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Citation: **114**, 8775 (2001); doi: 10.1063/1.1356017

View online: <http://dx.doi.org/10.1063/1.1356017>

View Table of Contents: <http://aip.scitation.org/toc/jcp/114/20>

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# Intermolecular exchange-induction and charge transfer: Derivation of approximate formulas using nonorthogonal localized molecular orbitals

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(Received 13 November 2000; accepted 24 January 2001)

Previous work on the efficient evaluation of the second-order exchange repulsion energy [Mol. Phys. **89**, 1313 (1996)] is extended to exchange induction and charge transfer energies. The approximations outlined in the previous work are shown to be sufficient to simplify all new terms in the exchange induction and charge transfer energy terms. Both variational and couple perturbed Hatree–Fock approaches are discussed as is the use of these new energy terms in conjunction with hybrid “quantum mechanical/molecular mechanics” methods [specifically the effective fragment potential method, J. Chem. Phys. **105**, 1968 (1996)]. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356017]

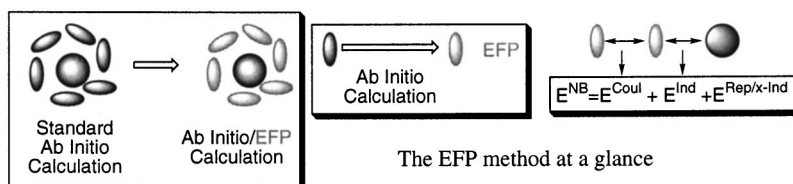
## I. INTRODUCTION

Theories of intermolecular interactions were among the first successful application of physical laws at the molecular level.<sup>1</sup> While the initial focus was on the long-range electrostatic contributions to intermolecular forces,<sup>2–4</sup> purely quantum mechanical contributions, such as dispersion,<sup>5</sup> were quickly identified as the theory of wave mechanics emerged. Furthermore, quantum mechanics was shown<sup>6</sup> to give rise to significant short-range interactions via the Pauli exclusion principle. The original functional forms of these energy terms, derived for simple atomic systems, form the basis of most molecular mechanics interaction potentials used today.

Comprehensive molecular theories of both the short- and long-range interactions have also been developed, usually using intermolecular perturbation theories<sup>7,8</sup> (IMPTs) modified to account for exchange interactions for the former.<sup>5,9–15</sup> Furthermore, some of the resulting methods have been implemented in computer programs, so that accurate numerical values for the various intermolecular interaction terms can be computed for a given molecular system.<sup>15,16</sup> The computational cost is roughly that of regular electronic structure calculations requiring a two-electron integral transformation, so that the practical applicability to very large systems is similarly limited. However, the accurate values for the various intermolecular interaction terms for smaller representative systems can be used to parametrize the molecular mechanics interaction potentials mentioned above, that can be applied to much larger systems.

There have been some attempts to use the *equations* derived using IMPT, rather than the numerical results, to generate less empirical intermolecular interaction potentials. Significant advances have been made in the long-range interactions so that, for example, the long-range electrostatic interaction energy can be evaluated with near arbitrary accuracy without empirical parametrization, by using a distributed multipole expansion.<sup>17</sup> Recent studies by Kairys and Jensen<sup>18</sup> as well as Freitag, Gordon, Jensen, and Stevens<sup>19</sup> have shown how to correct this interaction for short-range charge penetration effects.

This treatment of electrostatic interactions forms the basis of the effective fragment potential (EFP) method.<sup>20</sup> The EFP method is a hybrid method in which only the active part of a molecular system is treated with *ab initio* quantum mechanics while the rest is replaced by one or more EFPs. An EFP represents the static electrostatic potential by a distributed multipole expansion<sup>17</sup> (charges through octupoles at all atomic centers and bond midpoints), while the electronic polarizability is represented by dipole polarizability tensors for each valence (localized) molecular orbital.<sup>21–23</sup> The induced dipoles on a given EFP are induced in part by the induced dipoles on other EFPs, and the induction term thus describes many-body effects. Both expressions can be systematically improved by including higher order terms or more expansion points, but the current form has proved sufficient thus far. Both the multipole expansion and polarizability terms are calculated by one separate *ab initio* calculation.



The EFP method at a glance

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The complexity of the exchange terms has made an analogous nonempirical treatment more challenging. However, recently Jensen and Gordon presented a computationally efficient expression for the exchange repulsion term that depends solely on the properties of the isolated molecules.<sup>20(c),24,25</sup> In this paper we present similar expressions for the exchange induction energy, including charge transfer. In the resulting EFP method, *all* EFP parameters are generated *automatically* and by a *single ab initio calculation* (or by a few calculations for large systems<sup>23</sup>), so that an EFP is tailor made for each particular system, at a particular level of theory. Thus, this method shares two unique and very important features with *ab initio* quantum mechanics: (1) *No reliance on empirical parameters*, which may be unavailable for, or not transferable to, a particular system. (2) *The results can be systematically improved* both with respect to the level of theory and to the sophistication of the mathematical treatment.

This paper is organized as follows. First, we review a previous derivation of the Coulomb and exchange repulsion energies by Fröman and Löwdin.<sup>26,27</sup> This derivation does not rely on perturbation theory and is therefore more consistent with the subsequent treatment of the exchange induction and charge transfer terms. Furthermore, the Löwdin approach can be more easily extended to restricted open shell Hartree–Fock (ROHF), generalized valence bond (GVB), and multiconfigurational self-consistent-field (MCSCF) wave functions in future studies. Second, we review the approximations that lead to a computationally tractable expression for the Coulomb and exchange repulsion energy. Third, the classical induction energy is discussed. Fourth, new expressions for the exchange induction and charge transfer are derived and simplified by using the approximations reviewed for the Coulomb, exchange repulsion, and classical induction energies. In all cases we consider EFP/EFP and *ab initio*/EFP interactions separately, since different assumptions must be made for each case. Finally, our findings are summarized and future directions are discussed.

