



# Evaluation of the charge penetration energy between non-orthogonal molecular orbitals using the Spherical Gaussian Overlap approximation

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Received 28 September 1999

## Abstract

An overlap dependent formula for evaluating the charge penetration energy between non-orthogonal molecular orbitals is derived using the Spherical Gaussian Overlap approximation. When combined with an accurate multipole representation of the electrostatic energy, such as in the effective fragment potential method, ab initio electrostatic energies are generally reproduced to within 0.2 kcal/mol for a variety of molecular dimers and basis sets. The only larger error is for the DMSO dimer, where the electrostatic energy is overestimated by 0.7 kcal/mol. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The multipole expansion is a powerful tool for the analysis and modeling of intermolecular interactions [1]. Converged expansions can now routinely be obtained even for relatively large molecules by using distributed expansions [1,2]. However, the multipole expansion is not valid inside a charge distribution. As a result, the interaction energy of two molecules with overlapping charge distributions calculated using multipoles will be in error even if the multipole expansions are converged. At the equilibrium separation of relatively strongly interacting molecules this error can be substantial. For example, at the equilibrium geometry of the formamide–formaldehyde dimer charge penetration contributes roughly 1.80 kcal/mol (0.2388 kcal/mol = 1 kJ/mol) to the

10.16 kcal/mol electrostatic interaction energy [3]. This error is generally referred to as the (electrostatic or Coulombic) charge penetration energy ( $E^{\text{pen}}$ ). Charge penetration can have similar effects on the multipole expansions of the induction and dispersion energies, and here the effect is generally referred to as ‘damping’. Several damping functions have been explored for the induction [4] and, especially, dispersion [1] energy, but the electrostatic charge penetration energy has received relatively little attention.

In general, it is known that  $E^{\text{pen}}$  decays exponentially with distance [5]. Furthermore, Murrell and Teixeira-Dias [6] have shown that  $E^{\text{pen}}$  and the exchange repulsion energy ( $E^{\text{XR}}$ ) behave similarly, and suggested the following relation

$$E^{\text{XR}} = -E^{\text{pen}}(a + bR),$$

where  $a$  and  $b$  are empirical parameters and  $R$  is the intermolecular separation.

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Stone [1] has suggested a  $E^{\text{pen}}$ -damping function based on a functional form derived for the hydrogen atom. A similar damping form is used in the effective fragment potential (EFP) method, a hybrid QM/MM method in which part of a system is treated ab initio and the rest with EFPs [7,8]. Currently, the  $E^{\text{pen}}$  correction is done for the ab initio/EFP interaction energy. Work on a similar correction for the EFP/EFP interaction is ongoing [9].

In this Letter we present a different, overlap dependent, approximation to  $E^{\text{pen}}$ , which contains no adjustable parameters. The Letter is organized as follows. First, we demonstrate the origin of  $E^{\text{pen}}$  for a simple system consisting of two spherical Gaussians. Second, we relate the resulting expression to molecular systems using the Spherical Gaussian Overlap approximation [10]. Finally, we demonstrate the utility of this new approach for molecular dimers of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ ,  $(\text{CH}_3)_2\text{CO}$ , and  $(\text{CH}_3)_2\text{SO}$ .

## 2. Theory

The electron–electron (e–e) repulsion energy between two identical spherical Gaussians,

$$\chi_i(\mathbf{r}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha|\mathbf{r} - \mathbf{R}_i|^2) \quad (1a)$$

and

$$\chi_j(\mathbf{r}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha|\mathbf{r} - \mathbf{R}_j|^2), \quad (1b)$$

is (assuming double occupancy) [11]

$$E_{e-e} = 4 \langle \chi_i \chi_i | \chi_j \chi_j \rangle = \frac{4}{R_{ij}} \text{erf}(\sqrt{\alpha} R_{ij}), \quad (2)$$

where  $R_{ij}$  is the distance between the Gaussian centers. For this simple case, a charge penetration contribution can easily be isolated by expanding [12] the error function and truncating after the second term,

$$\begin{aligned} E_{e-e} &= \frac{4}{R_{ij}} \left( 1 - \frac{1}{2\sqrt{\alpha} R_{ij}} \exp(-\alpha R_{ij}^2) \right) \\ &= \frac{4}{R_{ij}} - \frac{2}{\sqrt{\alpha} R_{ij}^2} S_{ij}^2 = E_{e-e}^{\text{class}} + E_{e-e}^{\text{pen}}, \end{aligned} \quad (3)$$

where  $S_{ij}$  is the Gaussian overlap integral,  $\exp(-\frac{1}{2}\alpha R_{ij}^2)$ .

