

Exchange repulsion between effective fragment potentials and ab initio molecules

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Abstract The exchange repulsion energy and the Fock operator for systems that contain both effective fragment potentials and ab initio molecules have been derived, implemented, and tested on six mixed dimers of common solvent molecules. The implementation requires a balance between accuracy and computational efficiency. The gradient of the exchange repulsion has also been derived. Computational timings and the current challenges facing the implementation of the gradient are discussed.

Keywords Effective fragment potential · QM-EFP · Exchange repulsion · Solvent

1 Introduction

The effective fragment potential (EFP) method has been used to successfully model a variety of intermolecular interactions, including solvent effects on ions and chemical reaction mechanisms, solvent effects on electronically excited states, mixed clusters of water with benzene, and the study of liquids. The original implementation [1], called EFP1, was designed exclusively for the water molecule. It can be used to study a system exclusively containing EFP1

potentials, or a system in which EFP1 water potentials solvate an ab initio solute within the general atomic and molecular electronic structure system (GAMESS) [2, 3].

The second implementation [4], called EFP2, is a general model potential that can be generated for any molecular species. An EFP2 can interact with other EFP2 molecules via electrostatics, polarization, exchange repulsion, dispersion [5], and charge transfer [6]. Gradients for each interaction type have been derived and implemented, allowing the structural geometry to be optimized.

An EFP2 can be used in the presence of an ab initio quantum mechanics (QM) molecule in GAMESS to calculate energies at fixed geometries. Single point energies are described through electrostatics, polarization, and exchange repulsion interaction energies. Only single-point energies may be calculated when an ab initio molecule is present, because the gradient expression is not currently available for the exchange repulsion energy, and the currently implemented EFP2–ab initio exchange repulsion energy is an approximate one [7]. The development of the EFP-QM dispersion interaction is currently in progress, in a manner analogous to the EFP2–EFP2 prescription that was implemented previously [5].

The exchange repulsion can be well accounted for at the Hartree–Fock (HF) level of theory. The Morokuma–Kitaura analysis [8] and the reduced variational space (RVS) analysis developed by Stevens and Fink [9] are both well-known methods for assessing the exchange repulsion and other contributions to the HF energy and are available in many electronic structure programs, including GAMESS. The focus of the present work is on developing the theory for the EFP2-QM exchange repulsion interaction, as well as the implementation of an efficient computer code. The ultimate goal is to implement the analogous dispersion term as well, since that would provide a level of theory that

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is of second order perturbation theory quality, as has been demonstrated for EFP2–EFP2 interactions [10–14]. The current implementation of the exchange repulsion provides a HF-quality model that can be used, for example, to model non-aqueous solvent effects on chemical processes, such as reaction mechanisms and UV spectroscopy. As has been demonstrated previously [10–14], EFP2 including the dispersion interactions provides intermolecular interactions whose quality is equivalent to that of second-order perturbation theory (MP2). The expectation is that once the EFP2-QM dispersion interaction has been derived and implemented, the quality of EFP2-QM calculations of intermolecular interactions will also be of MP2 quality.

Section 2 of the present work considers the rigorous expressions for the EFP-QM exchange repulsion energy [15] and the corresponding Fock matrix [15] and gradient expressions [16]. Implementations, results, and timings are presented in Sect. 3. Successful and less successful approximations are detailed in Sect. 4. Potential future directions and the required derivatives for the gradient are discussed in Sect. 5. Conclusions are drawn in Sect. 6.

2 Theory

The EFP2–EFP2 exchange repulsion energy expression [6] has previously been used to calculate the inter-fragment exchange repulsion (among EFP2 potentials). An analogous (not derived) expression is available in GAMESS for the EFP–ab initio exchange repulsion energy (between EFP2 potentials and ab initio molecules). The expression [6] for the exchange repulsion energy with no approximations is

$$\begin{aligned}
 E^{\text{XR}} = & -2 \sum_{i \in A} \sum_{j \in B} (ij|ij) \\
 & - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[V_{ij}^A + G_{ij}^A + V_{ij}^B + G_{ij}^B \right] \\
 & + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[\sum_{k \in A} S_{kj} (V_{ik}^B + 2J_{ik}^B) + \sum_{l \in B} S_{il} (V_{ij}^A + 2J_{ij}^A) \right. \\
 & \left. - \sum_{k \in A} \sum_{l \in B} S_{kl} (ik|lj) \right] \quad (1)
 \end{aligned}$$

The integrals in Eq. 1 are defined as follows:

$$(ij|ij) = \iint \phi_i^*(r_1) \phi_j(r_1) \frac{1}{r_{12}} \phi_i^*(r_2) \phi_j(r_2) dr_1 dr_2 \quad (2)$$

$$S_{ij} = (i|j) = \int \phi_i^*(r_1) \phi_j(r_1) dr_1 \quad (3)$$

$$V_{ij}^A = \sum_{l \in A} \left(i \left| \frac{Z_l}{R_{li}} \right| j \right) = \sum_{l \in A} \int \phi_i^*(r_1) \frac{Z_l}{R_{li}} \phi_j(r_1) dr_1 \quad (4)$$

$$G_{ij}^A = 2J_{ij}^A - K_{ij}^A \quad (5)$$

All orbital indices refer to molecular orbitals (MOs). MO ϕ_i is always on molecule *A* (the ab initio molecule in the case of EFP2/ab initio exchange repulsion) while MO ϕ_j is always on molecule *B* (always an EFP2). Electrons 1 and 2 are represented by r_1 and r_2 , respectively. Z_l is the atomic number of the l th atom and R_{li} is the distance between electron 1 and the l th atom. S_{ij} is an intermolecular overlap integral, and V_{ij} contains the electron-nuclear attraction terms. J_{ij}^A is commonly referred to as a Coulomb integral and represents the electrostatic repulsion between electron 1 and electron 2. K_{ij}^A is a quantum mechanical exchange integral. A sum is located on both integrals in Eq. 5. J_{ij}^A and K_{ij}^A can be defined as follows, where the orbital k always resides on molecule *A*

$$\begin{aligned}
 J_{ij}^A = & \sum_{k \in A} (ij|kk) = \sum_{k \in A} \iint \phi_i^*(r_1) \phi_j(r_1) \frac{1}{r_{12}} \phi_k^*(r_2) \phi_k(r_2) \\
 & \times dr_1 dr_2 \quad (6)
 \end{aligned}$$

$$\begin{aligned}
 K_{ij}^A = & \sum_{k \in A} (ik|jk) = \sum_{k \in A} \iint \phi_i^*(r_1) \phi_k(r_1) \frac{1}{r_{12}} \phi_j^*(r_2) \phi_k(r_2) \\
 & \times dr_1 dr_2 \quad (7)
 \end{aligned}$$

