



# Application of the overlap model to calculating correlated exchange energies

Matthew P. Hodges<sup>\*</sup>, Richard J. Wheatley

*School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK*

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## Abstract

We develop methods for approximating correlated exchange energies which require only Hartree–Fock self-consistent field (SCF) exchange energies and SCF and correlated charge density overlaps. We benchmark the methods using results calculated for the water dimer at the second-order Møller–Plesset (MP2) level using symmetry-adapted perturbation theory. Assuming that the exchange/overlap ratio is transferable between SCF and MP2 calculations gives a weighted RMS error of 3.2% with no fitted parameters. Including a single overall scaling parameter gives an error of 2.3%. © 2000 Published by Elsevier Science B.V.

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## 1. Introduction

Modelling the water dimer accurately has proven to be computationally very demanding, and this task has drawn considerable effort from the scientific community over the last few decades. One of the most sensitive tests of a model potential for this system is in the determination of the vibration–rotation–tunneling spectrum, and only very recently, using state of the art computational techniques, has it been possible to attain near spectroscopic accuracy [1]. The work in Ref. [1] represents a continuation of earlier work on the same system [2,3] and employs symmetry-adapted perturbation theory (SAPT) [4,5]. The success of the SAPT method stems partly from the fact that both intramolecular and intermolecular

correlation effects can systematically be considered. However, SAPT is computationally demanding even for systems as small as the water dimer, and more approximate methods are still required for larger molecules.

Interactions between molecules may be divided into long-range (multipolar) and short-range (overlap and exchange–repulsion) contributions. Long-range interactions, including the effects of intramolecular correlation, can be obtained from monomer calculations, but more computationally demanding dimer calculations are required for short-range interactions. Here we concentrate on the exchange–repulsion (called exchange here for brevity) which is a dominant component of the intermolecular potential energy at short range. The exchange energy is relatively straightforward to compute at the uncorrelated (Hartree–Fock, i.e. HF) level. However, correlation corrections are also important as there is a delicate

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<sup>\*</sup> Corresponding author. Fax: +44-115-951-3562; e-mail: pczmph@unix.ccc.nottingham.ac.uk

balance between long-range and short-range terms near the minima of the potential energy surface. Correlated exchange energies are difficult to obtain, even approximately. Their magnitude, relative to the HF exchange, is system-dependent, and may vary considerably as a function of the relative orientations of the interacting molecules [6].

The development of accurate ab initio potentials will therefore benefit from methods which can provide high-quality exchange energies for a reasonable computational cost. In this Letter we report the development of methods which can be used to estimate correlated exchange energies from quantities which are easy to evaluate, namely charge density overlaps and HF exchange energies. We report results for the water dimer at the MP2 level, because SAPT results are available for comparison, though the methods are completely general and applicable to higher levels of correlation and to systems too large for SAPT calculations. With reference to the use of the MP2 method, we note a recent study by Heßelmann and Jansen who calculated first-order exchange energies with a reference determinant constructed using a Brueckner doubles (BD) methodology [7]. Six configurations of the water dimer were studied, and the BD and MP2 results were comparable with exchange energies calculated at the CCSD level with an infinite-order summation of the intramolecular correlation corrections [8,9]. This indicates that the MP2 results are a reasonable approximation to highly correlated calculations.

## 2. Methods

The charge density overlap between two molecules separated by a distance  $R$ , with relative orientations denoted by  $\Omega$ , is defined as

$$S_\rho(R; \Omega) = \int \rho_A(\mathbf{r}) \rho_B(\mathbf{r}) d^3\mathbf{r} \quad (1)$$

where  $\rho_A$  and  $\rho_B$  are the ground-state charge densities of isolated monomers A and B, respectively. Note that the charge density only has to be calculated once per molecule at each level of theory being considered, if the internal coordinates remain fixed. The basic premise of the overlap model (see Ref. [10] for previous applications) is that the exchange

energy can be related to the charge density overlap by the approximate relationship

$$E_{\text{exch}}(R; \Omega) \approx K \times S_\rho^x(R; \Omega) \quad (2)$$

where the exchange/overlap ratio  $K$  is a constant and the exponent  $x$  is expected to be close to unity. We now generalize this relationship by allowing the exchange/overlap ratio to depend on the intermolecular coordinates. Assuming  $x = 1$ , we write

$$E_{\text{exch}}(R; \Omega) = K(R; \Omega) \times S_\rho(R; \Omega) \quad (3)$$

and we will henceforth refer to (geometry-independent)  $K$  as an overlap *parameter*, and to  $K(R; \Omega)$  as an overlap *function*.

