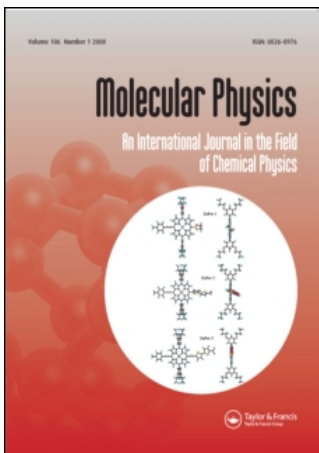


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Intermolecular potential energy extrapolation method for weakly bound systems: Ar₂, Ar–H₂ and Ar–HF dimers

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Two methods are presented and compared for modifying the intermolecular potential energy extrapolation routine SIMPER, to overcome the problems occurring at small intermolecular separation associated with the use of a Coulomb approximation. The first modification uses a charge density overlap pseudopotential added to the effective Hamiltonian of each interacting fragment. The second treats the problem perturbatively, truncating the polarization expansion series at third order. The methods are used to produce potential energy curves for Ar₂ dimer and several one-dimensional cuts through the Ar–H₂ and Ar–HF potential energy surfaces. Both approaches are competitive with supermolecule dimer calculations at high levels of theory, and significantly reduce the computational cost.

1. Introduction

In the description of weakly bound systems within the framework of the Born–Oppenheimer approximation, two complementary methods are mainly used: a supermolecule approach based on application of standard molecular orbital techniques and a perturbative approach using one of the various formulations of intermolecular perturbation theory. Both supermolecular and perturbative approaches have their advantages and disadvantages in studies of weak intermolecular forces in van der Waals molecules.

The supermolecule *ab initio* approach to calculating intermolecular forces is conceptually very simple. Calculations are carried out on the interacting system at each relative geometry and the intermolecular potential is then obtained by subtracting the energies of the two monomers from the energy of the dimer. Highly accurate *ab initio* supermolecule calculations are possible for the lightest dimers, but become more expensive and challenging for dimers containing larger atoms or molecules. The problem is largely one of calculating the dispersion contribution to intermolecular forces.

When dispersion forces dominate, large and flexible basis sets and a high-level treatment of electron correlation are required to calculate intermolecular forces. In addition, for molecule–molecule systems, a very large number of geometry points is essential to cover fully the complete configuration space. When choosing the correlation treatment, it is important that the method be size-consistent, so that the energy of the supermolecule at infinite separation is equal to the sum of the monomer energies. The leading size-consistent method is currently coupled-cluster with single, double and perturbative triple substitutions, CCSD(T). Møller–Plesset perturbation methods, such as second-order, MP2, and fourth-order, MP4, are also used. The second-order MP2 method is much cheaper than coupled-cluster calculations, but less accurate than CCSD(T); the fourth-order MP4 method requires computational time similar to CCSD(T), but without proven advantage in accuracy.

Intermolecular perturbation methods, such as symmetry-adapted perturbation theory [1] and intermolecular perturbation theory [2], provide a decomposition of the interaction energy into physically meaningful terms, which gives more insight into the nature of the intermolecular potential than supermolecule calculations. Some low-order contributions to the interaction energy can be obtained from *ab initio* calculations on the isolated monomers, which avoids the need for a supermolecule calculation at every geometry. The main problem with

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intermolecular perturbation methods lies in the calculation of exchange-repulsion and higher-order terms. Exchange-repulsion interactions cannot be defined rigorously from monomer-based perturbation theory and ‘Coulomb’ interactions become rapidly more expensive to calculate at higher orders.

Our solution to this problem is to develop a treatment which improves the description of each component of the interaction energy individually, including dispersion, exchange-repulsion and electrostatic contributions, by scaling low-level supermolecule calculations. In our previous work [3], a new approach was first reported for improving supermolecule *ab initio* intermolecular potentials, the systematic intermolecular potential extrapolation routine, SIMPER. It is a scaling method which involves combining quantities obtained from ‘low’ level dimer calculations (exchange-repulsion and Coulomb energies) with quantities obtained from ‘high’ level monomer calculations (charge density overlaps, first-order Coulomb interaction energies and dispersion energy coefficients) in order to estimate the resulting potential energy surfaces at the ‘high’ level of theory. The definition of ‘low’ and ‘high’ levels of theory is flexible and depends on technological limitations only. The ‘low’ level must be computationally affordable to produce multidimensional potential energy surfaces and ‘high’ level is required only in a few monomer calculations.