Approximations can be made to Eq. 1 to reduce the computational time required to calculate the energy. For example, the spherical Gaussian orbital (SGO) approximation [17] can be applied to the exchange integral to cast it in terms of the intermolecular overlap integral, S_{ij} . Therefore, Eq. 2 can be approximated as

$$(ij|ij) \approx 2 \sqrt{\frac{-2 \ln S_{ij} S_{ij}^2}{\pi R_{ij}}} \quad (8)$$

Consider the terms in Eq. 1 that depend upon the intermolecular overlap integral (to the first power), S_{ij} . These electron-nuclear attraction integrals and two-electron integrals, $V_{ij}^A + G_{ij}^A$ and $V_{ij}^B + G_{ij}^B$, can be rewritten to avoid the computationally costly two-electron integrals by replacing them with the Fock matrix elements of the monomers and the kinetic energy integrals T_{ij} :

$$\begin{aligned}
 V_{ij}^A + G_{ij}^A = & F_{ij}^A - T_{ij} = \sum_{k \in A} F_{ik}^A S_{kj} - T_{ij} \\
 V_{ij}^B + G_{ij}^B = & F_{ij}^B - T_{ij} = \sum_{l \in B} F_{jl}^B S_{il} - T_{ij} \quad (9)
 \end{aligned}$$

The Fock matrix elements of the monomers are obtained by performing a HF calculation. Once the Fock matrix is obtained in the atomic orbital (AO) basis, it is transformed to the MO basis using the MO eigenvectors obtained during the HF procedure. This matrix is stored on disk after the transformation and is readily available.

By neglecting many of the smaller and off-diagonal integrals that depend upon the intermolecular overlap to the second power, some simplifications can be made. Specifically, a nuclear-electron attraction integral and a two-electron integral can be approximated as shown in Eqs. 10 and 11.

$$S_{ij}S_{kj}V_{ik}^B \approx S_{ij}^2V_{ii}^B\delta_{ik} \quad (10)$$

$$S_{ij}S_{kl}(ik|lj) \approx S_{ij}^2(ii|jj)\delta_{ik}\delta_{lj} \quad (11)$$

Any integrals that remain are approximated by using classical point-charge models

$$S_{ij}^2V_{ij}^B \Rightarrow S_{ij}^2\left(\sum_{j \in B} -Z_j R_{ij}^{-1}\right) \quad (12)$$

$$S_{ij}^2(ii|jj) \Rightarrow S_{ij}^2 R_{ij}^{-1} \quad (13)$$

The exchange repulsion energy in Eq. 1 can consequently be approximated as [6]

$$\begin{aligned} E^{XR} \approx & -2 \sum_{i \in A} \sum_{j \in B} 2 \sqrt{\frac{-2 \ln S_{ij}}{\pi}} \frac{S_{ij}^2}{R_{ij}} \\ & - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[\sum_{k \in A} F_{ik}^A S_{kj} + \sum_{l \in B} F_{jl}^B S_{li} - 2T_{ij} \right] \\ & + 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^2 \left[- \sum_{J \in B} Z_J R_{ij}^{-1} + 2 \sum_{l \in B} R_{il}^{-1} \right. \\ & \left. - \sum_{l \in A} Z_l R_{ij}^{-1} + 2 \sum_{k \in A} R_{kj}^{-1} - R_{ij}^{-1} \right] \quad (14) \end{aligned}$$

Equation 14 has been implemented in GAMESS and is used to calculate the exchange repulsion energy between EFP2 potentials. Equation 14 has also been implemented previously to permit the calculation of the exchange repulsion energy between an EFP2 and an ab initio QM molecule; however, this equation has not previously been extensively tested for EFP2-QM applications. When a QM molecule is present, its orbitals are localized at the end of the self-consistent field (SCF) process and the exchange repulsion energy given by Eq. 14 is calculated. However, an important assumption that is used to derive Eqs. 1 and 14 is not rigorously correct when a QM molecule is present. In general, in HF theory,

$$F^A \phi_i = \sum_{k \in A} F_{ik}^A \phi_k \quad (15)$$

In Eq. 15, F^A is the Fock operator on molecule A and the $\{\phi_i\}$ are the MOs. Equation 15 is used to derive Eqs. 1 and 14, but this equation is not strictly valid when an EFP2 is present, because the EFP2 is not accounted for in the Fock operator [15]. Therefore, Eq. 14 should not be used without modification. An energy expression has been derived for E^{XR} that takes into account that both EFP2 potentials and ab initio molecules are present in the system. This expression [8] is given without approximation in Eq. 16.

$$\begin{aligned} E^{XR} = & -2 \sum_{i \in A} \sum_{j \in B} (ij|ij) - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \\ & \times \left[2 \left(V_{ij}^A + G_{ij}^A \right) + \sum_{l \in B} F_{jl}^B S_{li} \right] + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \\ & \times \left[\sum_{k \in A} S_{kj} \left(F_{ik}^A + V_{ik}^B + J_{ik}^B \right) + S_{ij} \left(V_{jj}^A + J_{jj}^A \right) \right. \\ & \left. - \sum_{k \in A} S_{kj} (ik|jj) \right] \quad (16) \end{aligned}$$

To calculate the exchange repulsion energy (Eq. 16) efficiently during the HF SCF iterations, approximations must be applied. Because the orbitals on the ab initio molecule are canonical (not-localized) MOs obtained during the SCF iterations, some of the approximations applied to Eq. 1 cannot be used to approximate Eq. 16. The SGO approximation [17] can still be applied to the exchange integral in the leading term of Eq. 16, but the way in which it is applied must be modified. The success of the SGO approximation depends upon the availability of localized orbitals, so the integrals over MOs on molecule A are transformed to the AO basis,

$$(ij|ij) = \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu j} (\mu j | \nu j) \quad (17)$$

where μ and ν are basis functions on the ab initio molecule. The AOs are better suited for the SGO approximation because they are localized on the atomic centers.