## II. THE COULOMB ENERGY AND EXCHANGE REPULSION ENERGY

### A. Derivation

The restricted Hartree–Fock (RHF) energy of a closed shell system is usually expressed in terms of orthogonal molecular orbital (MOs)  $\{\phi\}$ ;  $E^{\text{nuc}}$  is the nuclear repulsion energy; please refer to Refs. 24 and 28 for additional notation),

$$E = 2 \sum_m h_{mm} + \sum_m \sum_n (2 \langle mm|nn \rangle - \langle mn|mn \rangle) + E^{\text{nuc}}$$

$$= 2 \sum_m h_{mm} + \sum_m \sum_n G_{mn} + E^{\text{nuc}}. \quad (1)$$

However, the expression for the nonorthogonal MO ( $\{\psi\}$ ) case,

$$E = 2 \sum_m \sum_n h_{mn} S_{mn}^{-1} + \sum_m \sum_n \sum_r \sum_s (2 \langle mn|rs \rangle - \langle mr|ns \rangle) S_{mn}^{-1} S_{rs}^{-1} + E^{\text{nuc}} \quad (2)$$

is easily obtained through the following substitution:

$$\phi_m = \sum_n S_{mn}^{-1/2} \psi_n, \quad (3)$$

where  $S_{mn} = \langle \psi_m | \psi_n \rangle$ . The effect of orthogonalization is easily isolated by<sup>26,27</sup>

$$\mathbf{S}^{-1} = \mathbf{1} - \mathbf{P}, \quad (4)$$

so that

$$E = 2 \sum_m h_{mm} + \sum_m \sum_n G_{mn} - 2 \sum_m \sum_n F_{mn} P_{mn}$$

$$+ \sum_m \sum_n \sum_r \sum_s (2 \langle mn|rs \rangle - \langle mr|ns \rangle) P_{mn} P_{rs}$$

$$+ E^{\text{nuc}}, \quad (5)$$

where

$$F_{mn} = h_{mn} + G_{mn}. \quad (6)$$

To proceed further, we consider a bimolecular system ( $A \cdots B$ ) where the RHF wave function of isolated  $A$  and  $B$  is expressed in terms of orthonormal MOs. Thus only the intermolecular overlap is nonzero,

$$\mathbf{S} = \begin{array}{|c|c|} \hline \begin{array}{c} 1 \quad 0 \\ 0 \quad \ddots \quad 1 \end{array} & \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \\ \hline \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} & \begin{array}{c} 1 \quad 0 \\ 0 \quad \ddots \quad 1 \end{array} \\ \hline \end{array}$$

Defined this way, the first two terms of Eq. (5) consists of the energy of isolated  $A$  and  $B$  ( $E_A$  and  $E_B$ ) plus the Coulombic and exchange interaction between the two molecules ( $E^{\text{Coul}}$  and  $E^{\text{Exch}}$ , respectively),

$$2 \sum_m h_{mm} + \sum_m \sum_n G_{mn} + E^{\text{nuc}}$$

$$= \sum_{i \in A} \left( 2h_{ii}^A + \sum_{k \in A} G_{ik}^A \right) + \sum_{j \in B} \left( 2h_{jj}^B + \sum_{l \in B} G_{jl}^B \right)$$

$$+ 2 \sum_{i \in A} \sum_{j \in B} (V_{ii}^B + V_{jj}^A + 2 \langle ii|jj \rangle)$$

$$- 2 \sum_{i \in A} \sum_{j \in B} \langle ij|ij \rangle + E^{\text{nuc}}$$

$$= E_A + E_B + E^{\text{Coul}} + E^{\text{Exch}}, \quad (7)$$

The third term of Eq. (5) can be simplified further by isolating Fock matrix elements for the molecules  $A$  and  $B$ ,

$$\sum_m \sum_n F_{mn} P_{mn} = \sum_m \sum_{i \in A} F_{mi}^A P_{mi} + \sum_m \sum_{j \in B} F_{mj}^B P_{mj}$$

$$+ \sum_m \sum_{i \in A} (V_{mi}^B + G_{mi}^B) P_{mi}$$

$$+ \sum_m \sum_{j \in B} (V_{mj}^A + G_{mj}^A) P_{mj}. \quad (8)$$

If the basis set is large enough to approach the basis set limit the MOs will approach the exact solution to the integro-differential equation,

$$\hat{F}^A \psi_i = \sum_{k \in A} F_{ik}^A \psi_k, \quad (9)$$

then

$$F_{mi}^A = \sum_{k \in A} F_{ik}^A S_{mk}. \quad (10)$$

Previous studies by Jensen and Gordon<sup>24,25</sup> have shown that relatively modest basis sets satisfy Eq. (10) with sufficient accuracy. Using Eq. (10), Fröman and Löwdin<sup>26</sup> showed early on that the first term in Eq. (8) vanishes (and similarly for the second term),

$$\begin{aligned} \sum_m \sum_{i \in A} F_{mi}^A P_{mi} &= \sum_m \sum_{i \in A} \sum_{k \in A} F_{ik}^A S_{km} P_{mi} \\ &= \sum_{i \in A} \sum_{k \in A} F_{ik}^A \tilde{S}_{ki} = 0 \end{aligned} \quad (11)$$

by taking advantage of the following property of  $\mathbf{P}$ :

$$\mathbf{P} = \mathbf{1} - \mathbf{S}^{-1} = \mathbf{1} - (\mathbf{1} + \tilde{\mathbf{S}})^{-1} = \tilde{\mathbf{S}}(\mathbf{1} + \tilde{\mathbf{S}})^{-1} \Rightarrow \mathbf{P}\mathbf{S} = \tilde{\mathbf{S}}. \quad (12)$$

Combining Eqs. (7), (8), and (11) we arrive at the following equation for the total energy:

$$\begin{aligned} E &= E_A + E_B + E^{\text{Coul}} + E^{\text{Exch}} + \sum_m \sum_{i \in A} (V_{mi}^B + G_{mi}^B) P_{mi} \\ &+ \sum_m \sum_{j \in B} (V_{mj}^A + G_{mj}^A) P_{mj} \\ &+ \sum_m \sum_n \sum_r \sum_s (2\langle mn|rs\rangle - \langle mr|ns\rangle) P_{mn} P_{rs} \\ &= E_A + E_B + E^{\text{Coul}} + E^{XR}. \end{aligned} \quad (13a)$$

Equation (13) defines the exchange repulsion energy<sup>26,27</sup> ( $E^{XR}$ ) which has two contributions: the intermolecular exchange and energy terms due to the orthogonality requirement.