The SAPT method has been used to calculate exchange energies at about 2500 configurations of the water dimer [1], and we use the  $E_{\text{exch}}^{(10)}$ ,  $E_{\text{exch}}^{(11)}$  and  $E_{\text{exch}}^{(12)}$  components from these calculations. The  $E_{\text{exch}}^{(10)}$  component is the exchange energy calculated using HF determinants, and the  $E_{\text{exch}}^{(11)}$  and  $E_{\text{exch}}^{(12)}$  components are correlation corrections to the exchange energy which approximately correspond to contributions up to the MP2 level [11]. We therefore define the SCF and MP2 exchange energies as follows:

$$E_{\text{exch}}^{\text{SCF}} = E_{\text{exch}}^{(10)}, \quad (4)$$

$$E_{\text{exch}}^{\text{MP2}} = E_{\text{exch}}^{(10)} + E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)}. \quad (5)$$

We calculate monomer charge densities using CADPAC [12] at the SCF and MP2 levels of theory using the same basis set described in Refs. [1–3], and evaluate the charge density overlaps, using the GMUL program [13], at the same set of geometries as used in the SAPT calculations. This procedure is made more efficient by first simplifying the charge density using a Gaussian multipole expansion [13], terminated at rank 4.

Because the exchange energies span more than six orders of magnitude, we have examined the effect of several weighting schemes in trial fits of the data. Using the Levenberg–Marquardt method, the quantity we minimize and report is the weighted RMS % error defined as

$$\Delta = 100 \times \left[ \frac{\sum_i w_i \left( \frac{E_i^{\text{fit}} - E_i^{\text{calc}}}{E_i^{\text{calc}}} \right)^2}{\sum_i w_i} \right]^{1/2}. \quad (6)$$

Here  $w_i$  is the weight for energy  $E_i^{\text{calc}}$  which is approximated in the fit by  $E_i^{\text{fit}}$ . We define a Gaussian/Log weighting scheme, for which the weights are given by

$$w_i = \exp\left\{-\alpha \left[\ln\left(E_i^{\text{calc}}/E^{\text{ref}}\right)\right]^2\right\} \quad (7)$$

where we have chosen  $E^{\text{ref}} = 20 \text{ kJ mol}^{-1}$  (roughly the exchange energy at the dimer minimum), and  $\alpha = 1/\ln(10)$ , so the weights decrease by a factor of 10 as the energy increases/decreases by a factor of 10 from this reference energy. We also give some results for a uniform weighting scheme where  $w_i = 1$ , but do not recommend this as the error tends to be dominated by contributions from very small energies, so the quality of the fit in important regions of the potential energy surface may be poor.

### 3. Results

The SCF and MP2 exchange energies are plotted against one another in Fig. 1, and it is evident that a

Table 1  
Results of fitting MP2 exchange energies using Eq. (8)

Weighting scheme	$\lambda$	$\Delta$
Gaussian/Log	1.0	18.52
	1.220	4.226
Uniform	1.0	21.28
	1.221	11.33

simple scaling factor can be used to approximate the MP2 data such that

$$E_{\text{exch}}^{\text{MP2}} \approx \lambda \times E_{\text{exch}}^{\text{SCF}} \quad (8)$$

The optimized scaling parameters  $\lambda$ , and errors  $\Delta$ , resulting from this approximation are given in Table 1. If we assume that  $\lambda = 1$  then for both weighting schemes the error incurred by using the SCF rather than MP2 exchange energies is about 20%. This is a measure of the significant effect of correlation on the exchange energy. If we have sufficient data to fit  $\lambda$ , then this single scaling parameter gives us a reasonably successful method of estimating the MP2 exchange energies.