A similar analysis can be performed for the charge penetration contribution to the electron–nuclear (e–n) attraction energy. In order to facilitate a direct comparison to Eq. (3), two +2 nuclear charges are placed at each of the Gaussian centers, so that

$$E_{e-n} = -4 \left\langle \psi_i \left| \frac{2}{R_{ij}} \right| \psi_j \right\rangle = -\frac{8}{R_{ij}} \text{erf}(\sqrt{2\alpha} R_{ij}). \quad (4)$$

Again, a charge penetration term is easily isolated,

$$E_{e-n} = -\frac{8}{R_{ij}} + \frac{4}{\sqrt{2\alpha} R_{ij}^2} S_{ij}^4 = E_{e-n}^{\text{class}} + E_{e-n}^{\text{pen}}. \quad (5)$$

As expected, the magnitude of the charge penetration energy is significantly larger for the e–e repulsion, leading to a net negative charge penetration energy. Furthermore, for relatively small values of  $S_{ij}$ ,

$$E^{\text{pen}} = E_{e-e}^{\text{pen}} = -\frac{2}{\sqrt{\alpha} R_{ij}^2} S_{ij}^2 \quad (6)$$

is a reasonable approximation.

Though derived for a very simple system, Eq. (6) can be used to estimate the charge penetration energy for pairs of non-orthogonal molecular orbitals (MOs) through the Spherical Gaussian Overlap (SGO) approximation [10]. In the SGO approximation each non-orthogonal MO-pair ( $\psi_i$  and  $\psi_j$ ) is approximated by a pair of identical spherical Gaussians centered at the respective MO centroids of charge,

$$\psi_i(\mathbf{r}) \approx \chi_i(\mathbf{r}) \quad \text{and} \quad \psi_j(\mathbf{r}) \approx \chi_j(\mathbf{r}). \quad (7)$$

The exponent  $\alpha$  is obtained by requiring that the Gaussian overlap is equal to the MO overlap  $S_{ij} = \langle \psi_i | \psi_j \rangle$ ,

$$S_{ij} = \exp(-\frac{1}{2}\alpha R_{ij}^2) \quad (8a)$$

and hence

$$\alpha = -\frac{2}{R_{ij}^2} \ln S_{ij}, \quad (8b)$$

so that

$$E_{ij}^{\text{pen}} = -2 \left( \frac{1}{-2 \ln S_{ij}} \right)^{1/2} \frac{S_{ij}^2}{R_{ij}}. \quad (9)$$

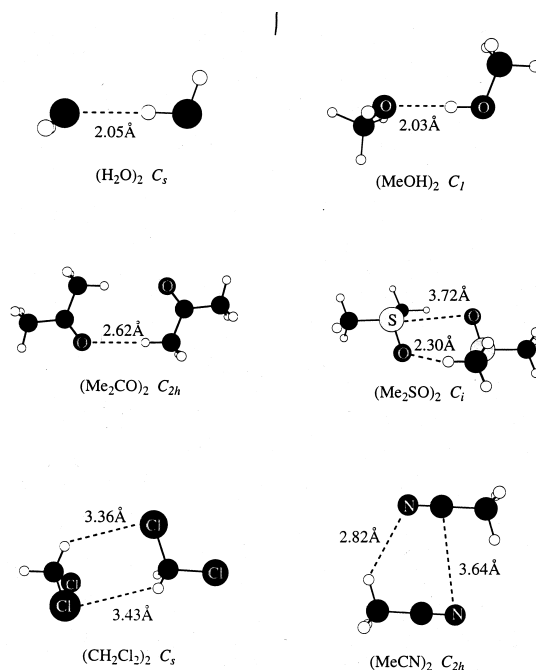


Fig. 1. Dimer geometries used in Tables 1–3. See text for explanations on how they were obtained.