The exchange repulsion energy can be expressed explicitly in terms of the intermolecular overlap by expanding  $\mathbf{P}$ ,

$$\begin{aligned} \mathbf{P} &= \tilde{\mathbf{S}}(\mathbf{1} + \tilde{\mathbf{S}})^{-1} \\ &\approx \tilde{\mathbf{S}}(\mathbf{1} - \tilde{\mathbf{S}} + \tilde{\mathbf{S}}^2 - \dots) = \tilde{\mathbf{S}} - \tilde{\mathbf{S}}^2 + \tilde{\mathbf{S}}^3 - \dots. \end{aligned} \quad (14)$$

A truncation after the second term has proven sufficient for many applications,<sup>14(c),16,24,25</sup> so that  $\mathbf{P}$  takes the following form:

$$\begin{aligned} P_{ij} &= \tilde{S}_{ij} = S_{ij}, \\ P_{ik} &= \tilde{S}_{ik}^2 = \sum_{j \in B} S_{ij} S_{jk}, \\ P_{jl} &= \tilde{S}_{jl}^2 = \sum_{i \in A} S_{ji} S_{il}. \end{aligned} \quad (15)$$

The second term in  $E^{XR}$  thus takes the form

$$\begin{aligned} \sum_m \sum_{j \in B} (V_{mj}^A + G_{mj}^A) P_{mj} &= \sum_{j \in A} \sum_{j \in B} S_{ij} (V_{ij}^A + G_{ij}^A) \\ &+ \sum_{j \in A} \sum_{j \in B} S_{ij} \sum_{l \in B} S_{il} (V_{lj}^A + J_{lj}^A). \end{aligned} \quad (16)$$

Here we note that all terms in Eq. (16) involve two products of MOs on molecules  $A$  and  $B$  (e.g.,  $\psi_i \psi_j$ ) and thus scale as  $S^2$ . Thus, in evaluating the last term of Eq. (13a) only terms that scale as  $S^2$  are included,

$$\begin{aligned} \sum_m \sum_n \sum_r \sum_s (\langle mn|rs\rangle - \langle mr|ns\rangle) P_{mn} P_{rs} \\ = - \sum_{i \in A} \sum_{j \in B} S_{ij} \sum_{k \in A} \sum_{l \in B} S_{kl} \langle ik|jl\rangle. \end{aligned} \quad (17)$$

Thus, we arrive at the familiar form<sup>12,16,24</sup> of the exchange repulsion energy to second order in  $\mathbf{S}$ ,

$$\begin{aligned} E^{XR} &= -2 \sum_{i \in A} \sum_{j \in B} \langle ij|ij\rangle - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} [V_{ij}^A + G_{ij}^A + V_{ij}^B \\ &+ G_{ij}^B] + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[ \sum_{k \in A} S_{kj} (V_{ik}^B + J_{ik}^B) \right. \\ &\left. + \sum_{l \in B} S_{il} (V_{lj}^A + J_{lj}^A) - \sum_{k \in A} \sum_{l \in B} S_{kl} \langle ik|lj\rangle \right]. \end{aligned} \quad (18)$$

## B. Approximations

### 1. The EFPI/EFP Coulomb energy

The classical Coulomb energy derived above has the following form ( $E_{AB}^{\text{nuc}}$  is the intermolecular nuclear repulsion energy),

$$E^{\text{Coul}} = 2 \sum_{i \in A} \sum_{j \in B} (V_{ii}^B + V_{jj}^A + 2\langle ii|jj\rangle) + E_{AB}^{\text{nuc}}. \quad (19)$$

Expansion of the one- and two-electron operators in one or two Taylor series, respectively,

$$\begin{aligned} |\mathbf{r}_1 - \mathbf{R}_j|^{-1} &\approx |\mathbf{R}_a - \mathbf{R}_j|^{-1} + \dots, \\ |\mathbf{r}_1 - \mathbf{r}_2|^{-1} &\approx |\mathbf{R}_a - \mathbf{R}_b|^{-1} + \dots, \end{aligned} \quad (20)$$

leads to the well-known multipole expansion of the Coulomb energy,<sup>7</sup>

$$E^{\text{Coul}} = \sum_{a \in A} \sum_{b \in B} \left[ \frac{q_a q_b}{R_{ab}} - \frac{q_a \mathbf{R}_{ab} \cdot \boldsymbol{\mu}_b}{R_{ab}^2} - \frac{q_b \mathbf{R}_{ab} \cdot \boldsymbol{\mu}_a}{R_{ab}^2} + \dots \right], \quad (21)$$

where  $q$  can be either an electronic or nuclear charge. Within the EFP method, the multipole expansion of the molecular densities of  $A$  and  $B$ , calculated separately by *ab initio* methods, is done using Stone's distributed multipole analysis method,<sup>17</sup> and using expansion points at each atom and bond midpoint. If the two electron densities do not overlap Eq. (21) can be systematically improved by including more expansion points and higher order terms to reproduce  $E^{\text{Coul}}$  to arbitrary accuracy.

## 2. The *ab initio*/EFP Coulomb energy

The *ab initio*/EFP Coulombic interaction energy between the *ab initio* molecule (*A*) and the EFP molecule (*B*) is obtained by expanding the operator terms connected only with molecule *B*,

$$\begin{aligned} |\mathbf{r}_1 - \mathbf{R}_l|^{-1} &\approx |\mathbf{R}_b - \mathbf{R}_l|^{-1} + \dots, \\ |\mathbf{r}_1 - \mathbf{r}_2|^{-1} &\approx |\mathbf{r}_1 - \mathbf{R}_b|^{-1} + \dots, \end{aligned} \quad (22)$$

so that

$$\begin{aligned} E^{\text{Coul}} &\approx \sum_{l \in A} \sum_{b \in B} \left[ \frac{Z_l q_b}{R_{lb}} - \frac{Z_l \mathbf{R}_{lb} \cdot \boldsymbol{\mu}_b}{R_{lb}^2} + \dots \right] \\ &\quad + 2 \sum_{i \in A} \left\langle i \left| \sum_{b \in B} \left[ \frac{q_b}{R_{1b}} - \frac{\mathbf{R}_{1b} \cdot \boldsymbol{\mu}_b}{R_{1b}^2} + \dots \right] \right| i \right\rangle \\ &\approx \sum_{l \in A} \sum_{b \in B} \left[ \frac{Z_l q_b}{R_{lb}} - \frac{Z_l \mathbf{R}_{lb} \cdot \boldsymbol{\mu}_b}{R_{lb}^2} + \dots \right] + 2 \sum_{i \in A} V_{ij}^{\text{EFP}, B}. \end{aligned} \quad (23)$$

In the EFP method this energy is evaluated using MOs of molecule *A* optimized in the presence of *B*. Evaluated in this way  $E^{\text{Coul}}$  is actually the sum of the classical Coulomb and induction energy, and this point will be discussed further in Sec. III A 2.

## 3. The EFP/EFP exchange repulsion energy

The second order exchange repulsion energy involves two-electron integrals in the MO basis and is thus computationally expensive to evaluate. Jensen and Gordon<sup>24</sup> have proposed several approximations that eliminate all two-electron integrals, and included the resulting equation in the effective fragment potential method.<sup>25</sup> We briefly review the approximations here.

