc}B} + \sum_l (2 \langle nj| ll \rangle - \langle nl| jl \rangle) + V_{nj}^{\text{nuc}A} + \sum_k (2 \langle nj| kk \rangle - \langle nk| jk \rangle) \right] S_{ij}. \tag{13}
\]

Further simplification includes
\[
T_{nj} + V_{nj}^{\text{nuc}B} + \sum_l (2 \langle nj| ll \rangle - \langle nl| jl \rangle) = F_{nj}^{B} = 0, \tag{14}
\]
where \( n \) and \( j \) belong to the virtual and occupied orbitals of molecule B, respectively. This is because, for CMOs, the off-diagonal elements of the Fock operator are zero. Likewise,
\[
T_{in} + V_{in}^{\text{nuc}A} + \sum_k (2 \langle in| kk \rangle - \langle ik| nk \rangle) = F_{in}^{A} = 0, \tag{15}
\]
in \( i \in \text{occ}A, n \in \text{vir}B \).

In Eq. (15), \( i \) is an index for the MOs of A and \( \Psi_{n}^{(0)} \) is assumed to be orthogonal to all the MOs of A. This is enforced by the following approximate orthonormalization procedure
\[
\Phi_{n}^{(0)} = \frac{1}{\sqrt{1 - \sum_{\text{all}} (S_{nm})^2}} \left( \Psi_{n}^{(0)} - \sum_{m} S_{nm} \Psi_{m}^{(0)} \right), \tag{16}
\]
in \( n \in \text{vir}B \),

where \( \Phi \) is the MO after orthonormalization. To simplify Eq. (14) further, two sets of approximations can be applied. The first set [Eqs. (17) and (18)] neglects the exchange integrals and approximates the Coulomb integrals with the multipole expansion as the electrostatic potential of the molecule, truncated at the quadrupole:
\[
V_{\text{in}}^{\text{nuc}B} + \sum_j (2 \langle in| jj \rangle - \langle ij| nj \rangle) \approx V_{\text{in}}^{\text{EFB}}, \tag{17}
\]
where \( i \in \text{occ}A, n \in \text{vir}B \),
\[
V_{nj}^{\text{nuc}A} + \sum_k (2 \langle nj| kk \rangle - \langle nk| jk \rangle) \approx V_{nj}^{\text{EFA}}, \tag{18}
\]
where \( n \in \text{vir}B, j \in \text{occ}A \).

The superscripts EFA and EFB represent the potentials of molecules A and B, respectively, described by a distributed multipole expansion. The other possible set of approximations [Eqs. (19) and (20)] set the Fock matrix to zero if the two indices are either from different molecules (Eq. (19)) or from the occupied and virtual orbitals of the same molecule (Eq. (20)).
\[
V_{\text{in}}^{\text{nuc}B} + \sum_j (2 \langle in| jj \rangle - \langle ij| nj \rangle) = F_{in}^{B} - T_{in} \approx -T_{in}, \tag{19}
\]
in \( i \in \text{occ}A, n \in \text{vir}B \),
\[ V_{nj}^{\text{nuca}} + \sum_k (2\langle nj | k k\rangle - \langle nk | j k \rangle) = F_{nj}^A - T_{nj} \approx -T_{nj}, \]
\[ n \in \text{vir}_B, \ j \in \text{occ}_B. \]  

Different combinations of Eqs. (17)–(20) can result in four possible formulae (see the Appendix). Previously, it was demonstrated that the combination of Eqs. (17) and (20) gives the most accurate numerical results when compared with values obtained from a reduced variational space (RVS) analysis.\(^{10,13}\) When the valence virtual orbitals (see Sec. II B) are used, numerical tests show that this combination still gives the best results (see the Appendix).