This is done for each MO-pair to yield the total charge penetration energy,

$$E^{\text{pen}} = \sum_{i,j} E_{ij}^{\text{pen}}. \quad (10)$$

We note that the SGO charge penetration energy is very similar to the SGO exchange energy derived earlier [10],

$$2\langle \psi_i \psi_j | \psi_i \psi_j \rangle = 4 \left( \frac{-2 \ln S_{ij}}{\pi} \right)^{1/2} \frac{S_{ij}^2}{R_{ij}}. \quad (11)$$

Since the exchange energy scales similarly to the exchange repulsion energy this observation is consistent with the previous empirical observations that the charge penetration energy and exchange repulsion energy scale similarly with respect to intermolecular separation [6]. The utility of both Eqs. (9) and (11) depends on the extent to which the overlap region can be described by a spherical Gaussian [10]. Previous studies [10,13] of Eq. (11) indicate that reliable results can be obtained for several different molecular dimers as long as localized molecular orbitals are

used. Next we present a similar investigation for Eq. (9).

### 3. Methodology

To test how the addition of the charge penetration term (Eqs. (9) and (10)) improves the EFP electrostatic interaction energies, a set of ab initio and electrostatic calculations are performed on six different dimers (Fig. 1) using the GAMESS package [14]. Three different basis sets are used: 6-31 + G(d,p)<sup>1</sup>, 6-31 + + G(2d,2p)<sup>2</sup> and Sadlej's polarized valence triple zeta (pVTZ) [16] basis set. In the latter basis set (14s10p4d/10s6p4d/6s4p) primitive Gaussians

<sup>1</sup> The following diffuse sp-shell exponents were used: C = 0.0438, N = 0.0639, O = 0.0845, S = 0.0405, Cl = 0.0483 [15].

<sup>2</sup> The diffuse hydrogen exponent used was 0.0360. The two d exponents on the non-hydrogen atoms were obtained by multiplying the standard d exponent from the 6-31G(d,p) basis set by 2.0 and 0.5. Likewise for the two p exponent on the hydrogen atoms.

Table 1

Electrostatic interaction energies (in kcal/mol) obtained from ab initio and distributed multipole calculations and the charge penetration correction ( $E^{\text{pen}}$ ) calculated using Eq. (9)

	Ab initio	EFP				
	ES	ES	Localized MOs		Canonical MOs	
			$E^{\text{pen}}$	ES + $E^{\text{pen}}$	$E^{\text{pen}}$	ES + $E^{\text{pen}}$
Water dimer	−8.21	−7.12	−1.04	−8.16	−0.33	−7.45
Methanol dimer	−8.12	−6.89	−1.04	−7.93	−0.62	−7.51
Dichloromethane dimer	−1.73	−1.47	−0.14	−1.61	−0.10	−1.57
Acetonitrile dimer	−5.12	−4.53	−0.35	−4.88	−0.33	−4.86
Acetone dimer	−3.33	−2.66	−0.49	−3.15	−0.26	−2.92
DMSO dimer	−10.88	−8.42	−1.75	−10.17	−0.99	−9.41

All energies are given in kcal/mol and calculated at the RHF/6-31 + G(d,p)//6-31 + G(d,p) level of theory.

are contracted to [7s5p2d/5s3p2d/3s2p] for the third/second/first row elements. The dimer geometries were obtained by first fully optimizing the dimer geometry at the RHF/6-31 + G(d,p) level of theory, and then superimposing the free RHF/6-31 + G(d,p) monomer geometries on the dimer structure. This was done to allow a fair comparison between the ab initio and the multipole calculations since the latter utilizes the free monomer geometries.

The ab initio electrostatic energies are evaluated using the Morokuma–Kitaura energy decomposition scheme [17]. The classical electrostatic energy is the interaction energy between two distributed multipole expansions (charges through octupoles<sup>3</sup> at each atomic center and bond midpoint). The multipoles are obtained by a distributed multipole analysis [2] of the ab initio charge density of each monomer. The LMOs were obtained using the Edmiston–Ruedenberg localization scheme [18].