The intermolecular exchange integral can be greatly simplified by approximating the orbital product as a spherical Gaussian,

$$\begin{aligned} \psi_i \psi_j &\approx \left( \frac{2\alpha}{\pi} \right)^{3/2} S_{ij} e^{-2\alpha|\mathbf{r} - 1/2(\mathbf{R}_i + \mathbf{R}_j)|^2}, \\ \text{where } \alpha &= -\frac{2}{R_{ij}^2} \ln S_{ij}. \end{aligned} \quad (24)$$

With this spherical Gaussian overlap approximation<sup>29</sup> the exchange integral can be cast in terms of the intermolecular overlap,

$$\langle ij | ij \rangle \approx 2 \sqrt{\frac{-2 \ln S_{ij}}{\pi}} \frac{S_{ij}^2}{R_{ij}}. \quad (25)$$

Jensen and Gordon<sup>25</sup> have demonstrated that the intermolecular exchange energy for six molecular dimers can be reproduced to within 0.25 kcal/mol provided that LMOs are used. The use of canonical MOs in, e.g., the water dimer leads to 0.70 kcal/mol error compared to 0.02 kcal/mol for LMOs.<sup>29</sup>

The second term in Eq. (18) can be simplified using the Landshoff approximation<sup>30</sup> [Eq. (10)],

$$V_{ij}^A + G_{ij}^A = F_{ij}^A - T_{ij} = \sum_{k \in A} F_{ik}^A S_{kj} - T_{ij}. \quad (26)$$

Finally, the last term in Eq. (18) can be greatly simplified by first neglecting many of the smaller integrals all together,

$$S_{ij} S_{kj} V_{ik}^B \approx S_{ij}^2 V_{ii}^B \delta_{ik}$$

and

$$S_{ij} S_{kl} \langle ik | lj \rangle = S_{ij}^2 \langle ii | jj \rangle \delta_{ik} \delta_{lj}. \quad (27)$$

The remaining integrals have classical analogs and can be modeled accurately using a point charge model for the MOs,

$$\begin{aligned} |\mathbf{r}_1 - \mathbf{R}_j|^{-1} &\approx |\mathbf{R}_i - \mathbf{R}_j|^{-1} \Rightarrow S_{ij}^2 V_{ij}^B = S_{ij}^2 \left( \sum_{j \in B} -Z_j R_{ij}^{-1} \right), \\ |\mathbf{r}_1 - \mathbf{r}_2|^{-1} &\approx |\mathbf{R}_i - \mathbf{R}_j|^{-1} \Rightarrow S_{ij}^2 \langle ii | jj \rangle = S_{ij}^2 R_{ij}^{-1}. \end{aligned} \quad (28)$$

As before, both approximations work very well for LMOs, but both lead to unacceptable errors for canonical MOs.

The combined use of all approximations leads to the following equation:<sup>24</sup>

$$\begin{aligned} E^{XR} &\approx -2 \sum_{i \in A} \sum_{j \in B} 2 \sqrt{\frac{-2 \ln S_{ij}}{\pi}} \frac{S_{ij}^2}{R_{ij}} \\ &\quad - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[ \sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - 2 T_{ij} \right] \\ &\quad + 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^2 \left[ \sum_{j \in B} -Z_j R_{ij}^{-1} + 2 \sum_{l \in B} R_{il}^{-1} \right. \\ &\quad \left. + \sum_{l \in A} -Z_l R_{lj}^{-1} + 2 \sum_{k \in A} R_{kj}^{-1} - R_{ij}^{-1} \right]. \end{aligned} \quad (29)$$

This equation requires only the computation of intermolecular overlap and electronic kinetic energy integrals, i.e., no two-electron integrals other than those calculated once for the isolated molecules. It contains *no adjustable parameters*, only fixed parameters computed for the isolated molecules, such as the LMOs in some AO basis, Fock matrices in the LMO bases, and the LMO centroids of charge. The accuracy of the approximate exchange repulsion formula has been demonstrated by reproducing the exact  $E^{XR}$  values for five different intermolecular dimers to within 0.5 kcal/mol at the 6-31++G(2d,2p) level of theory.<sup>25</sup> Furthermore, aggressive screening of the overlap and kinetic energy integrals (made possible by their short-range nature) leads to a less than  $N^2$  scaling with respect to cluster size ( $N$ ) as demonstrated for water and methanol clusters.<sup>25</sup> Since all approximations are physically motivated and based on LMOs the new but very similar approximations outlined below are expected to yield similar accuracy and efficiency.

## III. INDUCTION

The induction energy arises when the charge density of one molecule responds to the presence of another. Within MO theory, the response of *A* due to *B* is treated by mixing in virtual MOs from both *A* and *B* to obtain a new set of occupied MOs,

$$\psi_i^A(A \leftarrow B) = \sum_m^{\text{vir } A} U_{mi} \psi_m + \sum_n^{\text{vir } B} U_{ni} \psi'_n. \quad (30)$$

The energy resulting from the latter term is often called charge transfer, though in the limit of a complete basis set on  $A$ , this energy should go to zero. Since the two terms give rise to very different energy expressions, we consider the charge transfer term in the next section, and focus on the energy expression due to the first term here (which we call induction).

### A. Classical induction

The classical induction energy of molecule  $A$  due to  $B$  is obtained by substituting the first term of Eq. (30) into Eq. (19),<sup>16,31</sup>

$$\begin{aligned} E_A^{\text{ind}} &= E^{\text{Coul}}(A \leftarrow B) \\ &= 4 \sum_{i \in A} \sum_{j \in B} \sum_{m \in A}^{\text{vir}} U_{mi} (V_{mi}^B + 2 \langle mi | jj \rangle) \\ &= 4 \sum_{i \in A} \sum_{m \in A}^{\text{vir}} U_{mi} V_{mi}^{\text{ES}, B}. \end{aligned} \quad (31)$$

There is a similar induction energy due to molecule  $B$  being polarized by  $A$ .

### 1. Ab initio EFP induction

If molecule  $B$  is described by an EFP, so that  $V_{mi}^{\text{ES}, B} \approx V_{mi}^{\text{EFP}, B}$ , and the MOs on  $A$  are optimized for the isolated  $A$ , so that the corresponding Fock matrix is diagonal, Eq. (31) can be written in terms for a new Fock matrix,

$$\begin{aligned} E_A^{\text{ind}} &= 4 \sum_{i \in A} \sum_{m \in A}^{\text{vir}} U_{mi} V_{mi}^{\text{EFP}, B} \\ &= 4 \sum_{i \in A} \sum_{m \in A}^{\text{vir}} U_{mi} (F_{mi}^A + V_{mi}^{\text{EFP}, B}) \\ &= 4 \sum_{i \in A} \sum_{m \in A}^{\text{vir}} U_{mi} F_{mi}'^A. \end{aligned} \quad (32)$$

This equation is solved by finding a new set of MOs that diagonalizes  $F_{mi}'^A$ . In this way,  $E_A^{\text{ind}} = 0$  and  $E^{\text{Coul}}$  is comprised of both the Coulomb and induction energy.