Applying Eqs. (17) and (20) to Eq. (13) results in
\[ CT_{A(B)} = 2 \sum_{i} \sum_{n} U_{in} \left( V_{inB}^{\text{EFB}} + \sum_{j} T_{nj}S_{ij} \right). \]  

The mixing coefficient matrix element \( U_{in} \) is approximated as\(^{10}\)
\[ U_{in} \approx \frac{\langle \psi_i^{A(0)} | V_{EFB} | \psi_n^{B(0)} \rangle}{\varepsilon_i^A - \varepsilon_n^A} = \frac{\langle \Psi_i^{A(0)} | V_{EFB} | \Psi_n^{B(0)} \rangle}{F_{in}^A - F_{nn}^A}, \]
\[ i \in \text{occ}_A, \ n \in \text{vir}_B. \]  

In Eq. (22) \( V_{\text{EFB}} \) is the multipole potential defined in Eq. (17). \( \varepsilon_i^A \) is the orbital energy of \( \Psi_i^A \), which equals the corresponding diagonal element of the Fock matrix, \( F_{ii}^A \), \( \varepsilon_n^A \) on the other hand, is the orbital energy of \( \Psi_n^B \) when it is assumed to be orthonormal to the virtual MOs of molecule A (enforced by Eq. (16)). \( \varepsilon_n^A \) can also be written as a Fock matrix element, \( F_{nn}^A \), in an analogous manner:
\[ F_{nn}^A = T_{nn} + V_{nn}^{\text{nuca}} + \sum_i (2\langle ni | ii\rangle - \langle ni | ni \rangle), \]
\[ = T_{nn} + V_{nn}^{\text{EFA}} - \sum_i \langle ni | ni \rangle, \ n \in \text{vir}_B. \]  

The last equality in Eq. (23) is obtained using Eq. (18). It is important to realize that \( F_{nn}^A \) is not related to \( F_{nn}^B \). The latter is the orbital energy of \( \psi_n^B \) determined by diagonalizing the Fock matrix of isolated B. Therefore \( F_{nn}^A \) is not a quantity that can be obtained from the preparative \textit{ab initio} calculation on the isolated molecule that is used to construct an EFP. Since \( \psi_n^A \) and \( \psi_i^A \) are from different molecules, the exchange term \( \langle ni | ni \rangle \) and the potential energy due to the multipole charge distribution on fragment A, \( V_{nn}^{\text{EFA}}, \) in Eq. (23) are relatively small and can be neglected. \( F_{nn}^A \approx T_{nn} \) (Numeral tests were done previously to justify this approximation.\(^{10}\)) Hence the final form for the mixing coefficient matrix U is
\[ U_{in} \approx \frac{V_{inB}^{\text{EFB}}}{F_{ii}^A - T_{nn}}. \]  

Combining Eqs. (21) and (24) and replacing \( \psi_n^B \) with Eq. (16), one obtains the final form of the charge transfer energy expression as
\[ CT_{A(B)} = 2 \sum_{i} \sum_{n} \frac{1}{1 - \sum_{m} (S_{nm})^2} \times \frac{V_{inB}^{\text{EFB}} - \sum_{m} S_{nm} V_{nm}^{\text{EFB}}}{(F_{ii}^A - T_{nn})} \times \left[ V_{EFB} - \sum_{m} S_{nm} V_{nm}^{\text{EFB}} + \sum_{j} S_{ij} \left( T_{nj} - \sum_{m} S_{nm} T_{mj} \right) \right]. \]  

Since the final CT energy formulation is unaltered by the use of the quasiatomic minimal-basis-set orbitals, the expression for the gradient remains unchanged from the one that was derived previously.\(^{10}\)

B. QUAMBOs and valence virtual orbitals (VVOs)

Quasiatomic minimal-basis-set orbitals (QUAMBOs), developed by Ruedenberg and co-workers,\(^{12}\) have the following attributes: (i) the number of QUAMBOs equals the number of minimal basis set molecular orbitals for the system. (ii) The QUAMBOs deviate minimally from the minimal basis set orbitals of the corresponding free atoms of that system. Thus QUAMBOs can be viewed as slightly deformed minimal basis atomic orbitals. (iii) The formulation of QUAMBOs is independent of the atomic basis sets used.

The projection of the QUAMBOs onto the SCF virtual space selects a subspace, called the virtual valence space, which yields a good approximation to the most important correlating orbitals. The most time-consuming part of an EFP CT calculation is the computation of the one-electron potential terms. Fundamentally, the bottleneck is the huge number of canonical virtual orbitals compared to the number of occupied orbitals. Hence, the motivation for using QUAMBOs as the basis for EFP-EFP charge transfer calculations is the expectation that the dramatically reduced number of virtual orbitals will diminish the cost of a CT calculation significantly while these chemically important "valence virtual orbitals" can capture most of the CT interaction.