In the original formulation of the method [3], (here called SIMPER-0 to distinguish it from new methods to be considered later), the induction and dispersion components of the Coulomb energy were not separated, but scaled using the ratio of dispersion energy coefficients evaluated at ‘high’ and ‘low’ levels of theory, $C_6^{\text{high}}/C_6^{\text{low}}$. The MP2 theory was used as the ‘low’ level and C_6^{high} was taken from effective dipole oscillator strength distribution (DOSD) results [4]. The method worked well for small rare-gas systems. For example, for the He₂ and Ne₂ dimers, agreement within about 0.4 cm⁻¹ was seen between the SIMPER-0 results and *ab initio* interaction energies obtained using CCSD(T) theory. However, for the Ar₂ dimer, the SIMPER-0 energy near the equilibrium was about 25% too shallow. For this system, the value of the C_6 dispersion coefficient at the MP2 level of theory is in much worse agreement with accurate values than C_8 and C_{10} , which provides an explanation for the discrepancy in the results. It was concluded that methods using a separate scaling for each C_n component are required.

In subsequent studies [5], the SIMPER method was improved by using a separate scaling for each C_n dispersion coefficient in the dispersion energy (see section 2.1) and potential energy curves were

constructed for homonuclear and heteronuclear rare-gas dimers including He, Ne and Ar atoms. This method (here called SIMPER-1) showed much better results than SIMPER-0, and for some systems (Ne–Ar, Ne–Ne, for example) achieved an accuracy of about 1–2% in the binding energy. For the Ar₂ dimer, the accuracy in the binding energy was improved to 5.2%. However, for this system, as well as for the Ar–H₂ dimer, the SIMPER-0 and SIMPER-1 methods could not be used to calculate potential energy surfaces at small internuclear separation. The partitioning of the interaction energy into Coulomb and exchange-repulsion contributions becomes unstable due to ‘collapse’ of the Coulomb wavefunction in this region [6] and, therefore, the Coulomb component of the interaction energy needs to be obtained in a different way.

In this paper, two different ways to tackle the ‘Coulomb collapse’ problem are discussed (sections 2.2–2.4) and the new methods are tested by applying them to Ar₂, Ar–H₂ and Ar–HF systems, and comparing the potential energy curves obtained with the best available reference data for each system (sections 3.2 and 3.3). These systems are chosen as they are weakly bound complexes bound mainly by dispersion forces, but with induction forces playing an increasing role from Ar₂ to Ar–HF. The SIMPER-1 method was found to fail at short range for all three dimers, so they are of immediate interest for testing the new approaches. The extensive body of experimental data from high-resolution microwave [7–9] and infrared [10–12] spectroscopy has made it possible to determine reliable empirical potentials for Ar₂ [13], Ar–H₂ [14] and Ar–HF [15, 16], which are used to assess the results.

2. Theory

An outline of how each component of the total interaction energy is treated in the SIMPER-1 approach and how the different interaction energy contributions are extrapolated, is given in section 2.1. The difficulties which emerge when the SIMPER-1 routine is used at small intermolecular separation are discussed in section 2.2. These are associated with the use of the Coulomb approximation. Two methods to prevent the Coulomb collapse are then presented. The first method, SIMPER-1K (section 2.3), is based on solution of the Schrödinger equation in the Coulomb approximation. In this approach, in order to prevent the Coulomb collapse an extra ‘charge density overlap’ operator is added to the interaction Hamiltonian. The second method, SIMPER-1P (section 2.4), treats the problem of calculating the Coulomb energy perturbatively to finite order, rather than infinite order.

2.1. SIMPER-1 methodology

In the SIMPER-1 approach [5], the intermolecular potential energy surface is first divided into a short-range exchange-repulsion interaction energy, E_{exch} , and a Coulomb interaction energy, E_{Coul} , dominating at long range.

The Coulomb interaction energy between the molecules is obtained by performing a modified supermolecule calculation, where the monomer energies are calculated using monomer-centred basis sets and the dimer wavefunction is expanded in simple product functions, which are not antisymmetrized between electrons on the different molecules:

$$\begin{aligned} \psi_{\text{Coul}}(1, \dots, n) \\ = \sum_{a,b} \psi_a^A(1, \dots, n_A) \times \psi_b^B(n_A + 1, \dots, n). \end{aligned} \quad (1)$$

Here n_A is the number of electrons of A and n is the total number of electrons in the AB dimer. In a self-consistent field (SCF) calculation, this ‘SCF Coulomb’ wavefunction is a simple product of two determinants and the molecular orbitals are chosen to minimize the energy in the usual way. In second-order Møller–Plesset perturbation theory (MP2), the Coulomb wavefunction also includes products of doubly excited determinants of A (B) with the SCF determinant of B (A), and products of singly excited determinants of both A and B; the molecular orbitals and orbital energies are taken from the SCF Coulomb wavefunction and the amplitudes are obtained from the usual MP2 procedure.