The SGO approximation defines two localized molecular orbitals (LMOs) as two spherical (s-type) Gaussian functions [17]

$$\phi_i = \left(\frac{2\alpha}{\pi} \right)^{\frac{3}{4}} e^{-\alpha|r-R_i|^2} \quad \text{and} \quad \phi_j = \left(\frac{2\alpha}{\pi} \right)^{\frac{3}{4}} e^{-\alpha|r-R_j|^2} \quad (18)$$

One can then obtain the corresponding exchange integral as [18]

$$\langle \phi_i \phi_j | \phi_i \phi_j \rangle \approx 2 \left(\frac{\alpha}{\pi} \right)^{\frac{3}{2}} e^{-\alpha R_{ij}^2} \quad (19)$$

In the SGO approximation [17], α is obtained by equating the Spherical Gaussian overlap with the actual overlap of the appropriate LMOs

$$e^{-\frac{1}{2}\alpha R_{ij}^2} = S_{ij} \quad (20)$$

Taking the log of both sides leads to Eq. 21

$$\alpha_{ij} = -\frac{2}{R_{ij}^2} \ln S_{ij} \quad (21)$$

Two-electron integrals over s-type primitives A, B, C, D are obtained as follows [18]:

$$\begin{aligned}
 (AB|CD) &= 2\pi^{5/2} / \left[(\alpha + \beta)(\gamma + \delta)(\alpha + \beta + \gamma + \delta)^{1/2} \right] \\
 &\quad \times \exp \left[-\alpha\beta / (\alpha + \beta) |R_A - R_B|^2 - \gamma\delta / (\gamma + \delta) \right. \\
 &\quad \quad \left. \times |R_C - R_D|^2 \right] \\
 &\quad \times F_0 \left[(\alpha + \beta)(\gamma + \delta) / (\alpha + \beta + \gamma + \delta) \right. \\
 &\quad \quad \left. \times |R_p - R_Q|^2 \right] \quad (22)
 \end{aligned}$$

In Eq. 22 γ is the exponent for function C, δ is the exponent for function D, R_p is the center of the product Gaussian resulting from function A and B, R_Q is the center of the product Gaussian resulting from function C and D.

Substituting $\alpha_{\mu j}$ for α and β , $\alpha_{\nu j}$ for γ and δ , and defining R_p and R_Q , one obtains

$$\begin{aligned}
 \langle \mu j | \nu j \rangle &= 2\pi^{5/2} / \left[(2\alpha_{\mu j})(2\alpha_{\nu j})(2\alpha_{\mu j} + 2\alpha_{\nu j})^{1/2} \right] \\
 &\quad \times \exp \left[-\alpha_{\mu j}^2 / (2\alpha_{\mu j}) |R_{\mu j}|^2 - \alpha_{\nu j}^2 / (2\alpha_{\nu j}) |R_{\nu j}|^2 \right] \\
 &\quad \times F_0 \left[\left(2\alpha_{\mu j} \right) (2\alpha_{\nu j}) / (2\alpha_{\mu j} + 2\alpha_{\nu j}) \right. \\
 &\quad \quad \left. \times \left| \left(\frac{R_\mu - R_j}{2} \right) - \left(\frac{R_\nu - R_j}{2} \right) \right|^2 \right] \quad (23)
 \end{aligned}$$

Equation 23 can be simplified to

$$\langle \mu j | \nu j \rangle = \frac{2}{\sqrt{\pi}} \sqrt{\frac{2\alpha_{\mu j}\alpha_{\nu j}}{\alpha_{\mu j} + \alpha_{\nu j}}} S_{\mu j} S_{\nu j} F_0 \left[\frac{1}{4} \left(\frac{2\alpha_{\mu j}\alpha_{\nu j}}{\alpha_{\mu j} + \alpha_{\nu j}} R_{\mu\nu}^2 \right) \right] \quad (24)$$

F_0 is the incomplete gamma function $F_0[t] = \frac{1}{2} \left(\frac{\pi}{t} \right)^{1/2} \text{erf} \left(t^{1/2} \right)$. Equation 24 provides a value for the integral $\langle \mu j | \nu j \rangle$. Transforming the integral in Eq. 24 to the MO basis gives Eq. 17 [15].

The one-electron nuclear attraction term, V_{ij}^A , is efficiently calculated without approximation. Approximations based on the SGO approximation have been proposed for the two-electron integrals [8] J_{ij}^A and K_{ij}^A . Just as for the exchange integral defined in Eq. 17, this approximation must make use of the AOs on the ab initio molecule. J_{ij}^A can be expressed as

$$J_{ij}^A = (ij|kk) = \sum_{\mu} \sum_{\lambda} \sum_{\sigma} C_{\mu i} C_{\lambda k} C_{\sigma k} (\mu j | \lambda \sigma) \quad (25)$$

Applying the multipole approximation to Eq. 25 gives

$$(\mu j | \lambda \sigma) \approx S_{\lambda\sigma} \left(\mu | R_{I_{Q,\lambda\sigma}}^{-1} | j \right) \quad (26)$$

Next, the SGO approximation is applied to Eq. 26. For s-type primitives, the approximate electron-nuclear attraction integral in Eq. 26 can be written as [18]

$$\begin{aligned}
 (A | (-Z_I / r_{I1}) | B) &= \frac{-2\pi}{(\alpha + \beta)} Z_I \exp \left[-\alpha\beta / (\alpha + \beta) |R_A - R_B|^2 \right] \\
 &\quad \times F_0 \left[(\alpha + \beta) |R_p - R_I|^2 \right] \quad (27)
 \end{aligned}$$

where Z_I is the atomic number of atom I, α the orbital exponent of orbital A, β the orbital exponent on orbital B, R_A the center of A, R_B the center of B, R_p the center of the product Gaussian formed from A and B, and R_I is the position of atom I.