## 2. EFP/EFP induction

If molecule  $A$  is also represented by EFPs,  $V_{mi}^{\text{EFP}, B}$  is simplified further by a Taylor expansion about the centroid of charge of MO  $i$  ( $\mathbf{R}_i$ ) truncated after the second term (the first term is zero),

$$V_{mi}^{\text{EFP}, B} \approx \langle m | \mathbf{r}_1 - \mathbf{R}_i | i \rangle \cdot (\nabla \hat{V}^{\text{EFP}, B})_{\mathbf{R}_i} = -\mu_{mi} \cdot \mathbf{F}_i^{\text{EFP}, B}, \quad (33)$$

where  $\mathbf{F}_i^{\text{EFP}, B}$  is the electric field of EFP  $B$  at  $\mathbf{R}_i$ . When combined with the response function  $\{\mu_{mi}\}$  describes the change in the dipole of MO  $i$  induced by  $B$ ,<sup>31</sup>

$$\begin{aligned} E^{\text{ind}} &= 2 \sum_{i \in A} \sum_{m \in A}^{\text{vir}} U_{mi} V_{mi}^{\text{EFP}, B} \\ &= -2 \sum_{i \in A} \sum_{m \in A}^{\text{vir}} U_{mi} \mu_{mi} \cdot \mathbf{F}_i^{\text{EFP}, B} \\ &= -\frac{1}{2} \sum_{i \in A} \mu_i^{\text{ind}, A} \cdot \mathbf{F}_i^{\text{EFP}, B}. \end{aligned} \quad (34)$$

In the EFP method, the induced MO dipoles are calculated by using the LMO dipole polarizability tensors ( $\alpha$ ),<sup>20</sup>

$$\mu_{i,x}^{\text{ind}, A} = \sum_a^{x,y,z} \alpha_{ax}^i F_{ia}^{\text{EFP}, B}. \quad (35)$$

## B. EFP/EFP exchange induction

We start with a slightly simplified version of Eq. (19),

$$\begin{aligned} E^{XR} &= -2 \sum_{i \in A} \sum_{j \in B} \langle ij | ij \rangle - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} [V_{ij}^A + G_{ij}^A + V_{ij}^B \\ &\quad + G_{ij}^B] + 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^2 [V_{ii}^B + 2J_{ii}^B + V_{jj}^A + 2J_{jj}^A \\ &\quad - \langle ii | jj \rangle] \end{aligned} \quad (36)$$

obtained by applying the approximation of Eq. (27). The substitution of the first term of Eq. (30) into Eq. (36) and some algebraic simplifications (summation of  $i$  and  $k$  can be interchanged and  $F_{im} = 0$ ) yield

$$\begin{aligned} E_A^{XI} &= E^{XR}(A \leftarrow B) \\ &= -2 \sum_{i \in A} \sum_{j \in B} \sum_m^{\text{vir } A} U_{mi} \langle mj | ij \rangle - 4 \sum_{i \in A} \sum_{j \in B} \sum_m^{\text{vir } A} U_{mi} S_{mj} \left[ \sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - T_{ij} \right] \\ &\quad - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \sum_m^{\text{vir } A} \left\{ U_{mi} [-2T_{mj}] + \sum_k U_{mk} [2 \langle ij | mk \rangle - \langle ik | jm \rangle] \right\} + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \sum_m^{\text{vir } A} U_{mi} S_{mj} \left[ V_{ii}^B + 2 \sum_{l \in B} \langle ii | ll \rangle \right. \\ &\quad \left. + V_{jj}^A + 2 \sum_{k \in A} \langle kk | jj \rangle - \langle ii | jj \rangle \right] + 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^2 \left\{ \sum_m^{\text{vir } A} U_{mi} \left[ V_{im}^B + 2 \sum_l \langle im | ll \rangle + \langle im | jj \rangle \right] + 2 \sum_m^{\text{vir } A} \sum_k U_{mk} \langle mk | jj \rangle \right\}. \end{aligned} \quad (37)$$



The second term has already been simplified using Eq. (26), and the expression can be further simplified using the same kinds of approximations discussed in Sec. II B.

In the first term in Eq. (37),  $\psi_i\psi_j$  can be approximated as before [Eq. (24)] and if the virtual MOs on A are localized,  $\psi_m\psi_j$  can be approximated similarly,

$$\psi_m\psi_j \approx \left(\frac{2\beta}{\pi}\right)^{3/2} S_{mj} e^{-2\beta|\mathbf{r}-\frac{1}{2}(\mathbf{R}_m+\mathbf{R}_j)|^2},$$

where  $\beta = -\frac{2}{R_{mj}^2} \ln S_{mj}$ . (38)

Thus,

$$\langle m|j|ij\rangle \approx 2\sqrt{\frac{2\alpha\beta}{\alpha+\beta}} S_{ij} S_{mj} F_0 \left[ \frac{2\alpha\beta}{\alpha+\beta} R_{im}^2 \right],$$

where  $\frac{2\alpha\beta}{\alpha+\beta} = \frac{-4 \ln S_{ij} \ln S_{mj}}{\pi(\ln S_{mj} R_{ij}^2 + \ln S_{ij} R_{mj}^2)}$  (39)

and  $F_0[t] = 1/2(\pi/t)^{1/2} \text{erf}(t^{1/2})$ . For  $\psi_m = \psi_j$ , Eq. (39) reduces to Eq. (25) and we expect similar accuracy for both equations.