The exchange-repulsion interaction energy E_{exch} is defined as the difference between the counterpoise-corrected supermolecular interaction energy E_{int} and the Coulomb interaction energy E_{Coul} , and the Coulomb interaction energy is further separated into different contributions using perturbation theory:

$$\begin{aligned} E_{\text{int}} &= E_{\text{exch}} + E_{\text{Coul}} \\ &= E_{\text{exch}} + \left(E_{\text{Coul}}^{(1)} + E_{\text{disp}}^{(2)} + E_{\text{Coul}}^{\text{rest}} \right), \end{aligned} \quad (2)$$

where $E_{\text{Coul}}^{(1)}$ is the first-order Coulomb interaction energy calculated from the unperturbed ground-state charge densities, $E_{\text{disp}}^{(2)}$ is the second-order dispersion energy and $E_{\text{Coul}}^{\text{rest}}$ contains the induction energy, $E_{\text{ind}}^{(2)}$, and higher-order contributions.

The intermolecular exchange-repulsion energy is extrapolated using the charge density overlap model [17], assuming that the ratio of the exchange-repulsion energy and the charge-density overlap integral, S_ρ , is a function of the intermolecular geometry, but not the

level of theory:

$$E_{\text{exch}}^{\text{high}}(R, \theta) \approx E_{\text{exch}}^{\text{low}}(R, \theta) \times \frac{S_\rho^{\text{high}}(R, \theta)}{S_\rho^{\text{low}}(R, \theta)}, \quad (3)$$

$$S_\rho(R, \theta) = \int \rho_{\text{el}}^A(\mathbf{r}) \rho_{\text{el}}^B(\mathbf{r}) \, d\mathbf{r}, \quad (4)$$

where (R, θ) denotes the intermolecular geometry and $\rho_{\text{el}}^A(\mathbf{r})$ and $\rho_{\text{el}}^B(\mathbf{r})$ are unperturbed ground state electron densities.

The intermolecular dispersion energy is written as a damped multipolar series:

$$E_{\text{disp}}^{(2)} = - \sum_n C_n \times f_n(bR) \times R^{-n}, \quad (5)$$

where b is the scaling parameter in the Tang–Toennies damping function [18] $f_n(bR)$ (an incomplete gamma function of order $n+1$). At the ‘low’ level of theory, this parameter is determined uniquely at each point on the potential energy surface from the ‘low’ level dispersion energy and the ‘low’ level dispersion energy coefficients. The damping functions are then extrapolated by assuming [19] that the scaling parameter, b , is proportional to $(C_6/C_8)^{1/2}$, such that

$$b^{\text{high}} \times \left(\frac{C_8^{\text{high}}}{C_6^{\text{high}}} \right)^{1/2} \approx b^{\text{low}} \times \left(\frac{C_8^{\text{low}}}{C_6^{\text{low}}} \right)^{1/2}. \quad (6)$$

For the atom–diatom systems, Ar–HF and Ar–H₂, the dispersion energy coefficients are anisotropic and can be evaluated for each intermolecular angle by expanding in Legendre polynomials [15]. The improved scaling parameter, b^{high} , obtained at each point on the potential energy surface is used together with the more accurate ‘high’ level dispersion energy coefficients, C_n^{high} , to extrapolate the dispersion energy using equation (5).

The first-order Coulomb interaction energy is obtained at ‘low’ and ‘high’ levels of theory from the appropriate one-electron density matrices. The ‘low’ level $E_{\text{Coul}}^{(1)}$ is simply replaced by the ‘high’ level $E_{\text{Coul}}^{(1)}$ in equation (2).

The resulting SIMPER-1 interaction energy is the sum of the extrapolated exchange-repulsion and dispersion energies, the high-level first-order Coulomb energy and the higher-order Coulomb energy, $E_{\text{Coul}}^{\text{rest}}$, which is not extrapolated. The SIMPER-1 extrapolation is therefore a true *ab initio* method, which requires no fitting parameters at any stage of the procedure.

2.2. The Coulomb collapse

In the ‘Coulomb’ or ‘polarization’ approximation (1), the wavefunction ψ_{Coul} is made from functions which do not satisfy the Pauli principle for all n electrons of the complex. The function $\psi_a^A(1, \dots, n_A)$ is antisymmetric

with respect to the permutation of electrons $(1, \dots, n_A)$, and $\psi_b^B(n_A + 1, \dots, n)$ is antisymmetric with respect to the permutation of electrons $(n_A + 1, \dots, n)$. By definition, their product has the same properties, but has no extra symmetry with respect to the intermolecular exchanges, i.e. those exchanging electrons between the sets $(1, \dots, n_A)$ and $(n_A + 1, \dots, n)$.