Since $\alpha = \beta$, Eq. 27 becomes

$$\begin{aligned}
 (A | (-Z_I / r_{I1}) | B) &= \frac{-2\pi}{(2\alpha_{\mu j})} Z_I \\
 &\quad \times \exp \left[-\alpha_{\mu j}^2 / (2\alpha_{\mu j}) |R_A - R_B|^2 \right] F_0 \left[(2\alpha_{\mu j}) |R_p - R_I|^2 \right] \quad (28)
 \end{aligned}$$

Using the $\alpha_{\mu j}$ defined by the SGO approximation in Eq. 21,

$$\begin{aligned}
 (A | (-Z_I / r_{I1}) | B) &= \frac{-2\pi}{(2\alpha_{\mu j})} Z_I \\
 &\quad \times \exp \left[-2 / \left(-2 \times |R_A - R_B|^2 \right) |R_A - R_B|^2 \ln |S_{\mu j}| \right] \\
 &\quad \times F_0 \left[(2\alpha_{\mu j}) |R_p - R_I|^2 \right] \quad (29)
 \end{aligned}$$

Multiplying Eq. 29 by SGO prefactors and simplifying

$$(A | (-Z_I / r_{I1}) | B) = - \left(\frac{8\alpha_{\mu j}}{\pi} \right)^{1/2} Z_I S_{\mu j} F_0 \left[(2\alpha_{\mu j}) |R_p - R_I|^2 \right] \quad (30)$$

Therefore,

$$\begin{aligned}
 J_{ij}^A = (ij|kk) &= \sum_{\mu} \sum_{\lambda} \sum_{\sigma} C_{\mu i} C_{\lambda k} C_{\sigma k} (\mu j | \lambda \sigma) \\
 &\approx - \sum_{\mu} \sum_{\lambda} \sum_{\sigma} C_{\mu i} C_{\lambda k} C_{\sigma k} \left(\frac{8\alpha_{\mu j}}{\pi} \right)^{1/2} S_{\mu j} S_{\lambda j} F_0 \left[2\alpha_{\mu j} R_{P_{\mu j} Q_{\lambda\sigma}}^2 \right] \quad (31)
 \end{aligned}$$

Equation 31 is the proposed approximation to Eq. 25.

Approximations based on multipole expansions can be used to simplify all of the terms that depend upon the overlap squared [15]

$$F_{ik}^A + V_{ik}^B + J_{ik}^B \approx F_{ik}^A + V_{ik}^{\text{ES},B} \approx F_{ik}^A + V_{ik}^{\text{EFP},B} \quad (32)$$

$$(ik|jj) \approx \left(i | |r_1 - R_J|^{-1} | k \right) = V_{ik}^J \quad (33)$$

Because the one-electron nuclear attraction integral involves only one MO on B with the nuclei on molecule A, it can be replaced [15] with a classical point-charge approximation:

$$V_{ij}^A \approx \sum_{j \in B} \sum_{I \in A} \frac{-Z_I}{R_{jI}} \quad (34)$$

The remaining unapproximated terms in Eq. 16, the Fock matrix elements and the overlap integrals are calculated exactly. Finally, taking into account all of the foregoing approximations, the exchange repulsion energy becomes [15]

$$E^{\text{XR}} \approx -2 \sum_{i \in A} \sum_{j \in B} (ij|ij)^{\text{SGO}} - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[2 \left(V_{ij}^A + G_{ij}^{\text{A,SGO}} + \sum_{l \in B} F_{jl}^B S_{li} \right) \right] + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[\sum_{k \in A} S_{kj} (F_{ik}^A + V_{ik}^{\text{EFP},B}) \right] + S_{ij} \left(\sum_{l \in A} -Z_l R_{lj}^{-1} + \sum_{k \in A} V_{kk}^j \right) - \sum_{k \in A} S_{kj} V_{ik}^j \quad (35)$$

Before the desired EFP2-ab initio gradient can be calculated, an exchange repulsion Fock operator must be added to the one-electron part of the Fock matrix. The contribution of the EFP2 exchange repulsion to the Fock operator was derived by setting the variational derivative of the exchange repulsion energy to zero [15]. By adding this Fock operator to the Fock matrix of the ab initio molecule, exchange repulsion effects are incorporated into the HF calculation as the ab initio orbitals are being optimized during the SCF iterations. The exchange repulsion Fock operator is defined [8] as

$$V_{mi}^{\text{XR}} = - \sum_{j \in B} (mj|ij) - \frac{1}{2} \sum_{j \in B} S_{mj} \left[2 \left(V_{ij}^A + G_{ij}^A \right) + \sum_{l \in B} F_{jl}^B S_{li} \right] - \frac{1}{2} \sum_{j \in B} S_{ij} \left[2 \left(V_{mj}^A + G_{mj}^A \right) + \sum_{l \in B} F_{jl}^B S_{lm} \right] - \sum_{k \in A} \sum_{j \in B} S_{kj} [4(kj|mi) - (km|ji) - (ki|jm)] + \sum_{j \in B} S_{mj} \left[\sum_{k \in A} S_{kj} (F_{ik}^A + V_{ik}^B + J_{ik}^B) - (ik|jj) + S_{ij} (V_{ij}^A + J_{ij}^A) \right] + \sum_{j \in B} S_{ij} \left[\sum_{k \in A} S_{kj} (F_{mk}^A + V_{mk}^B + J_{mk}^B) - (mk|jj) \right] + \frac{1}{2} \sum_{n \in A} \sum_{k \in A} \sum_{j \in B} S_{kj} S_{nj} [4(nk|im) - (nm|ik) - (ni|mk)] + 2 \sum_{k \in A} \sum_{j \in B} S_{kj}^2 (jj|mi) \quad (36)$$