The penultimate term of Eq. (37) can be approximated by a multipole expansion as before [cf. Eq. (28)], and similarly for the last term only now the first nonvanishing term is the dipole term [cf. Eq. (33)]:

$$2S_{ij}^2 \sum_m^{\text{vir A}} U_{mi} V_{mi}^B \approx -2S_{ij}^2 \left( \sum_m^{\text{vir A}} U_{mi} \mu_{im}^A \cdot \mathbf{F}_{\text{nuc}}^B \right)$$

$$= -\frac{1}{2} S_{ij}^2 (\mu_i^{\text{ind,A}} \cdot \mathbf{F}_{\text{nuc}}^B) \quad (40)$$

and similarly,

$$2S_{ij}^2 \sum_m^{\text{vir A}} U_{mi} \langle im|jj\rangle \approx -\frac{1}{2} S_{ij}^2 (\mu_i^{\text{ind,A}} \cdot \mathbf{F}_j^B). \quad (41)$$

Here we have made use of the fact that the individual LMO induced dipoles are known [cf. Eq. (34)]. Finally, the integrals in the fourth term are first simplified by a multipole expansion about the centroid of charge on LMO  $k(\mathbf{R}_k)$ ,

$$S_{ij} U_{mk} \langle ij|mk\rangle \approx -S_{ij} U_{mk} (\mu_{mk}^A \cdot \langle i|\hat{\mathbf{F}}(\mathbf{R}_k)|j\rangle). \quad (42)$$

The resulting one electron integral involves  $\psi_i\psi_j$  and can be further simplified via Eq. (24),

$$\langle i|\hat{\mathbf{F}}(\mathbf{R}_k)|j\rangle \approx 8\sqrt{\frac{2\alpha^2}{\pi}} \mathbf{R}_{Pk} F_1[2\alpha R_{Pk}^2] \equiv \mathbf{F}_{ij}^{k,\text{SGO}}, \quad (43)$$

where  $F_1[t] = \frac{1}{2}t^{-1}(F_0[t] - e^{-t})$  and  $\mathbf{R}_{Pk} = \frac{1}{2}(\mathbf{R}_i + \mathbf{R}_j) - \mathbf{R}_k$ . Combining all approximations leads to the following approximate equation for the exchange induction energy of A:

$$E_A^{\text{XI}} = -2 \sum_{i \in A} \sum_{j \in B} \sum_m^{\text{vir A}} U_{mi} 2\sqrt{\frac{2\alpha\beta}{\alpha+\beta}} S_{ij} S_{mj} F_0 \left[ \frac{2\alpha\beta}{\alpha+\beta} R_{im}^2 \right] - 4 \sum_{i \in A} \sum_{j \in B} \sum_m^{\text{vir A}} U_{mi} S_{mj} \left[ \sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - T_{ij} \right]$$

$$- 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \sum_m^{\text{vir A}} \left\{ U_{mi} [-2T_{mj}] + \sum_k U_{mk} [2\mu_{mk}^A \cdot \mathbf{F}_{ij}^{k,\text{SGO}} - \mu_{ik}^A \cdot \mathbf{F}_{jm}^{i,\text{SGO}}] \right\}$$

$$+ 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \sum_m^{\text{vir A}} U_{mi} S_{mj} \left[ \sum_{j \in B} -Z_j R_{ij}^{-1} + 2 \sum_{l \in B} R_{il}^{-1} + \sum_{l \in A} -Z_l R_{lj}^{-1} + 2 \sum_{k \in A} R_{kj}^{-1} - R_{ij}^{-1} \right]$$

$$- \frac{1}{2} \sum_{i \in A} \sum_{j \in B} S_{ij}^2 \left\{ \mu_i^{\text{ind,A}} \cdot \mathbf{F}_{\text{nuc}}^B + 2 \sum_l \mu_l^{\text{ind,A}} \cdot \mathbf{F}_l^B + \mu_i^{\text{ind,A}} \cdot \mathbf{F}_j + 2 \sum_k \mu_k^{\text{ind,A}} \cdot \mathbf{F}_j^B \right\}. \quad (44)$$

Finally, we discuss the form of the expansion coefficients  $\{U_{mi}\}$ , which are given by the coupled Hartree–Fock equation,<sup>16</sup>

$$\mathbf{A}\mathbf{U} = \mathbf{V}^{\text{ES,B}} \Rightarrow$$

$$\mathbf{U} = \mathbf{A}^{-1} \mathbf{V}^{\text{ES,B}} \Rightarrow$$

$$U_{mi} = \sum_{k \in A} \sum_{m'}^{\text{vir A}} V_{km'}^{\text{ES,B}} (A_{km',im}^A)^{-1}. \quad (45)$$

Here,  $V^{\text{ES,B}}$  denotes the electrostatic potential of molecule B, which in the EFP methodology is approximated by the multipole expansion of  $V^{\text{EFP,B}}$  as before [cf. Eq. (33)],

$$V_{km'}^{\text{ES,B}} \approx V_{km'}^{\text{EFP,B}} \approx -\mu_{km'} \cdot \mathbf{F}_{\text{EFP,B}}^B. \quad (46)$$

The matrix  $\mathbf{A}$  in Eq. (45) has the following elements:<sup>28</sup>

$$A_{mi,m'k}^A = \delta_{ik} F_{mm'}^A - \delta_{mm'} F_{ik}^A - (4\langle mi|m'k\rangle - \langle mm'|ik\rangle - \langle mk|m'i\rangle) \quad (47)$$

for (localized) noncanonical MOs. Here we simplify  $\mathbf{A}$  in a manner similar to  $\mathbf{S}$ , by separating  $\mathbf{A}$  into a diagonal matrix  $\mathbf{D}$  and a nondiagonal remainder,

$$\mathbf{A} = \mathbf{D} + \tilde{\mathbf{A}}$$

$$= \mathbf{D}(\mathbf{1} + \mathbf{D}^{-1}\tilde{\mathbf{A}}), \quad (48)$$

whereby

$$\begin{aligned}
\mathbf{A}^{-1} &= (\mathbf{1} + \mathbf{D}^{-1} \tilde{\mathbf{A}})^{-1} \mathbf{D}^{-1} \\
&\approx (\mathbf{1} - \mathbf{D}^{-1} \tilde{\mathbf{A}} + \dots) \mathbf{D}^{-1} \\
&\approx \mathbf{D}^{-1} - \mathbf{D}^{-1} \tilde{\mathbf{A}} \mathbf{D}^{-1}.
\end{aligned} \quad (49)$$

Thus, approximating  $\mathbf{A}$  by

$$A_{mi,m'k}^A \approx \delta_{ik} F_{mm'}^A - \delta_{mm'} F_{ik}^A \quad (50)$$

leads to the following expression for  $\mathbf{A}^{-1}$ :

$$\begin{aligned}
A_{mi,m'k}^{-1} &\approx \frac{\delta_{ik} \delta_{mm'}}{(\varepsilon_m^A - \varepsilon_i^A)} - (1 - \delta_{ik} \delta_{mm'}) \\
&\quad \times \frac{\delta_{ik} F_{mm'}^A - \delta_{mm'} F_{ik}^A}{(\varepsilon_m^A - \varepsilon_i^A)(\varepsilon_{m'}^A - \varepsilon_k^A)}.
\end{aligned} \quad (51)$$

The familiar IMPT (canonical MO) expression is thus the first term of Eq. (51) where  $\varepsilon_i^A \equiv F_{ii}^A$ .