The full description of QUAMBOs is given in Ref. 12 A summary of how QUAMBOs are constructed is given here.

The free-atom minimal basis atomic orbital \( A_i^* \) can be expressed in terms of the occupied and virtual

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SCF MOs:
\[ A_j^* = \sum_n^{\text{occ}} \phi_n a_{nj}^* + \sum_{v}^{\text{vir}} \phi_v a_{vj}^*, \]  
(27)

where \( a_{nj}^* = \langle \phi_n | A_j^* \rangle \) and \( a_{vj}^* = \langle \phi_v | A_j^* \rangle \).

Note that the * here does not represent complex conjugate, but is merely a symbol to distinguish the free-atom minimal basis atomic orbitals from QUAMBOs. The QUAMBO \( A_j \) can be similarly expanded as
\[ A_j = \sum_n^{\text{occ}} \phi_n a_{nj} + \sum_{v}^{\text{vir}} \phi_v a_{vj}, \]  
(28)

with \( a_{nj} = \langle \phi_n | A_j \rangle \) and \( a_{vj} = \langle \phi_v | A_j \rangle \).  
(29)

For both the free-atomic minimal basis orbitals, \( A_j^* \) and QUAMBOs, \( A_j \), the index \( j \) runs from 1 to \( M \), with \( M \) being the total number of minimal basis set valence atomic orbitals in the molecule. One can write \( M = N + P \), where \( P \) is the number of virtual valence orbitals. The \( M \)-dimensional space spanned by the QUAMBOs must also be spanned by the \( N \) occupied SCF MOs plus the appropriate number (\( P \)) of orbitals in the \( N \)-dimensional SCF virtual space. Calling these virtual orbitals \( \phi_p \), QUAMBO \( A_j \) can be expressed in terms of the SCF occupied MOs and these \( \phi_p \):
\[ A_j = \sum_n^{\text{occ}} \phi_n a_{nj} + \sum_{p}^{\text{val,vir}} \phi_p b_{pj}, \]  
(30)

and
\[ \phi_p = \sum_{v}^{\text{vir}} \phi_v T_{vp}. \]  
(31)

In Eq. (30) \( p \) goes up to the number of minimal basis set virtual orbitals, which equals the number of the VVO, \( P \).

The QUAMBO \( A_j \) is constructed in such a way that it deviates as little as possible from the free-atomic minimal basis atomic orbital \( A_j^* \). This corresponds to minimizing the square deviation,\(^{12}\)
\[ \langle A_j - A_j^* \rangle A_j - A_j^* \rangle = 2[1 - \langle A_j | A_j^* \rangle] = 2[1 - (D_j)^{1/2}], \]  
(32)

where
\[ D_j = \sum_n^{\text{occ}} \langle \phi_n | A_j^* \rangle^2 + \sum_{p}^{\text{val,vir}} \langle \phi_p | A_j^* \rangle^2, \]  
(33)

with the normalization condition \( \langle A_j | A_j \rangle = 1 \) and \( \langle A_j^* | A_j^* \rangle = 1 \).

A constrained Lagrange minimization leads to
\[ A_j = D_j^{-1/2} \left( \sum_n^{\text{occ}} \phi_n (\phi_n | A_j^* \rangle + \sum_{p}^{\text{val,vir}} \phi_p (\phi_p | A_j^* \rangle \right). \]  
(34)

So, the QUAMBOs are the normalized projection of the free-atomic minimal-basis atomic orbitals \( A^* \) onto the space spanned by the SCF MOs. Combining Eqs. (29) and (34), and

\[ A_j = \sum_{n=1}^{\text{occ}} (D_j^{-1/2} \langle \phi_n | A_j^* \rangle) \phi_n \]  
+ \[ \sum_{p=1}^{\text{val,vir}} D_j^{-1/2} \sum_v \phi_v T_{vp} \left( \sum_w \phi_w T_{wp} | A_j^* \right) \]  
\[ = \sum_n (D_j^{-1/2} a_{nj}^*) \phi_n + \sum_v \sum_w \left( \sum_p D_j^{-1/2} T_{vp} T_{wp} \right) \]  
\[ \times \langle \phi_v | A_j^* \rangle \phi_v \]  
\[ = \sum_n a_{nj}^* \phi_n + \sum_v a_{vj}^* \phi_v. \]  
(35)