Use of the Coulomb approximation is not correct, because it fails to describe exchange-repulsion interactions, which tend to increase exponentially as the intermolecular separation decreases. Although the Coulomb approximation works sufficiently well at long range, exchange-repulsion dominates at short intermolecular distances. As a result of violation of the Pauli principle, the Coulomb interaction energy ‘collapses’ when the molecules approach each other and acquires physically unreal negative values (see figure 1 and note the change of scale).

Two different ways to overcome the Coulomb collapse problem are now investigated. The SIMPER-1K method involves adding a charge-overlap pseudopotential to the Hamiltonian, calculating the Coulomb energy, then correcting it to second order in the pseudopotential. The SIMPER-1P method involves calculating the Coulomb energy using intermolecular perturbation theory and truncating the resulting expansion at second or third order.

2.3. Pseudopotential method (SIMPER-1K)

The total Hamiltonian of the complex is denoted as H . A zero-order Hamiltonian H^0 is introduced as the sum of the Hamiltonians H^i of the isolated molecules i :

$$H^0(1, \dots, n) = H^A(1, \dots, n_A) + H^B(n_A + 1, \dots, n), \quad (7)$$

where the operator H^A acts only on the coordinates of the electrons and nuclei of molecule A, and similarly for H^B . The interaction operator V is then

$$V = H - H^0 = H - (H^A + H^B). \quad (8)$$

In the Coulomb approximation, at small intermolecular separations, the electrons of molecule A are influenced by the ‘Coulomb’ potential of molecule B and can be unphysically transferred onto molecule B. In order to discourage charge transfer between the molecules, we add an extra ‘charge density overlap’ operator $V_{\text{eff}}(K) = K \times \hat{S}_\rho$ to the interaction operator V , where

$$\hat{S}_\rho = \sum_{j(A)} \sum_{j(B)} \delta(\mathbf{r}_{j(A)j(B)}) \quad (9)$$

and $j(A)$, $j(B)$ are the electron coordinates of molecules A and B.

The Coulomb wavefunctions at SCF level, $\psi_{\text{Coul, SCF}}^K$, and at correlated (MP2) level, $\psi_{\text{Coul, MP2}}^K$, are then calculated in the same way as described previously (equation (1) and accompanying text), with the additional $V_{\text{eff}}(K)$ operator included in the Hamiltonian. The Coulomb wavefunction and the corresponding Coulomb interaction energy, E_{Coul}^K , depend on the parameter K . In the region of the potential where no ‘Coulomb collapse’ occurs, this (weak) dependence on K is unwanted and perturbation theory is used to remove it. The operator $V_{\text{eff}}(K)$ is treated as the perturbation and all terms in the SCF Coulomb energy, which are first-order or second-order in the parameter K , are

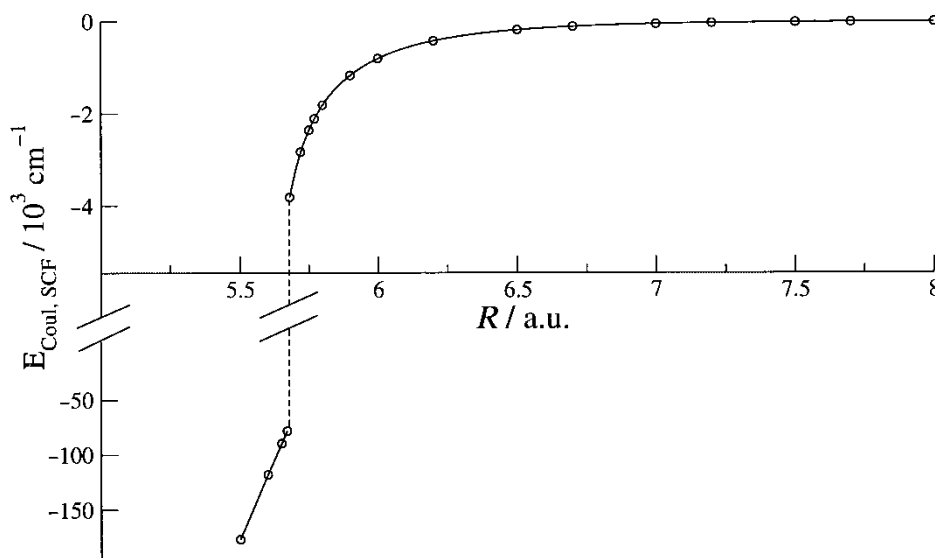


Figure 1. The SCF Coulomb interaction energy $E_{\text{Coul, SCF}}$ for Ar_2 dimer as a function of the Ar–Ar interatomic separation R , showing the ‘Coulomb collapse’ at $R \approx 5.7$ atomic units. The results are obtained with the aug-cc-pVTZ basis set.