### C. *Ab initio*/EFP exchange induction

As mentioned above, the expression for  $E^{XR}$  in Eq. (29) assumes localized MOs fully optimized for isolated molecule  $A$  and  $B$ . If molecule  $A$  is treated by *ab initio* methods neither assumption is valid, since the MOs are optimized in the presence of  $B$  in their canonical basis. Thus if only Eq. (15) [and not Eq. (11)] is used to simplify Eq. (8),

$$\begin{aligned}
\sum_m \sum_n F_{mn} P_{mn} &\approx \sum_{i \in A} \sum_{j \in B} S_{ij} [F_{ij}^A + V_{ij}^A + G_{ij}^A + V_{ij}^B \\
&\quad + G_{ij}^B] + \sum_{i \in A} \sum_{j \in B} S_{ij} \left[ \sum_{k \in A} S_{kj} (F_{ik}^A \right. \\
&\quad \left. + V_{ik}^B + J_{ik}^B) + \sum_{l \in B} S_{il} (V_{lj}^A + J_{lj}^A) \right]
\end{aligned} \quad (52)$$

and Eq. (27) is applied only to  $\psi_i \psi_j$  a more general expression for  $E^{XR}$  is obtained,

$$\begin{aligned}
E^{XR} &= -2 \sum_{i \in A} \sum_{j \in B} \langle ij | ij \rangle - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \\
&\quad \times \left[ 2(V_{ij}^A + G_{ij}^A) + \sum_{l \in B} F_{jl}^B S_{li} \right] \\
&\quad + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[ \sum_{k \in A} S_{kj} (F_{ik}^A + V_{ik}^B + J_{ik}^B) \right. \\
&\quad \left. + S_{ij} (V_{jj}^A + J_{jj}^A) - \sum_{k \in A} S_{kj} \langle ik | jj \rangle \right].
\end{aligned} \quad (53)$$

Since  $\psi_i$  is not localized, Eq. (24) cannot be used directly, but must rather be applied to the localized AOs in which  $\psi_i$  is expanded,

$$\begin{aligned}
\psi_i \psi_j &= \sum_{\mu} C_{\mu i} \chi_{\mu} \psi_j \\
&\approx \sum_{\mu} C_{\mu i} \left( \frac{2\alpha}{\pi} \right)^{3/2} S_{\mu j} e^{-2\alpha|\mathbf{r} - 1/2(\mathbf{R}_{\mu} + \mathbf{R}_j)|^2}.
\end{aligned} \quad (54)$$

The integral  $\langle \mu j | v j \rangle$  can thus be approximated as before [Eq. (39)], while the remaining integrals in the second, third, and fourth term reduce to one of two types. The first type ( $V_{ij}^A$ ) reduces to

$$\langle \mu | \hat{V}^A | j \rangle \approx - \left( \frac{8\alpha}{\pi} \right)^{1/2} S_{\mu j} \sum_{l \in A} Z_l F_0[2\alpha R_{Pl}^2] \equiv V_{\mu j}^{A,SGO} \quad (55)$$

while the second type ( $G_{ij}^A$ ) is first simplified by a multipole expansion (about the Gaussian product center of  $\lambda$  and  $\sigma$ ,  $\mathbf{R}_Q$ ) and then further by Eq. (54),

$$\begin{aligned}
\langle \mu j | \lambda \sigma \rangle &\approx S_{\lambda \sigma} \langle \mu | R_{1Q}^{-1} | j \rangle \\
&\approx - \left( \frac{8\alpha}{\pi} \right)^{1/2} S_{\mu j} S_{\lambda \sigma} F_0[2\alpha R_{PQ}^2] \equiv I_{\mu j}^{\lambda \sigma,SGO}.
\end{aligned} \quad (56)$$

The resulting  $G$  matrix

$$2\langle \mu j | \lambda \sigma \rangle - \langle \mu \lambda | j \sigma \rangle = 2I_{\mu j}^{\lambda \sigma,SGO} - I_{\mu \lambda}^{j \sigma,SGO} = G_{\mu j}^{\lambda \sigma,SGO} \quad (57)$$

is subsequently transformed to the MO basis to yield  $G_{ij}^{A,SGO}$ . The remaining integrals can be treated with multipole expansions,

$$F_{ik}^A + V_{ik}^B + J_{ik}^B = F_{ik}^A + V_{ik}^{ES,B} \approx F_{ik}^A + V_{ik}^{EFP,B} \equiv F_{ik}'^A \quad (58)$$

and [cf. Eq. (27)]

$$\langle ik | jj \rangle \approx \langle i | |\mathbf{r}_i - \mathbf{R}_j|^{-1} | k \rangle = V_{ik}^j. \quad (59)$$

The resulting exchange repulsion energy,

$$\begin{aligned}
E^{XR} &= -2 \sum_{i \in A} \sum_{j \in B} \langle ij | ij \rangle^{SGO} - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \\
&\quad \times \left[ 2(V_{ij}^{A,SGO} + G_{ij}^{A,SGO}) + \sum_{l \in B} F_{jl}^B S_{li} \right] \\
&\quad + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[ \sum_{k \in A} S_{kj} F_{jk}'^A + S_{ij} \left( \sum_{l \in A} -Z_l R_{lj}^{-1} \right. \right. \\
&\quad \left. \left. + \sum_{k \in A} V_{kk}^j \right) - \sum_{k \in A} S_{kj} V_{ik}^j \right]
\end{aligned} \quad (60)$$

can thereby be evaluated with minimal additional computational expense.