To find \( a_{nj}^* \) and \( a_{vj}^* \) requires the determination of the expansion coefficient matrix \( T \). The simultaneous minimization of the quantity in Eq. (32) for all QUAMBOs is equivalent to maximizing the sum
\[ \sum_j^{\text{min basis}} D_j = \sum_j \left[ \sum_n^{\text{occ}} \langle \phi_n | A_j^* \rangle^2 + \sum_p^{\text{val,vir}} \langle \phi_p | A_j^* \rangle^2 \right]. \]  
(36)

Equation (36) is ultimately achieved by maximizing the sum over the \( \phi_p \) (\( \varphi_{\text{sum}} \)). This is because the only variables in Eq. (36) are the elements of the expansion coefficient matrix \( T \) [Eq. (31)] for \( \varphi_p \).

\[ \varphi_{\text{sum}} = \sum_j \sum_p \langle \phi_p | A_j^* \rangle^2 \]  
\[ = \sum_j \sum_p \left( \sum_{v} T_{vp} \langle \phi_v | A_j^* \rangle \right) \left( \sum_{w} T_{wp} \langle \phi_w | A_j^* \rangle \right) \]  
\[ = \sum_p \sum_{v} \sum_{w} T_{vp} T_{wp} B_{vw}. \]  
(37)

\( T \) is defined in Eq. (31) and \( B_{vw} = \sum_j \langle \phi_v | A_j^* \rangle \langle \phi_w | A_j^* \rangle \) \[ = \sum_j a_{v}^* a_{w}^* \).\(^{12}\)

The B matrix is diagonalized, and the T matrix is formed from the \( p \) eigenvectors of B with the \( p \) largest eigenvalues, i.e., \( BT_p = \beta_p T_p \), where \( \beta_p \) is the \( p \)th eigenvalue of the matrix B. \( \varphi_{\text{sum}} = \sum_p \beta_p T_{vp} T_{wp} = \sum_p \beta_p \) is maximized. Once the matrix \( T \) is determined, the set of \( P \) valence virtual orbitals \( \varphi_p \) can be determined using Eq. (31). This effectively is a process of optimizing the valence virtual space in such a way that the QUAMBOs deviate least from the free-atomic minimal basis AOs. Subsequently, the normalized expansion coefficients \( a_{nj}^* \) and \( a_{vj}^* \) are obtained as in Eq. (35). Using these QUAMBOs as the atomic basis set, one can obtain orbital energies by diagonalizing the corresponding Fock matrix. These orbital energies are then used in the CT energy expression. The diagonalization also recovers the canonical occupied orbitals and generates the VVOs that are then used in the CT calculations.

III. NUMERICAL RESULTS AND DISCUSSION

A. Computational methodology

The codes for generating VVOs in the preparative \textit{ab initio} runs to generate an EFP, and for using VVOs to
calculate the EFP-EFP CT energy and gradient have been implemented in the electronic structure quantum chemistry package GAMESS. Five basis sets [6-31+G(d,p), 6-31++G(d,p), 6-311++G(3df,2p)] are used here to test the code. The five dimer systems (Fig. 1) chosen as the test systems are water–water, methanol–water, ammonia–water, ammonium–nitrate, and (ammonium–nitrate)$_4$.


At these optimized geometries with the aforementioned basis sets to obtain the benchmark CT energies. The benchmark CT gradients were computed by three-point numerical differencing the EFP CT energies, using step sizes of 0.001 bohr for translation and 0.001 radian for rotation. The CT energies and gradients for the dimer systems were computed at both equilibrium and non-equilibrium intermolecular distances. To demonstrate time saving for large systems, 7 (H$_2$O)$_{64}$ clusters, 10 (H$_2$O)$_{128}$ clusters, and 10 (H$_2$O)$_{256}$ clusters were chosen as test systems. Single point energy and single point energy + gradient calculations were carried out on a single Dell x86.64 CPU running at 2660 MHz. The aforementioned calculations were carried out using CMOs as well for comparison. All of the calculations were performed using GAMESS.