The expression for V_{mi}^{XR} in Eq. 36 includes no approximation. V_{mi}^{XR} is designed to be calculated for every pair of MOs m and i (both on the ab initio molecule) and added to the one-electron Fock matrix on every SCF iteration. When the approximations detailed in Eqs. 17–34 are applied to Eq. 36, one can obtain an approximate expression for V_{mi}^{XR}

$$V_{mi}^{\text{XR}} \approx - \sum_{j \in B} (mj|ij)^{\text{SGO}} - \frac{1}{2} \sum_{j \in B} S_{mj} \left[2 \left(V_{ij}^A + G_{ij}^{\text{A,SGO}} \right) + \sum_{l \in B} F_{jl}^B S_{li} \right] - \frac{1}{2} \sum_{j \in B} S_{ij} \left[2 \left(V_{mj}^A + G_{mj}^{\text{A,SGO}} \right) + \sum_{l \in B} F_{jl}^B S_{lm} \right] - \sum_{k \in A} \sum_{j \in B} S_{kj} \left[4 \left(kj|mi \right) - \left(km|ji \right) - \left(ki|jm \right) \right] + \sum_{j \in B} S_{mj} \left[\sum_{k \in A} S_{kj} \left(F_{ik}^A + V_{ik}^{\text{EFP},B} \right) - V_{ik}^j + S_{ij} \left(\sum_{l \in A} Z_l R_{lj}^{-1} + V_{kk}^j \right) \right] + \sum_{j \in B} S_{ij} \left[\sum_{k \in A} S_{kj} \left(F_{mk}^A + V_{mk}^{\text{EFP},B} \right) - V_{mk}^j \right] + \frac{1}{2} \sum_{n \in A} \sum_{k \in A} \sum_{j \in B} S_{kj} S_{nj} \left[4 \left(nk|im \right) - \left(nm|ik \right) - \left(ni|mk \right) \right] + 2 \sum_{k \in A} \sum_{j \in B} S_{kj}^2 V_{mi}^j. \quad (37)$$

3 Results and implementation

If Eqs. 35 and 37 are implemented as presented here, unpredictable and significant errors are introduced. By comparing each term against the full energy expression (cf., Eq. 16) and the Fock matrix operator (Eq. 36), it is clear that the approximated two-electron integrals in Eqs. 25–31 are the source of this error. Consider the contribution of the two-electron Coulomb integrals in Eq. 25. The contribution of these integrals to the energy, including the multiplication by the overlap integrals, can be written as

$$-2 \sum_i^A \sum_j^B S_{ij} (4(ij|kk)) \quad (38)$$

The sum of these contributions for each MO i , j , and k is presented for the water, methanol, and acetone dimers in Table 1. This table also provides a comparison of the exact two-electron integrals with the approximated integrals obtained by using the approximations that lead to Eqs. 25–31. Although the approximate integrals approach the exact values for some of the dimers shown in the table, other errors are large. The errors do not appear to be predictable.

Table 1 Comparison of exact and approximate Coulomb integral contributions to the energy

	Exact (h)	Approximate (h)	Error (kcal/mol)
Water	-0.091867	-0.052722	-24.56
Methanol	-0.121785	-0.123414	1.02
Acetone	-0.082931	-0.078245	-2.94

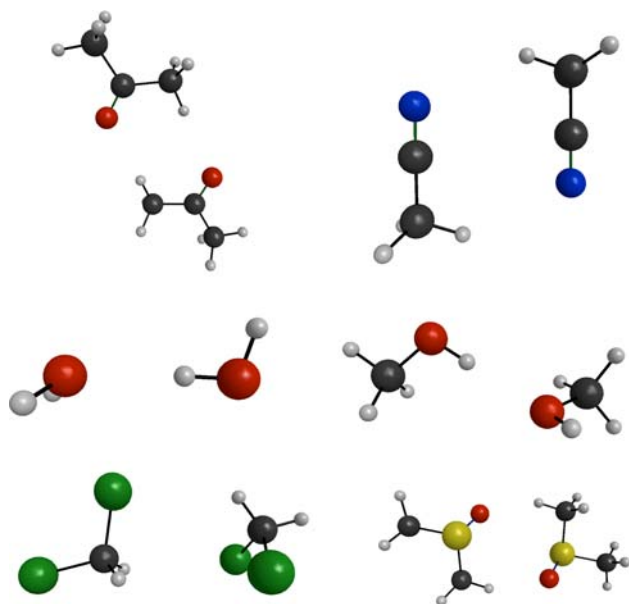


Fig. 1 The six dimers used to test the implementation of the EFP2/ab initio exchange repulsion. Starting with the structure in the top left corner and moving clockwise, the dimer structures are for acetone, acetonitrile, methanol, dimethylsulfoxide, dichloromethane, and water

The errors shown in Table 1 are mainly due to the multipole approximation (Eq. 26). The multipole approximation is inaccurate when the two electrons are not sufficiently far apart; for example, if they are both in basis functions on the ab initio molecule (μ, λ, σ).

One of the primary goals of the EFP2-QM method is to provide reliably accurate results. This cannot be accomplished with the errors that result from using Eq. 26. An alternative is to use the exact two-electron integrals instead of the approximate ones. That is, the two-electron integrals ($G_{ij}^A = 2J_{ij}^A - K_{ij}$) in Eq. 16 are calculated exactly while all other integral approximations used in Eq. 35 are retained. This modified Eq. 35 will be referred to below as Eq. 35'.

A test set of six dimers (shown in Fig. 1) was chosen to benchmark the energy and Fock matrix elements for the EFP2/ab initio exchange repulsion. The same test set was used to benchmark the EFP2 exchange repulsion energy and gradient for EFP2–EFP2 interactions [19]. Water, methanol, acetone, acetonitrile, dichloromethane, and dimethylsulfoxide (DMSO) dimers were optimized at the HF level of theory, with the resulting structures illustrated in Fig. 1. At the equilibrium dimer geometries, one monomer (B) was replaced by an EFP2, with the monomer internal geometry.

The series of six dimer exchange repulsion calculations based on Eq. 35' was benchmarked against the EFP2 method (both molecule A and B are EFP2s), the previously implemented EFP2/ab initio exchange repulsion energy using Eq. 14, and the Kitaura–Morokuma (KM) [8] energy decomposition. The 6–31+G(d,p) [20–22] basis set was used for the ab initio molecule in each dimer; the same

Table 2 Exchange repulsion energy values for water, methanol, dichloromethane, acetonitrile, acetone, and dimethylsulfoxide (DMSO) dimers. All units are in kcal/mol

	EFP2/EFP2	Eq. 14	Morokuma	Eq. 35'
Water	4.35	4.33	4.9	5.60
Methanol	4.34	7.84	5.15	5.94
Dichloromethane	0.27	2.22	0.79	0.87
Acetonitrile	2.05	9,145.39	2.21	2.28
Acetone	1.47	1.96	2.27	2.09
DMSO	6.31	Unconverged	6.38	7.53

basis set was used to generate each EFP2. The results are shown in Table 2. Equation 37 was added to the Fock matrix of the ab initio molecule at each iteration of the HF SCF process. For the DMSO dimer, SCF convergence was achieved by disabling the polarization interaction between the ab initio and EFP2 DMSO.