removed. This is done at all points on the potential energy surface, including those for which Coulomb collapse would occur at $K=0$. The expression for the Coulomb interaction energy used in SIMPER-1K is therefore

$$E_{\text{Coul}} = E_{\text{Coul}}^K - \langle \psi_{\text{Coul,SCF}}^K | V_{\text{eff}}(K) | \psi_{\text{Coul,SCF}}^K \rangle + \frac{1}{2} \langle \psi_{\text{Coul,SCF}}^K | [\kappa^{(1)}(K), V_{\text{eff}}(K)] | \psi_{\text{Coul,SCF}}^K \rangle, \quad (10)$$

where the operator $\kappa^{(1)}(K)$ is defined as the usual first-order orbital rotation operator resulting from the perturbation $V_{\text{eff}}(K)$. It is found from the response equation

$$\langle \psi_{\text{Coul,SCF}}^K | [X, [\kappa^{(1)}(K), H + V_{\text{eff}}(K)]] | \psi_{\text{Coul,SCF}}^K \rangle + \langle \psi_{\text{Coul,SCF}}^K | [X, V_{\text{eff}}(K)] | \psi_{\text{Coul,SCF}}^K \rangle = 0, \quad (11)$$

where X is an arbitrary single (de-)excitation operator. Equation (10) only includes the effect of the pseudo-potential on the SCF Coulomb energy. Its effect on the MP2 contribution to the Coulomb energy is much smaller, but may be considered in future work.

2.4. Perturbation expansion method (SIMPER-1P)

In SIMPER-1P, the Coulomb interaction energy is found perturbatively to a fixed order. This approach is based on the observations that, at medium to large separations, the unphysical charge transfer effects are almost entirely the result of higher-order terms in the polarization expansion, and truncation of the expansion at finite order recovers the major part of the ‘physical’ Coulomb interaction energy. Knowledge of the first-order perturbed wavefunction enables Coulomb interaction energies to be calculated to third order, and the exchange-repulsion energy is then calculated as the difference between the finite-order Coulomb interaction energy and the counterpoise-corrected total interaction energy.

The method for calculating finite-order Coulomb interaction energies is formulated using static response theory. The general expression for the SCF energy is

$$E_{\text{SCF}} = \langle \Psi | J | \Psi \rangle, \quad (12)$$

where $|\Psi\rangle$ is the product of two ground-state SCF wavefunctions of monomers A and B in the absence of interaction and the effective Hamiltonian J is defined as [20]

$$J = \exp(-\kappa)H \exp(\kappa), \quad (13)$$

where κ is the orbital rotation operator resulting from the intermolecular perturbation. In general, κ is obtained from the condition

$$\frac{\partial E_{\text{SCF}}}{\partial \kappa_X} = 0, \quad (14)$$

which leads to the response equation for $\kappa^{(1)}$ at first order in V :

$$\langle \Psi | [X, [\kappa^{(1)}, H^{(0)}]] | \Psi \rangle + \langle \Psi | [X, V] | \Psi \rangle = 0. \quad (15)$$

It should be noted that elements of the orbital rotation operator corresponding to occupied–occupied and virtual–virtual transformations are zero. In the Coulomb approximation, κ is a sum of operators restricted to the monomer subspaces.

The effective Hamiltonian is further expanded in powers of the perturbation [20]:

$$J^{(1)} = V + [\kappa^{(1)}, H^{(0)}], \quad (16)$$

$$J^{(2)} = \frac{1}{2} [\kappa^{(1)}, [\kappa^{(1)}, H^{(0)}]] + [\kappa^{(1)}, V], \quad (17)$$

$$J^{(3)} = \frac{1}{6} [\kappa^{(1)}, [\kappa^{(1)}, [\kappa^{(1)}, H^{(0)}]]] + \frac{1}{2} [\kappa^{(1)}, [\kappa^{(1)}, V]]. \quad (18)$$