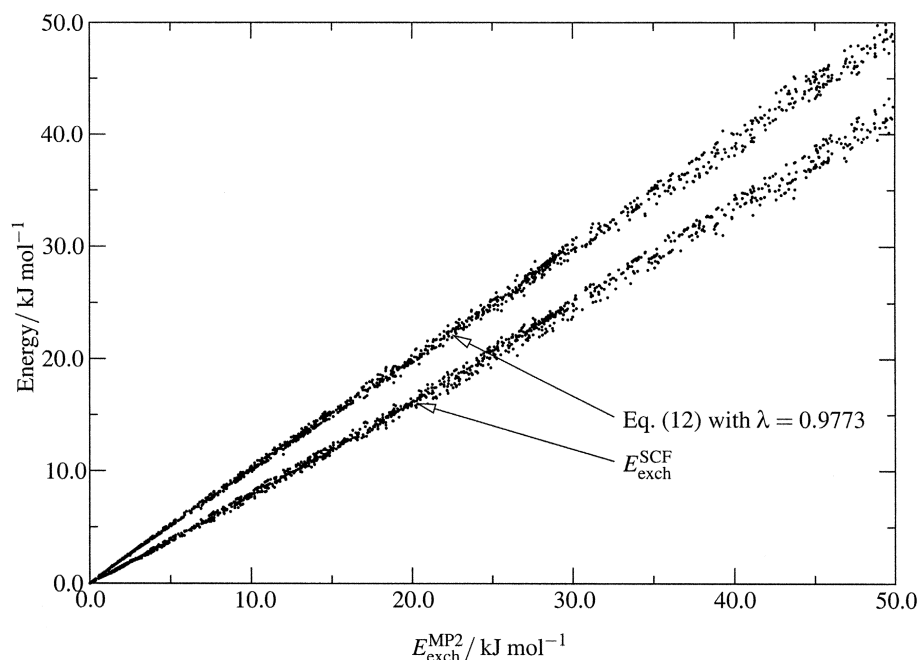


Fig. 1. Scatter plot of calculated SCF exchange energies (lower points) and fitted exchange energies (upper points) versus calculated MP2 exchange energies.

To look for more accurate methods, we first calculate overlap functions for the SCF and MP2 data, which by analogy with Eq. (3) are defined as

$$E_{\text{exch}}^{\text{SCF}}(R; \Omega) = K^{\text{SCF}}(R; \Omega) \times S_{\rho}^{\text{SCF}}(R; \Omega) \quad (9)$$

$$E_{\text{exch}}^{\text{MP2}}(R; \Omega) = K^{\text{MP2}}(R; \Omega) \times S_{\rho}^{\text{MP2}}(R; \Omega). \quad (10)$$

Since the charge density overlaps,  $S_{\rho}$ , can easily be calculated at the SCF and MP2 levels, we look for a relationship between  $K^{\text{SCF}}(R; \Omega)$  and  $K^{\text{MP2}}(R; \Omega)$ . We find that the two functions are very similar, and again we propose a one-parameter model which relates the two functions by a constant such that

$$K^{\text{MP2}}(R; \Omega) \approx \lambda \times K^{\text{SCF}}(R; \Omega) \quad (11)$$

and hence

$$E_{\text{exch}}^{\text{MP2}}(R; \Omega) \approx \lambda \times K^{\text{SCF}}(R; \Omega) \times S_{\rho}^{\text{MP2}}(R; \Omega), \quad (12)$$

$$\approx \lambda \times \left( \frac{E_{\text{exch}}^{\text{SCF}}(R; \Omega)}{S_{\rho}^{\text{SCF}}(R; \Omega)} \right) \times S_{\rho}^{\text{MP2}}(R; \Omega). \quad (13)$$

If we examine the value of  $\lambda$ , we see that it is close to unity for each intermolecular geometry. Furthermore, its uniformly-weighted mean value ( $\bar{\lambda}$ ) is not sensitive to the exclusion of data with very low weights and its standard deviation,  $\sigma$ , is small. For example, if we exclude data with Gaussian/Log weights less than 0.01 (6.9% of the points) then  $\bar{\lambda} = 0.9759$  and  $\sigma = 0.02778$ ; if we exclude data with weights less than 0.9 (74.8% of the points) then  $\bar{\lambda} = 0.9765$  and  $\sigma = 0.01583$ . In Table 2 we give the errors and values of  $\lambda$  from fits of the MP2 exchange energies using Eq. (12), along with the errors when  $\lambda = 1$ . For the Gaussian/Log weighting scheme, the error is about 3.2% when  $\lambda$  is fixed at unity, and about 2.3% when  $\lambda$  is treated as a param-

Table 2  
Results of fitting MP2 exchange energies using Eq. (12)

Weighting scheme	$\lambda$	$\Delta$
Gaussian/Log	1.0	3.245
	0.9773	2.266
Uniform	1.0	10.51
	0.9615	9.726

Table 3

Results of fitting SCF exchange energies using Eq. (2) (upper part) and Eq. (14) (lower part) with the Gaussian/Log weighting scheme

Parameters		$\Delta$
$K$	$x$	
7.389	1.0	9.630
5.498	0.9559	8.791
$K^{\text{HH}}$	$K^{\text{HO}}$	$K^{\text{OO}}$
9.270	7.863	6.422
		5.709

eter of the fit. It is worth noting that when we set  $\lambda = 1$  our model has no parameters. Either model represents a significant improvement over isotropic scaling of the SCF exchange energies, which for the same weighting scheme incurs an error of about 4.2%. The results with the uniform weighting scheme follow the same trend, although the errors are larger, and henceforth we will use only the (more reasonable) Gaussian/Log weighting. A scatter plot of the MP2 data versus the fitted function of Eq. (12), with  $\lambda = 0.9773$ , is shown in Fig. 1.