The KM energy decomposition provides the exact exchange repulsion for a given AO basis set. For all six dimers, Eq. 35' qualitatively reproduces the Morokuma exchange repulsion energy. Except for the DMSO dimer, Eq. 35' also quantitatively reproduces the Morokuma exchange repulsion energy. It is clear that Eq. 35' is more accurate than Eq. 14 when an ab initio molecule is present. However, the accuracy of Eqs. 35' and 37 come at the cost of computational expense. Table 3 provides the central processor unit (CPU) time required to complete a single-point energy calculation at the HF/EFP2 level of theory using Eq. 14, the full HF level of theory for a dimer and a HF/EFP2 calculation using Eqs. 35' and 37. All calculations were performed on a 1,200-MHz IBM Power4+. The cost associated with Eqs. 35' and 37 is more than a full HF dimer calculation.

To make the EFP2/ab initio exchange repulsion implementation more useful, especially for larger molecular systems, the efficiency must be improved. The first code modification was to calculate the exact two electron integrals in the AO basis and use the integrals in the AO basis to avoid the costly transformation to the MO basis.

Table 3 The total CPU time (in seconds) for the implementation of Eq. 14, a Hartree–Fock dimer calculation and the implementation of Eqs. 35' and 37

	Eq. 14	Hartree–Fock	Eqs. 35', 37
Water	0.4	1	1.8
Methanol	1.9	12.5	25.7
Dichloromethane	4.2	28.5	69.2
Acetonitrile	3.9	37.3	65.2
Acetone	4.0	136.1	273.5
DMSO	16.7	154.4	375.2

Table 4 The greatest deviation and the average deviation of the elements of the Fock matrix V_{mi} are provided (in Hartrees) for the water and methanol dimer. The number of elements within the Fock matrix which experienced a sign change is provided as well

Dimer	Greatest deviation	Average deviation	Qualitative changes
Water	6.20E–06	4.91E–06	2
Methanol	1.05E–03	1.72E–04	0

The exchange repulsion energy (Eq. 35') is only calculated once during a single-point energy calculation once the SCF process has converged. The Fock operator (Eq. 37) is calculated every SCF iteration. Additionally, more CPU time is spent determining the Fock matrix than the exchange repulsion energy. Fortunately, this cost can be reduced by examining the Fock matrix at various points in the iterative process. As illustrated in Table 4 for water and methanol, the repulsion contribution to the Fock matrix undergoes very small changes from iteration to iteration.

Because the Fock matrix does not change significantly over ten iterations, it is not useful to spend CPU time recalculating it every iteration. If the Fock matrix is calculated on the second iteration, and then re-calculated only when the iteration index is divisible by 4 (the 4th, 8th, 12th and so on), one obtains a significant speedup. On SCF iterations when the exchange repulsion Fock operator is not re-calculated, the most recently calculated Fock operator is used. Table 5 assesses the accuracy obtained using this approach. It is clear that there is essentially no accuracy lost by calculating the repulsion contribution to the Fock matrix only every fourth iteration. The corresponding CPU time comparison is presented in Table 6, where it is seen that considerable reduction in CPU time is achieved with virtually no loss of accuracy.

4 Other approximations

For the DMSO dimer the cost of forming the exact two-electron integrals needed to calculate $G_{ij}^A = 2J_{ij}^A - K_{ij}$

Table 5 The resulting exchange repulsion energies (in kcal/mol) when Eq. 37 is recalculated every SCF iteration is compared against the use of an approximate Eq. 37

	Eqs. 35', 37	Approx. V
Water	5.60	5.60
Methanol	5.94	5.94
Dichloromethane	0.87	0.87
Acetonitrile	2.28	2.28
Acetone	2.09	2.07
DMSO	7.53	7.54

Table 6 CPU time (in seconds) required to use Eq. 14 for a EFP2/QM calculation, a full Hartree–Fock dimer calculation and a EFP2/QM calculation which recalculates Eq. 37 on the second, fourth, and every other iteration number divisible by four

	Eq. 14	Hartree–Fock	Approx. V
Water	0.4	1	0.7
Methanol	1.9	12.5	5.9
Dichloromethane	4.2	28.5	14.6
Acetonitrile	3.9	37.3	11.7
Acetone	4	136.1	50.3
DMSO	16.7	154.4	63.2

without approximation is 23.6 s, roughly one-third of the time spent in the entire calculation (see last column in Table 6). If the number of two-electron integrals to calculate could be reduced, it would help reduce the largest bottleneck of the calculation.

The Schwarz inequality [23] can be a useful tool for avoiding the calculation of many integrals that are negligibly small (or zero). For example, if $(ijkl)$ is less than $\sqrt{(ij|ij) \times (kl|kl)}$, then a block of integrals can be skipped. The Schwarz inequality is commonly used in electronic structure programs to avoid calculating integrals that are too small to make significant contributions to the energy. The EFP2/ab initio algorithm for the exact two-electron integrals $G_{ij}^A = 2J_{ij}^A - K_{ij}$ calculates integrals of the form $(\xi\mu|\lambda\sigma)$ (where ξ is the only index on molecule B). In order to calculate the Schwarz inequality, one also needs the integrals $(\xi\mu|\xi\mu)$ and $(\lambda\sigma|\lambda\sigma)$. The $(\lambda\sigma|\lambda\sigma)$ integrals reside entirely on the QM molecule and are obtained during the HF calculation. The $(\xi\mu|\xi\mu)$ integrals are an entirely new (not presently calculated) class of integrals with two of the four indexes residing on the EFP2. Instead of calculating these integrals explicitly, the SGO approximation is used to obtain these integrals. The algorithm implemented to obtain Eq. 24 was modified to calculate $(\xi\mu|\xi\mu)$ efficiently.