In the SCF approximation, the Coulomb interaction energy can then be obtained [20] as the expectation value of the effective Hamiltonian at a given order of perturbation. The first-order Coulomb energy is

$$E_{\text{Coul,SCF}}^{(1)} = \langle \Psi | V | \Psi \rangle. \quad (19)$$

It corresponds to the interaction of two unperturbed charge distributions. The second-order Coulomb energy is

$$E_{\text{Coul,SCF}}^{(2)} = \frac{1}{2} \langle \Psi | [\kappa^{(1)}, V] | \Psi \rangle \quad (20)$$

and corresponds to the second-order induction. The third-order Coulomb energy is

$$E_{\text{Coul,SCF}}^{(3)} = \frac{1}{6} \langle \Psi | [\kappa^{(1)}, [\kappa^{(1)}, [\kappa^{(1)}, H^{(0)}]]] | \Psi \rangle + \frac{1}{2} \langle \Psi | [\kappa^{(1)}, [\kappa^{(1)}, V]] | \Psi \rangle \quad (21)$$

and corresponds to the third-order induction or hyperpolarization plus the interaction between two polarized charge densities.

The same technique can be applied when electron correlation is taken into account. For non-variational wavefunctions, such as MP2, CCSD, CCSD(T) etc., Lagrange’s method of undetermined multipliers can be applied to construct an energy functional which is variational in all parameters.

For example, the MP2 correlation energy is expressed as

$$E_{\text{MP2}} = \langle t | J | \Psi \rangle, \quad (22)$$

where $|t\rangle$ is a linear combination of doubly excited determinants with the restriction that all excitations

of individual electrons are restricted to monomer subspaces:

$$|t\rangle = \sum_{\mu} t_{\mu} |\mu\rangle.$$

The amplitudes t_{μ} must satisfy the equation

$$-\langle \Psi | J | \mu \rangle = \sum_{\nu} t_{\nu} \langle \mu | F^i \{ J \} - E_{\text{SCF}} | \nu \rangle, \quad (23)$$

where $F^i \{ J \}$ is the inactive Fock operator [21] of operator J and corresponds to the zero-order Hamiltonian in Møller–Plesset theory. The general expression for the MP2 correlation energy Lagrangian is therefore [20, 22]

$$E_{\text{MP2}} = 2\langle t | J | \Psi \rangle + \langle t | F^i \{ J \} - E_{\text{SCF}} | t \rangle + \langle \Psi | [\zeta, J] | \Psi \rangle, \quad (24)$$

where the last term is required to fulfil the Brillouin condition and ζ is a sum of single excitations with amplitudes defined by Lagrange multipliers.

The values of $\kappa^{(1)}$ defined by (15) are used in calculating the MP2 energies. Making the Lagrangian stationary with respect to t_{μ} and expanding in powers of V gives expressions for the zero-order amplitudes

$$\sum_{\nu} t_{\nu}^{(0)} \langle \mu | F^i \{ H^{(0)} \} - E_{\text{SCF}}^{(0)} | \nu \rangle = -\langle \Psi | H^{(0)} | \mu \rangle \quad (25)$$

and the first-order amplitudes

$$\begin{aligned} \sum_{\nu} t_{\nu}^{(1)} \langle \mu | F^i \{ H^{(0)} \} - E_{\text{SCF}}^{(0)} | \nu \rangle \\ = -\langle \Psi | J^{(1)} | \mu \rangle - \langle \mu | F^i \{ J^{(1)} \} - E_{\text{Coul,SCF}}^{(1)} | t^{(0)} \rangle. \end{aligned} \quad (26)$$

Expressions for the zero-order and first-order Lagrange multipliers ζ are obtained in a similar way, by making the Lagrangian stationary with respect to κ .

The MP2 Coulomb interaction energies at different orders are then obtained by expanding the Lagrangian in powers of V [20]:

$$E_{\text{Coul,MP2}}^{(1)} = \langle t^{(0)} | F^i \{ V \} - E_{\text{Coul,SCF}}^{(1)} | t^{(0)} \rangle + \langle \Psi | [\zeta^{(0)}, V] | \Psi \rangle, \quad (27)$$

$$\begin{aligned} E_{\text{Coul,MP2}}^{(2)} = & 2\langle t^{(0)} | J^{(2)} | \Psi \rangle + \langle t^{(1)} | J^{(1)} | \Psi \rangle + \langle t^{(1)} | F^i \{ J^{(1)} \} \\ & - E_{\text{Coul,SCF}}^{(1)} | t^{(0)} \rangle + \langle t^{(0)} | F^i \{ J^{(2)} \} \\ & - E_{\text{Coul,SCF}}^{(2)} | t^{(0)} \rangle + \langle \Psi | [\zeta^{(0)}, J^{(2)}] | \Psi \rangle, \end{aligned} \quad (28)$$