B. Accuracy

1. Model systems at equilibrium distances

Table I presents the CT energies of the five dimer systems at equilibrium separation and the cluster of four ammonium-nitrates. These energies are calculated in three ways: the RVS analysis to give benchmark CT energies, and EFP calculations using either CMOs or VVOs for the CT interaction. In most cases, the VVO-calculated CT energies are closer to the RVS CT energies than are those obtained from the CMOs. The variation of the VVO-calculated CT energies from basis to basis is small (<0.5 kcal/mol). In fact, the values hardly change for the three relatively small basis sets [6-31+G(d,p), 6-31++G(d,p), and 6-311++G(3df,2p)]. In addition, it is interesting to note that the CT energies calculated with VVOs using the largest basis set, 6-311++G(3df,2p), are always smaller than those from smaller basis sets. This is expected since the energy lowering from the CT interaction arises in part from insufficient monomer basis sets. Therefore, one expects the CT energy to decrease as one moves toward the complete basis set limit. Interestingly, this trend is not

### Table I. Charge transfer energies (kcal/mol) obtained from the RVS analysis, EFP (canonical occupied + virtual molecular orbitals), and EFP (occupied + valence virtual orbitals) for the five dimer systems and (ammonium-nitrate)$_4$ system with five basis sets. The dimer geometries were optimized with RHF/6-31+G(d,p). Boldface denotes benchmarking numbers.

<table>
<thead>
<tr>
<th>Basis sets</th>
<th>Water-water</th>
<th>Methanol-water</th>
<th>Ammonia-water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RVS</td>
<td>CMO</td>
<td>VVO</td>
</tr>
<tr>
<td>6-31+G(d,p)</td>
<td>0.55</td>
<td>-0.85</td>
<td>-0.51</td>
</tr>
<tr>
<td>6-31++G(d,p)</td>
<td>0.49</td>
<td>-0.75</td>
<td>-0.51</td>
</tr>
<tr>
<td>6-311++G(df,p)</td>
<td>0.47</td>
<td>-0.79</td>
<td>-0.51</td>
</tr>
<tr>
<td>6-311++G(d,p)</td>
<td>0.53</td>
<td>-0.82</td>
<td>-0.47</td>
</tr>
<tr>
<td>6-311++G(3df,2p)</td>
<td>0.65</td>
<td>-0.44</td>
<td>-0.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Basis sets</th>
<th>Ammonium-water</th>
<th>Ammonium-nitrate</th>
<th>(Ammonium-nitrate)$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RVS</td>
<td>CMO</td>
<td>VVO</td>
</tr>
<tr>
<td>6-31+G(d,p)</td>
<td>-2.33</td>
<td>-2.75</td>
<td>-2.05</td>
</tr>
<tr>
<td>6-31++G(d,p)</td>
<td>-2.21</td>
<td>-2.64</td>
<td>-2.04</td>
</tr>
<tr>
<td>6-311++G(3df,2p)</td>
<td>-2.85</td>
<td>-1.95</td>
<td>-1.79</td>
</tr>
</tbody>
</table>
observed consistently in the RVS calculations. For systems involving charged species, such as the ammonium-nitrate pair, one can encounter convergence problems and may need to adjust the convergence threshold in RVS calculations.

2. Non-equilibrium distances

It is important to ensure that one can predict the CT energy accurately, not only at the equilibrium distance but also at other, non-equilibrium, distances. It is particularly important to obtain the correct limiting behavior. Taking the equilibrium distance as zero and shorter distances as negative, the CT energies were calculated for the five dimer systems at various distances away from equilibrium, ranging from −0.5 to 1.2 Å. The five dimer systems exhibit similar behavior and therefore only the water dimer system is shown in Figure 2. In most cases, the CT energies predicted using VVOs agree better with the RVS results than do those obtained from CMOs. At ∼0.5 Å and longer than the equilibrium distances, CT energies approach zero as they should. As two molecules get closer, the magnitudes of the CT energies increase quickly. Both types of MOs predict the correct limiting behavior. The deviation from RVS CT energies increases for both types of MOs as the intermolecular distances get smaller than the equilibrium distances; but the VVO errors increase less rapidly, creating larger errors only at very small intermolecular distances. In general, VVOs tend to underestimate and CMOs overestimate the CT energies relative to the RVS values.