The Schwarz inequality has been implemented and the results are given in Table 7. The second column in Table 7 provides the same CPU time as was provided in the last column of Table 6. These computations were repeated after

Table 7 CPU time (in seconds) required to complete the EFP2/QM energy calculation with and without use of the Schwarz inequality

	w/Schwarz	w/o Schwarz
Water	0.7	0.7
Methanol	5.8	5.9
Dichloromethane	14.2	14.6
Acetonitrile	11.3	11.7
Acetone	46.0	50.3
DMSO	57.1	63.2

Table 8 Number of two-electron integrals required for dimer calculations

	Eqs. 35', 37	Hartree–Fock
Water	8.2E+06	2.3E+07
Methanol	1.1E+08	3.3E+08
Acetone	8.7E+08	2.9E+09
Acetonitrile	2.5E+08	7.6E+08
Dichloromethane	5.5E+08	1.7E+09
DMSO	1.4E+09	4.3E+09

the Schwarz inequality was implemented as the CPU time required for these calculations is given in the first column of Table 7. The systems with more basis functions (DMSO and acetone) benefit more from the Schwarz inequality than smaller systems. The larger the system, the greater the number of zero and nearly zero two electron integrals. By using the Schwarz inequality, the 23.6 s required to calculate the two-electron integrals for DMSO has been reduced to 17.5 s.

Table 8 provides the number of non-zero two-electron integrals required at the EFP2/QM and HF levels of theory using the G3Large basis set [24]. The number of EFP2/QM non-zero two-electron integrals includes all non-zero two-electron integrals on the QM molecule as well as the necessary EFP2/QM two-electron integrals. As the number of basis functions grows, the number of integrals that the EFP2/QM method avoids calculating grows when compared against the number of integrals required for a HF calculation. Therefore, the EFP2/QM method will be significantly more efficient than HF calculations while providing consistent, accurate results.

Semi-empirical methods have a long and successful history of ignoring many two-electron integrals while retaining qualitative accuracy. So, preliminary tests have been conducted to assess the possibility of employing semi-empirical approximations to avoid the calculation of many two-electron integrals. Traditionally, the complete neglect of differential overlap (CNDO) [25] simplifies the two-electron integral $(\xi\mu\lambda\sigma)$ to $(\xi\xi|\lambda\lambda)\delta_{\xi\mu}\delta_{\lambda\sigma}$. For the EFP2/ab initio integrals of interest here, the first index ξ resides on the EFP2 and must be considered as an entirely different basis set from μ . So, the zero differential overlap approximation can only be applied to the right-hand (ket) side of the $(\xi\mu\lambda\sigma)$ integral. This leads to $(\xi\mu\lambda\lambda)\delta_{\lambda\sigma}$ as a CNDO-like approximation for these two-electron integrals.

Neglect of diatomic differential overlap (NDDO) [25] is a less drastic approximation than CNDO. If basis functions λ and σ are on the same atom center (but not necessarily the same basis function), then the integral

Table 9 Exchange repulsion energies (in kcal/mol) for the three-center, NDDO, and CNDO methods compared to the predicted exchange repulsion energy from a Morokuma energy decomposition

	Three-center	NDDO	CNDO	Morokuma
Water	6.1	11.7	25.4	4.9
Methanol	6.2	18.8	39.6	5.15
Dichloromethane	0.85	2.4	6.1	0.79
Acetonitrile	5.3	14.1	25.3	2.21
Acetone	4.2	12.9	27.9	2.27
DMSO	11.4	33.0	80.5	6.38

$(\xi\mu\lambda\sigma)$ is not ignored. As noted earlier for CNDO, the NDDO approximation can only be applied to the ket side of the integral.

A third approximation, similar to NDDO, has also been considered, that excludes all four-center two-electron integrals. Unlike CNDO this third approach does not neglect any three-center integrals. Therefore, if ξ , μ , λ , and σ all reside on different atom centers, the $(\xi\mu\lambda\sigma)$ integral is not calculated. However, if a common atom center is shared between any two of the three ab initio basis functions (μ , λ and σ) then the integral is calculated. This approximation is referred to as the three-center method.

The results obtained using the CNDO-like, NDDO-like, and three-center methods are summarized in Table 9. The CNDO-like method is based on the most radical approximation of three methods, so it is no surprise that it suffers from the largest errors. The NDDO-like approximations are less radical, and the results are improved relative to those of CNDO, but the errors are still unacceptably large. Of the three methods, the three-center method provides the most accurate predicted exchange repulsion energies. In fact, for water, methanol, and dichloromethane dimers, the predicted energies are within 1.5 kcal/mol of the correct values. However, the errors grow to unacceptable levels for acetonitrile, acetone, and DMSO dimers.

Despite the fact that the three-center method does modestly well for three of the six dimers, it does not reduce the computational time requirement significantly. Of the 108 s required for the DMSO dimer calculation in the first column of Table 1, approximately 23.6 s are spent calculating the two-electron integrals. When the three-center method is used, the total time of the run is reduced to 104 s. Even though this saves roughly 17% of the time required to calculate the two-electron integrals, the accuracy suffers too much for it to be a useful approximation.

One consideration to keep in mind is that semi-empirical methods include approximations for the one-electron integrals as well as the two-electron integrals, and in methods

like CNDO and NDDO, these approximations are related to each other. To be consistent, one should introduce both the one-electron and two-electron approximations. None of the one-electron integral approximations were included in this present study. It is possible that the errors experienced in the two-electron integrals could be canceled or offset by errors associated with approximations associated with the one-electron integrals. In order to fairly assess the use of semi-empirical methods, the approximations to the one-electron integrals should be included as well. This will be the subject of a future study.

The Mulliken approximation [26, 27] approximates the $(\xi\mu|\lambda\sigma)$ two-electron integrals by replacing them with $\frac{1}{2}(\xi\mu|\lambda\lambda)S_{\sigma\lambda} + \frac{1}{2}(\xi\mu|\sigma\sigma)S_{\sigma\lambda}$. The Mulliken approximation has been tested for the water dimer, and it provides

inconsistent results. Though many integrals are approximated very closely, some individual integrals can experience unacceptable errors (as much as 1 kcal/mol for just one individual integral).