$$\begin{aligned} E_{\text{Coul,MP2}}^{(3)} = & 2\langle t^{(0)} | J^{(3)} | \Psi \rangle + 2\langle t^{(1)} | J^{(2)} | \Psi \rangle + 2\langle t^{(0)} | F^i \{ J^{(2)} \} \\ & - E_{\text{Coul,SCF}}^{(2)} | t^{(1)} \rangle + \langle t^{(0)} | F^i \{ J^{(3)} \} - E_{\text{Coul,SCF}}^{(3)} | t^{(0)} \rangle \\ & + \langle t^{(1)} | F^i \{ J^{(1)} \} - E_{\text{Coul,SCF}}^{(1)} | t^{(1)} \rangle \\ & + \langle \Psi | [\zeta^{(0)}, J^{(3)}] | \Psi \rangle + \langle \Psi | [\zeta^{(1)}, J^{(2)}] | \Psi \rangle. \end{aligned} \quad (29)$$

3. Results and discussion

3.1. Choice of parameter K in SIMPER-1K

In the SIMPER-1K approach, the total Hamiltonian of the interacting system, $H(K)$, depends on the external parameter K , which appears in the additional ‘charge density overlap’ operator V_{eff} . In this work, $K=3$ is used for the following reason. Figure 2 shows, in the SIMPER-1K approach, the dependence of the SCF Coulomb interaction energy on the value of parameter K for the Ar_2 dimer at an interatomic separation of $R=5$ atomic units. For this system, $R=5$ atomic units lies well inside the region of the ‘Coulomb collapse’ (see figure 1). The uncorrected SCF Coulomb interaction energy ($K=0$) at $R=5$ atomic units therefore has an unphysically low value of $E_{\text{Coul,SCF}} \approx -835 \times 10^3 \text{ cm}^{-1}$. As the value of K increases, the amount of unphysical ‘charge transfer’ decreases, until, when K is greater than a critical value of about two atomic units, the uncorrected Coulomb energy becomes stable at approximately $2 \times 10^3 \text{ cm}^{-1}$, as shown by the square symbols in figure 2.

Two corrections to the modified Coulomb energy with respect to K are also presented in figure 2. The correction to first order is represented by circles and corresponds to the first two terms in equation (10), and the correction to second order (the whole expression (10) for the corrected Coulomb energy) is shown by stars. These lines clearly define a lower limit in K for validity of the SIMPER-1K approach. For the Ar_2 dimer, the lowest value of parameter K that could be used is two atomic units. A similar investigation for the remaining two systems gave similar results and it is suggested that a suitable value for K is three atomic units. This value of K is expected to be valid for most closed-shell dimers until well inside the equilibrium separation.

3.2. Calculations on Ar_2 , Ar-H_2 and Ar-HF dimers

Interaction energies are calculated for each of the three systems using the SIMPER-1K and SIMPER-1P methods, and the *ab initio* MP2 and CCSD(T) supermolecule methods. The full counterpoise correction of Boys and Bernardi [23] is applied to the supermolecule calculations, which are done using Molpro [24].

In the SIMPER-1K method, as in the supermolecule calculations, the core orbitals are frozen. MP2 theory is used as a ‘low’ level of dimer calculation, i.e. the exchange-repulsion and Coulomb interaction energies are obtained at the MP2 supermolecule level and the results are combined with quantities obtained from higher levels of theory in order to estimate potential energy surfaces with better accuracy. The CCSD theory is used as the ‘high’ level to calculate monomer charge densities, which are then used to obtain charge density