#### 4. Results with conclusions

Table 1 lists the ab initio and multipole electrostatic energies for a series of dimers depicted in Fig. 1. Both canonical molecular orbitals (CMOs) and LMOs are tested.

The data in Table 1 indicates that the charge penetration correction term [Eqs. (9) and (10)] evalu-

ated using the LMOs clearly decreases the error in the electrostatic interaction energy calculated using multipoles. In most cases, the error is better than −0.2 kcal/mol compared to the ab initio values, except for the DMSO dimer, which is in error by −0.7 kcal/mol. In general, the SGO approximation underestimates the charge penetration correction.

The results in Table 1 quite clearly show that LMOs are a better choice of orbitals than CMOs when evaluating  $E^{\text{pen}}$  within the SGO approximation. The CMO-errors range from −0.16 kcal/mol for  $(\text{CH}_2\text{Cl}_2)_2$  to −1.47 kcal/mol for the DMSO dimer. The discrepancy between the LMO and CMO results becomes more significant when the charge penetration and thus the overlap is large, presumably since this constitutes a more severe test on the underlying assumptions of the SGO approximation. For this reason, in the remainder of this Letter we will be utilizing only the LMOs to calculate  $E^{\text{pen}}$ .

Table 2

Ab initio and multipole electrostatic energies as well as the charge penetration correction calculated using LMOs for various intermolecular separations of the water dimer

	Ab initio		EFP	
	ES	ES	$E^{\text{pen}}$	ES + $E^{\text{pen}}$
Water dimer	−8.21	−7.12	−1.04	−8.16
Water dimer + 0.5 Å	−4.07	−3.92	−0.14	−4.06
Water dimer − 0.5 Å	−21.26	−15.17	−7.82	−22.99

All energies are given in kcal/mol and calculated at the RHF/6-31 + G(d,p)//6-31 + G(d,p) level of theory.

<sup>3</sup> In the current implementation only the charge-octupole term is included.

Table 3

Ab initio and multipole electrostatic energies as well as the charge penetration correction calculated using LMOs calculated for the water dimer at various levels of theory

	Ab initio		EFP	
	ES	ES	$E^{\text{pen}}$	ES + $E^{\text{pen}}$
6-31 + G(d,p)	-8.21	-7.12	-1.04	-8.16
6-31 + +G(2d,2p)	-7.35	-6.18	-1.04	-7.22
pVTZ	-6.86	-5.69	-1.02	-6.71

All energies are given in kcal/mol.

Next we consider the effect of intermolecular separation on  $E^{\text{pen}}$  for the water dimer by increasing and decreasing the intermolecular separation of the equilibrium water dimer geometry by 0.5 Å. The results are shown in Table 2. As the distance between the water molecules is increased, the agreement between the ab initio and the  $E^{\text{pen}}$  corrected electrostatic energies becomes better. At the shorter water–water separation the error is larger (+1.7 kcal/mol), but the  $E^{\text{pen}}$  correction significantly improves the electrostatic energy compared to the uncorrected multipole energy which is in error by -6.09 kcal/mol.

Table 3 lists results for the water dimer at the 6-31 + G(d,p) equilibrium distance using more extensive basis sets. As more basis functions are added, the agreement between the ab initio and  $E^{\text{pen}}$  corrected multipole energies is essentially unaffected. The largest discrepancy is 0.15 kcal/mol for the pVTZ basis set. Interestingly, the charge penetration energy is nearly constant in all three cases while  $E^{\text{Coul}}$  increases with basis set size. This seems to indicate that the addition of more basis functions does not significantly change the intermolecular overlap, but rather the density distribution near the nuclei of the monomer.

## 5. Conclusion

We have derived an expression relating the overlap of non-orthogonal molecular orbitals to the charge penetration energy. When combined with an accurate multipole representation of the electrostatic energy, such as in the effective fragment potential method, our method is capable of reproducing the ab initio

electrostatic energies that are within 0.2 kcal/mol for a variety of molecular dimers and basis sets.

## Acknowledgements

This work was supported in part by the University of Iowa Department of Chemistry, a University of Iowa Biosciences Initiative Pilot Grant, and a Research Innovation Award from the Research Corporation. The computations were carried out on RS/6000 workstations generously provided by the University of Iowa.

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