5 Gradient considerations

The gradient (first derivative of the energy with respect to the nuclear coordinates) of the exchange repulsion energy was derived previously [16]. This is accomplished in two steps, giving rise to two equations. The first equation provides the derivative of the exchange repulsion energy with respect to the ab initio coordinates (x_a)

$$\begin{aligned}
 \frac{\partial E^{\text{XR}}}{\partial x_a} = & -2 \sum_{i \in A} \sum_{j \in B} (ij|ij)^a - 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^a \left[2(V_{ij}^A + G_{ij}^A) + \sum_{l \in B} F_{jl}^B S_{li} \right] \\
 & - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[2(V_{ij}^{A^a} + G_{ij}^{A^a}) + \sum_{l \in B} F_{jl}^B S_{li}^a \right] \\
 & + 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^a \left[\sum_{k \in A} S_{kj} (F_{ik}^A + V_{ik}^B + 2J_{ik}^B) + S_{ij} (V_{jj}^A + 2J_{jj}^A) - \sum_{k \in A} S_{kj} (ik|jj) \right] \\
 & + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[\sum_{k \in A} \left(S_{kj}^a (F_{ik}^A + V_{ik}^B + 2J_{ik}^B) + S_{kj} (F_{ik}^{A^a} + V_{ik}^{B^a} + 2J_{ik}^{B^a}) \right) + S_{ij}^a (V_{jj}^A + 2J_{jj}^A) \right. \\
 & \left. + S_{ij} (V_{jj}^{A^a} + 2J_{jj}^{A^a}) - \sum_{k \in A} [S_{kj}^a (ik|jj) + S_{kj} (ik|jj)^a] \right] \\
 & + \sum_{m \in A} \sum_{i \in A} \sum_{j \in B} S_{mi}^a \left[\begin{aligned} & 2(mj|ij) + S_{mj} \left(2(V_{ij}^A + G_{ij}^A) + \sum_{l \in B} F_{jl}^B S_{li} \right) \\ & + S_{ij} \left(2(V_{mj}^A + G_{mj}^A) + \sum_{l \in B} F_{jl}^B S_{lm} \right) \\ & - S_{mj} \left(\sum_{k \in A} S_{kj} (F_{ik}^A + V_{ik}^B + 2J_{ik}^B) + S_{ij} (V_{jj}^A + 2J_{jj}^A) - \sum_{k \in A} S_{kj} (ik|jj) \right) \\ & - S_{ij} \left(\sum_{k \in A} S_{kj} (F_{mk}^A + V_{mk}^B + 2J_{mk}^B) + S_{mj} (V_{jj}^A + 2J_{jj}^A) - \sum_{k \in A} S_{kj} (mk|jj) \right) \end{aligned} \right] \\
 & + \sum_{m \in A} \sum_{i \in A} \sum_{n \in A} \sum_{j \in B} S_{mn}^a S_{ij} \left[\begin{aligned} & 2[4(ij|mn) - (im|jn) - (in|jn)] \\ & - \sum_{k \in A} S_{kj} [4(ik|mn) - (im|kn) - (in|km)] \end{aligned} \right] \\
 & - \sum_{m \in A} \sum_{i \in A} \sum_{k \in A} \sum_{j \in B} S_{mk}^a S_{ij} \left[\begin{aligned} & S_{mj} (F_{ik}^A + V_{ik}^B + 2J_{ik}^B) + S_{kj} (F_{im}^A + V_{im}^B + 2J_{im}^B) + 4S_{ij} (jj|mk) \\ & - S_{mj} (ik|jj) - S_{kj} (im|jj) \end{aligned} \right] \tag{39}
 \end{aligned}$$

The second gradient expression is the first derivative of the energy with respect to the coordinates of the EFP (x_b):

$$\begin{aligned} \frac{\partial E^{\text{XR}}}{\partial x_b} = & -4 \sum_{i \in A} \sum_{j \in B} (ij^b | ij) - 2 \sum_{i \in A} \sum_{j \in B} S_{ij}^b \left[2(V_{ij}^A + G_{ij}^A) + \sum_{l \in B} F_{jl}^B S_{li} \right] \\ & - 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[2((i|V^A|j^b) + G_{ij}^{A^b}) + \sum_{l \in B} (F_{jl}^{B^b} S_{li} + F_{jl}^B S_{li}^b) \right] \\ & + 2 \sum_{i \in A} \sum_{j \in B} S_{ij} \left[\sum_{k \in A} S_{kj}^b (F_{ik}^A + V_{ik}^A + 2J_{ik}^A) + S_{kj} \left(\left(i \left| \sum_{J \in B} \frac{Z_J (x_1 - x_J)}{r_{1J}^3} \right| k \right) \right. \right. \\ & \left. \left. + 2 \sum_{l \in B} (ik|l^b l) \right) \right. \\ & \left. + S_{ij}^b (V_{jj}^A + 2J_{jj}^A) + S_{ij} V_{jj}^{A^b} + 2S_{ij} J_{jj}^{A^b} - \sum_{k \in A} S_{kj}^b (ik|jj) - \sum_{k \in A} S_{kj} (ik|jj)^b \right] \end{aligned} \quad (40)$$

Because of the product rule and the chain rule, many of the terms in Eqs. 39 and 40 do not contain a derivative. These equations will be readily implemented in the future.

6 Conclusions

The ab initio/EFP2 exchange repulsion energy and the corresponding exchange repulsion Fock operator have been implemented in GAMESS. Both expressions have been tested on six dimers and provide promising results. The accuracy of both expressions is excellent when the correct two-electron integrals are used in those instances in which potential approximations fail. The code has been made more efficient by avoiding the re-calculation of the Fock operator during every SCF iteration and by computing the integrals directly in the AO basis. The current computational bottleneck lies in the calculation of the two-electron integrals, and it is likely that an implementation of the Schwarz inequality will reduce this bottleneck. As it is currently implemented, the method is faster than a HF dimer calculation, yet it provides results that approach perturbation theory in accuracy. With this in mind, the method obtains very good results with modest efficiency. In actual applications of the EFP2-QM method, one will typically have one QM molecule or reacting system, plus many EFP (solvent) molecules. The greater the ratio of EFP molecules to QM molecules, the greater will be the overall computational efficiency.

The implementation of the analytic gradient will be reported in a future work. While the energy expression is in

itself very useful, as noted above, the availability of the analytic gradient will facilitate the computation of many other properties and processes, such as geometries of clusters,

vibrational frequencies, and molecular dynamics simulations.

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