We now turn to more approximate methods of the type described by Eq. (2), in which  $K$  is independent of orientation. We have also used an atomic decomposition of the water monomer charge density [13], and approximated the exchange energy as

$$E_{\text{exch}}(R; \Omega) \approx \left( K^{\text{HH}} \times S_{\rho}^{\text{HH}}(R; \Omega) \right) + \left( K^{\text{HO}} \times S_{\rho}^{\text{HO}}(R; \Omega) \right) + \left( K^{\text{OO}} \times S_{\rho}^{\text{OO}}(R; \Omega) \right) \quad (14)$$

where, for example,  $S_{\rho}^{\text{HH}}$  is the sum of four intermolecular overlaps between hydrogen atom charge densities. We consider the SCF and MP2 data separately.

The results of fitting the SCF exchange energies using the SCF charge density overlaps are given in Table 3. When using Eq. (2), it is apparent that treating  $x$  as a parameter of the fit leads to only a slight improvement relative to setting  $x = 1$ . Fitting the energies with atom–atom overlap parameters according to Eq. (14) proves to be a successful strategy, and the error is reduced from about 8.8%

when Eq. (2) is used and  $K$  and  $x$  are optimized, to about 5.7% when the three parameters  $K^{\text{HH}}$ ,  $K^{\text{HO}}$  and  $K^{\text{OO}}$  are optimized. It is interesting that the value of  $K^{\text{HO}}$  of 7.863 is close to the arithmetic mean of  $K^{\text{HH}}$  and  $K^{\text{OO}}$ , which is 7.846, and this suggests a simple combining rule for use in larger systems.

The results of fitting the MP2 exchange energies using the MP2 charge density overlaps are given in Table 4. From the observations made above it is expected that the overlap parameters will be close to the SCF values, and this is generally what we observe. In particular, the optimized SCF and MP2 atom–atom overlap parameters are very similar, and the combining rule  $K^{\text{HO}} = (K^{\text{HH}} + K^{\text{OO}})/2$  is again a good approximation. Using Eq. (2), the errors are comparable with the fits of the SCF data in Table 3, but for the atom–atom fit the error is slightly smaller at about 4.5%. This can be compared with the best fit using the isotropically scaled SCF exchange energies (Table 1) with an error of about 4.2%, and the best model using a scaling based on charge density overlaps (Table 2) which has an error of about 2.3%, although both the latter fits only used one parameter.

Because of the similarities between the SCF and MP2 overlap parameters, we also give in Table 4 the errors associated with approximating the MP2 data using the parameters derived from fitting the SCF data. The increase in the errors, relative to using the optimized MP2 parameters, is small. For example,

the error for the atom–atom fit increases from about 4.5% to 4.8% on making this assumption.

#### 4. Discussion and conclusions

We believe that this is the first time that correlated exchange energies and charge density overlaps have been compared. The observation that the SCF and MP2 overlap functions are very similar has allowed us to approximate correlated exchange energies to within 2–3% of the exact values. Two strategies for approximating results at the MP2 level, both requiring SCF exchange energies and SCF and MP2 charge density overlaps, have been proposed. The simpler of the two, requiring no fitted parameters, is to make the assumption that the SCF and MP2 overlap functions are identical, i.e. to use  $\lambda = 1$  in Eq. (12). The second requires an estimate of  $\lambda$  to be made, and this might be done by calculating a small number of MP2 exchange energies. Simpler models are formulated in Eqs. (2) and (14), with overlap parameters which are independent of the intermolecular coordinates. Although these are less accurate, they have the advantage that once the SCF parameters have been determined, for example by fitting a small number of SCF exchange energies, the MP2 overlap parameters may be assumed to be equivalent, and only the MP2 charge density overlaps need to be evaluated in order to obtain approximate MP2 exchange energies. Given that the charge density overlap calculations are relatively cheap to perform, this methodology would lead to significant computational savings for large systems, where even the SCF exchange energies are costly to evaluate accurately.

Several interesting questions remain which we have not addressed in this work. Firstly, whether or not the overlap functions are transferable to other correlated methods such as CCSD(T), which is commonly used in the study of weakly bound complexes. Secondly, basis set effects need to be examined. It may be the case that the parameters in our models are relatively independent of basis set, in which case it might be possible to approximate correlated exchange energies with large basis sets using uncorrelated calculations with smaller basis sets. The preliminary results presented here are encouraging, and we

Table 4  
Results of fitting MP2 exchange energies using Eq. (2) (upper part) and Eq. (14) (lower part) with the Gaussian/Log weighting scheme. The results in parentheses were obtained using the SCF parameters from Table 3

Parameters		$\Delta$
$K$	$x$	
7.263 (7.389)	1.0 (1.0)	9.517 (9.671)
6.025 (5.498)	0.9718 (0.9559)	9.183 (9.408)
$K^{\text{HH}}$	$K^{\text{HO}}$	$K^{\text{OO}}$
9.289 (9.270)	7.863 (7.863)	6.212 (6.422)
		4.528 (4.768)

intend to work towards answering some of the issues raised in future studies.

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