For water dimer (Fig. 2), the VVO-calculated CT energy error only becomes noticeable at about −0.2 Å, whereas the CMO-predicted CT energy starts to exhibit a noticeable discrepancy even around the equilibrium distance. The absolute deviation for VVO-predicted CT energies is generally smaller than that for the CMOs at all distances examined. Other dimer systems behave similarly. In all cases, VVOs underestimate the CT energies at −0.5 Å. However, this distance may not be of much physical significance and distance-dependent screening/scaling might be introduced in the future if necessary. In summary, one can expect VVO-predicted EFP-EFP CT interaction energies to be quite accurate in the region where most physical and chemical situations occur.

3. Gradients

The analytic EFP CT gradient code has been modified to use VVOs as an alternative option to calculate the EFP-EFP CT gradients. The benchmarking gradient results were computed using the numerical gradient code in GAMESS with a step size of 0.001 bohr for translation and 0.001 radians for rotation. Both analytic and numerical gradients are calculated at both the equilibrium and non-equilibrium distances. For all calculations, the differences between the analytic and numerical gradients using VVOs are within $10^{-7}$ hartree/bohr.

C. Efficiency/timing

Using valence virtual orbitals in the EFP CT formulation greatly reduces the number of orbitals used in EFP CT

FIG. 2. EFP-EFP charge transfer energies for water-water dimer at various distances with basis sets (a) 6-31+G(d,p), (b) 6-31++G(d,p), (c) 6-311++G(3df,2p), (d) 6-311++G(d,p), and (e) 6-311++G(3df,2p).
TABLE II. The CPU time spent for various terms in an EFP-EFP charge transfer energy calculation for one \((\text{H}_2\text{O})_{256}\) cluster. Other water clusters of the same size give similar results. \(T_{AA}\) is the kinetic energy integral of fragment A, \(S_{AB} \) and \(T_{AB}\) are the overlap and kinetic energy integrals between fragments A and B. \(V\) are the one-electron electrostatic potential integrals. For instance, \(V_{EFBA}\) represents the matrix elements of the electrostatic potential due to B. \(E_{CT}\) means assembling of all the terms and calculating the charge transfer energy once all of the required integrals are available. Times are in seconds.

<table>
<thead>
<tr>
<th></th>
<th>CMO</th>
<th>VVO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{AA})</td>
<td>31.66</td>
<td>16.42</td>
</tr>
<tr>
<td>(S_{AB}) and (T_{AB})</td>
<td>8.42</td>
<td>0.37</td>
</tr>
<tr>
<td>(V_{EFBA})</td>
<td>145.19</td>
<td>15.73</td>
</tr>
<tr>
<td>(V_{EFBA})</td>
<td>145.76</td>
<td>15.79</td>
</tr>
<tr>
<td>(V_{EFBA})</td>
<td>75.11</td>
<td>12.93</td>
</tr>
<tr>
<td>(V_{EFBA})</td>
<td>75.10</td>
<td>13.06</td>
</tr>
<tr>
<td>(E_{CT})</td>
<td>2.25</td>
<td>0.01</td>
</tr>
</tbody>
</table>

calculations, and this causes a significant reduction in the required computer time. Comparative CPU times for one of the \((\text{H}_2\text{O})_{256}\) clusters are shown in Table II. The time saving is global: for all of the terms in the CT energy formula [Eqs. (26) and (27)], the computational times drop by at least 50% compared to the times required for the analogous CMO calculations. The total CPU time for an EFP-EFP energy calculation and single point gradient calculation for the \((\text{NH}_4^+\text{–NO}_3^-)_4\) system are presented in Figures 3(a) and 3(b), respectively. For both energy and gradient calculations, the total CPU time increases linearly with the number of basis functions. For CMOs, the CPU time increases much more rapidly. The average total CPU time for the energy and gradient calculations, respectively, for the 7 \((\text{H}_2\text{O})_{64}\) clusters, 10 \((\text{H}_2\text{O})_{128}\) clusters, and 10 \((\text{H}_2\text{O})_{256}\) clusters are plotted as a function of the number of water molecules in Figures 4(a) and 4(b). A linear scaling is again observed. The use of VVOs significantly reduces the linear scaling coefficients. As the number of basis functions increases or the system size increases, the time saved by using VVOs is amplified. This is easily understood because the number of canonical virtual orbitals increases steeply while the number of minimal basis orbitals stays the same as the number of basis functions increases. Due to this new implementation, molecular dynamical (MD) simulations of EFP water clusters are able to run with CT included in the water potential.18 In general, one can expect a 50% or more time saving when using the recommended EFP basis set, 6-311++G(3df,2p).