The *ab initio*/EFP classical induction energy of molecule  $A$  is calculated by a variational energy minimization with Fock matrix elements that represent the electrostatic potential of fragment  $B$ . Similarly, the *ab initio*/EFP exchange induction energy can be evaluated variationally by including the following Fock matrix elements [the variational derivative of  $E^{XR}$  where  $m$  and  $i$  refer to any MO on  $A$ ; cf. Eq. (32)],



$$\begin{aligned}
V_{mi}^{XR} = & - \sum_{j \in B} \langle m|j\rangle \langle j|i\rangle - \frac{1}{2} \sum_{j \in B} S_{mj} \left[ 2(V_{ij}^A + G_{ij}^A) + \sum_{l \in B} F_{jl}^B S_{li} \right] - \frac{1}{2} \sum_{j \in B} S_{ij} \left[ 2(V_{mj}^A + G_{mj}^A) + \sum_{l \in B} F_{jl}^B S_{lm} \right] \\
& - \frac{1}{2} \sum_{k \in A} \sum_{j \in B} S_{kj} (4\langle kj|mi\rangle - \langle km|ji\rangle - \langle ki|jm\rangle) + \sum_{j \in B} S_{mj} \left[ \sum_{k \in A} S_{kj} (F_{ik}^A + \langle ik|jj\rangle) + S_{ij} (V_{jj}^A + J_{jj}^A) \right] \\
& + \sum_{j \in B} S_{ij} \left[ \sum_{k \in A} S_{kj} (F_{mk}^A + \langle mk|jj\rangle) \right] + \frac{1}{2} \sum_{k \in A} \sum_{k' \in A} \sum_{j \in B} S_{kj} S_{k'j} (4\langle k'k|mi\rangle - \langle k'm|ki\rangle - \langle k'i|km\rangle) \\
& + \sum_{k \in A} \sum_{j \in B} S_{kj}^2 \langle mi|jj\rangle,
\end{aligned} \quad (61)$$

where all intermolecular integrals are approximated as before. When the resulting MOs are used to evaluate Eq. (53) the resulting energy is the sum of the *ab initio*/EFP exchange repulsion and exchange induction energy.

#### IV. CHARGE TRANSFER

##### A. EFP/EFP charge transfer

If the wave function is allowed to respond by mixing in virtual MOs from the perturbing molecule,

$$\psi_i^A(A \leftarrow B) = \sum_n^{\text{vir } B} U_{n'i} \psi_n, \quad (62)$$

the exchange induction energy includes a “charge transfer” term, though if calculated correctly this term goes to zero within a complete basis set.<sup>7,8,15</sup> This change in the MOs affect all three energy terms related to molecule A, so Eq. (62) must be substituted into the energy of A, as well as the Coulomb and exchange repulsion energy. The result is a very simple expression for the second order charge transfer energy,

$$\begin{aligned}
E_A^{\text{CT}} = & E_A(A \leftarrow B) + E^{\text{Coul}}(A \leftarrow B) + E^{\text{XR}}(A \leftarrow B) \\
= & 2 \sum_n \sum_{i \in A} U_{n'i} \\
& \times \left( \sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - T_{ni} + \sum_{j \in A} S_{ij} T_{nj} \right). \quad (63)
\end{aligned}$$

The prime on  $n'$  in the response function is to indicate that the CPHF equations [Eq. (47)] assume orthogonal MOs. This is dealt with by including an orthogonality term

$$\begin{aligned}
\psi'_n = & \sum_p^{\text{all}} (\mathbf{S}^{-1})_{np} \psi_p \approx \sum_p^{\text{all}} (\mathbf{1} - \tilde{\mathbf{S}} + \cdots)_{np} \psi_p \\
\approx & \psi_n - \sum_m^{\text{all } A} S_{nm} \psi_m, \quad (64)
\end{aligned}$$

so that

$$\begin{aligned}
V_{in'}^{\text{ES},B} \approx & V_{in'}^{\text{EFP},B} \approx V_{in}^{\text{EFP},B} - \sum_{m \in A}^{\text{all}} S_{nm} V_{im}^{\text{EFP},B} \\
\approx & V_{in}^{\text{EFP},B} - \sum_{m \in A}^{\text{all}} S_{nm} \mu_{im} \cdot \mathbf{F}^{\text{EFP},B}. \quad (65)
\end{aligned}$$

The orthogonality (second) term in the middle equation insures that the energy gained by mixing linearly dependent MOs tends to zero in the limit of a complete basis. In practice  $U_{n'i}$  is set to zero if  $S_{nm}$  is above a certain threshold, otherwise the orthogonality term is approximated by a multipole expansion, while  $V_{in}^{\text{EFP},B}$  (i.e.,  $\psi_i \psi_n$ ) is simplified by the SGO approximation.

Finally, the **A** matrix is approximated by

$$A_{n',i,n''k}^{-1} \approx \frac{\delta_{ik} \delta_{n'n''}}{(\epsilon_n^A - \epsilon_i^A)}, \quad (66)$$

where  $\epsilon_n^A = T_{nn} + V_{nn}^{\text{EFP},A}$ . If the induced dipoles are included in  $\hat{V}^{\text{EFP},A}$  the effect of classical many-body effects on the charge transfer energy is included.

##### B. *Ab initio*/EFP charge transfer

Charge transfer for *ab initio*/EFP interactions can in principle be included by expanding the size of the Fock matrix to include some virtual MOs on fragment B. However, a larger Fock matrix will increase the cost of the diagonalization step during the SCF, which is undesirable. An alternative approach is to include an additional term in the existing Fock matrix element by taking the variational derivative of Eq. (63),

$$\begin{aligned}
V_{mi}^{\text{CT}} = & \sum_n U_{nm} \left( V_{ni}^A + G_{ni}^A + \sum_{l \in B} F_{jl}^B S_{li} + \sum_{j \in A} S_{ij} T_{nj} \right) \\
& + \sum_n U_{ni} \left( V_{nm}^A + G_{nm}^A + \sum_{l \in B} F_{nl}^B S_{nm} + \sum_{j \in A} S_{mj} T_{nj} \right) \\
& + \frac{1}{2} \sum_n U_{ni} \sum_{k \in A} (4\langle ni|mk\rangle - \langle nm|ik\rangle - \langle nk|im\rangle)
\end{aligned} \quad (67)$$

and approximate all integrals as outlined above.

## V. SUMMARY

Computationally efficient expressions for exchange induction [Eqs. (44) and (60)–(61)] and charge transfer [Eqs. (63) and (67)], to be used in conjunction with the effective fragment potential method, are derived. The derivation is accomplished by first deriving expressions that are rigorously correct to second order in the overlap and subsequently simplifying each term by a combination of three approximations: the multipole expansion, the Landshoff approximation, and the spherical Gaussian overlap approximation. All three approximations have previously been used successfully to yield accurate yet computationally classical induction and exchange repulsion energies (as outlined in Sec. II) and we expect similar accuracy for the new equations. The resulting implementation, to be described in a future paper, will thus yield *a completely general intermolecular interaction potential that depends solely on the properties of the isolated molecules*, made available by separate *ab initio* calculations.

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<sup>31</sup>When the coefficients are determined by an expansion, rather than variationally, higher order terms reduce the expression in Eq. (34) by a factor of 2: (a) L. C. Allen, *Phys. Rev.* **118**, 167 (1960); (b) R. M. Stevens, R. M. Pitzer, and W. N. Lipscomb, *J. Chem. Phys.* **38**, 550 (1963).