IV. CONCLUSION

The occupied + valence virtual orbitals have been implemented as an alternative for calculating the EFP-EFP charge transfer energy and gradient. QUAMBOs furnish a basis that can exactly expand the SCF occupied orbitals, and projection of QUAMBOs onto the virtual space select that part of the virtual space that contains the most important correlating orbitals. The number of QUAMBOs is constant for a particular
system. Therefore, the use of QUAMBOs to obtain VVOs improves the efficiency of EFP-EFP CT calculations markedly while retaining, and in some cases improving the accuracy of the CT energies.

**ACKNOWLEDGMENTS**

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**APPENDIX: CT ENERGY EXPRESSIONS FROM DIFFERENT APPROXIMATIONS**

The different combinations of Eqs. (18)–(21) lead to four possible formulae for CT energy of fragment A due to fragment B (Eqs. (A1)–(A4)). Four analogous formulae for the charge transfer energy of B due to A are not shown here.

\[
CT_{A(B)} \approx 2 \sum_{i} \sum_{n} \frac{1}{1 - \sum_{m} (S_{nm})^2} \frac{V_{EFB}^{in}}{F_{ii} - T_{nn}} \left[ V_{EFB}^{in} \sum_{m} S_{nm} V_{EFB}^{im} - \sum_{j} S_{ij} \left( V_{EFA}^{nj} \sum_{m} S_{nm} V_{EFA}^{mj} \right) \right],
\]

(A1)

\[
CT_{A(B)} \approx 2 \sum_{i} \sum_{n} \frac{1}{1 - \sum_{m} (S_{nm})^2} \frac{V_{EFB}^{in}}{F_{ii} - T_{nn}} \left[ -T_{in} + \sum_{m} S_{nm} T_{im} + \sum_{j} S_{ij} \left( T_{nj} - \sum_{m} S_{nm} T_{mj} \right) \right],
\]

(A2)

\[
CT_{A(B)} \approx 2 \sum_{i} \sum_{n} \frac{1}{1 - \sum_{m} (S_{nm})^2} \frac{V_{EFB}^{in}}{F_{ii} - T_{nn}} \left[ -T_{in} + \sum_{m} S_{nm} T_{im} - \sum_{j} S_{ij} \left( V_{EFA}^{nj} \sum_{m} S_{nm} V_{EFA}^{mj} \right) \right],
\]

(A3)
\[\begin{align*}
CT_A^{(B)} & \approx 2 \sum_i^\text{occA} \sum_n^\text{virB} \frac{1}{1 - \sum_m^\text{allA} (S_{nm})^2} \frac{V_{EFB \, in}}{F_{ii} - T_{nn}} - \sum_m^\text{allA} S_{nm} V_{EFB \, im} + \sum_j^\text{occB} S_{ij} \left( T_{nj} - \sum_m^\text{allA} S_{nm} T_{mj} \right) \left[ V_{EFB \, in} - \sum_m^\text{allA} S_{nm} V_{EFB \, im} \right].
\end{align*}\]

It is difficult to judge the accuracy of the four formulae without numerical results since the various approximations involve all the matrix elements, not just the expectation values of an operator. The accuracies could depend on various factors: basis sets, electronic structures of the molecules, the shape of the orbitals used, that is, canonical or localized.\(^{10}\)

In order to determine which formula is the best when using VVOs, the CT energies for the five dimer systems are presented in Table III.

In all cases tested, Eq. (A2) gives very large positive numbers that are unphysical. Equation (A1) significantly underestimates the magnitude of the CT energies. Equation (A3) shows unpredictable behavior: large positive numbers for water dimer and ammonium-water dimer and underestimated CT energies for the other three systems. Equation (A4) not only produces negative CT energies in all cases but also closest to the RVS benchmarking numbers.