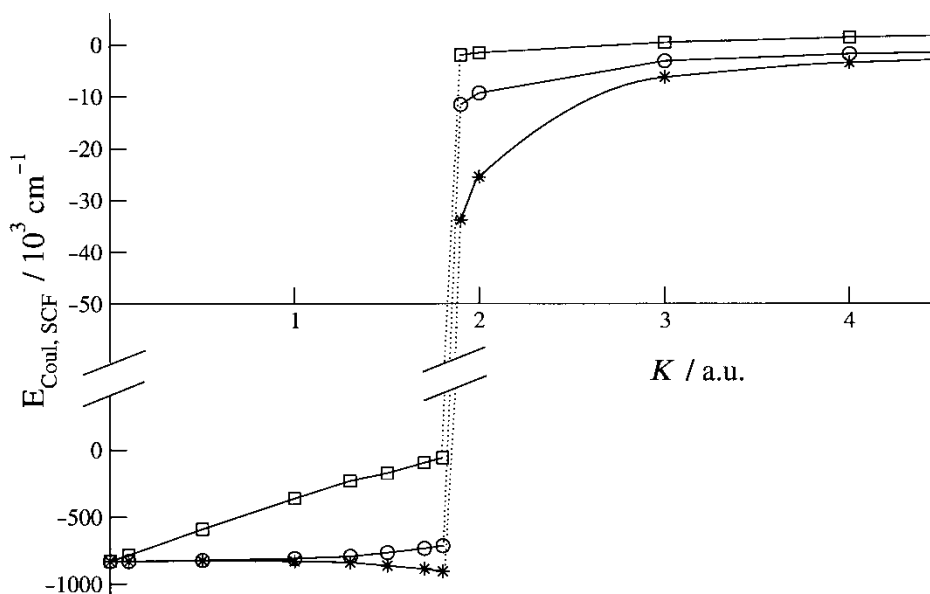


Figure 2. Modified SCF Coulomb interaction energy, $E_{\text{Coul,SCF}}^K$, and corrections to second order of the parameter K , for the Ar_2 dimer. Squares: $E_{\text{Coul,SCF}}^K$. Circles: $E_{\text{Coul,SCF}}^K$ plus the first-order correction (the second term in equation (10)). Stars: $E_{\text{Coul,SCF}}^K$ plus the first-order and second-order corrections (the second and third terms in equation (10)). The energies are calculated at $R = 5$ atomic units, with the SP-AV5Z basis set.

overlap integrals and first-order Coulomb interaction energies. Time-dependent configuration interaction with single and double substitutions, TD-CISD, is used to calculate dispersion energy coefficients. The method described in section 2.3 is used to obtain the SCF Coulomb interaction energy corrected to second order in the SCF charge density overlap. At $K = 0$ (SIMPER-1) the ‘Coulomb collapse’ occurs at short internuclear distances for the Ar_2 dimer ($R \approx 5.7$ atomic units) and near the equilibrium for the Ar-H_2 and Ar-HF systems ($R \approx 6.5$ atomic units).

In the SIMPER-1P approach, for technical reasons all electrons are correlated. In contrast to SIMPER-1K the method is not iterative and is expected to be faster for large systems. Coulomb interaction energies are calculated at the MP2 level to second or third order in V (SIMPER-1P-2, SIMPER-1P-3) and the exchange energy is defined as the difference between the counterpoise-corrected MP2 interaction energy and the Coulomb interaction energy in each case. As for SIMPER-1K, the first-order Coulomb energy and the exchange-repulsion energy are corrected using CCSD charge densities, and the dispersion energy is corrected using TD-CISD dispersion energy coefficients.

To obtain the dispersion energy accurately, the choice of basis set is important. The general-purpose correlation-consistent basis sets of Dunning and co-workers are widely used in the standard (cc-pVXZ) and augmented (aug-cc-pVXZ, d-aug-cc-pVXZ) forms from double- ζ ($X = \text{D}$) to quintuple- ζ ($X = 5$) [25]. In an attempt to improve basis sets for weak intermolecular

interactions, some authors include a few ‘bond-centred’ basis functions, located at or near the midpoint of the van der Waals bond and find it to be an effective way to recover most of the dispersion energy without needing basis functions with excessively large orbital angular momentum quantum numbers [26]. The basis set description can also be improved by shifting the exponents of the polarization functions. For the H (Ar, F) atoms, the exponents of each set of basis functions with angular momentum $l \geq 2$ ($l \geq 3$) are shifted to match the most diffuse p (d) functions [27]. This method is favoured by our group, because it performs equally well, has basis functions located only on nuclei and requires fewer basis functions. In this work the SP-AV5Z basis sets are used, obtained from the aug-cc-pV5Z basis sets of Dunning [28].

A polar coordinate system is used to define the geometries. The vector from the Ar atom to the F nucleus in HF, or to the H–H bond centre in H_2 , is denoted as \mathbf{R} and has length R . The angle between \mathbf{R} and the FH (or HH) direction is θ , which is zero at the linear Ar–F–H (or Ar–H–H) geometry.

3.3. Discussion

The calculated interaction energies are shown in tables 1–3, where the best available reference data for each system are also presented. In table 4 different contributions to the total energy at the potential minima are shown.

Overall, the MP2 method works better for the systems discussed in this paper than for those containing He or

Ne atoms (see [5]). The accuracy in the binding energy obtained with the MP2 method for the Ar₂ dimer is about 9% compared to the semi-empirical HFDID1 potential of Aziz [13]. For the T-shaped Ar–H₂ dimer, it is 12% compared to the XC (fit) potential of Bissonnette *et al.* [14]. Near the equilibrium geometry, the accuracy of the MP2 results is about 15% for linear Ar–F–H ($\theta = 0^\circ$) and 14% for linear Ar–H–F ($\theta = 180^\circ$), compared to the H6(4,3,2) potential of Hutson [15]. However, for the He₂ dimer, for example, the error in the MP2 results is about 37% compared to an accurate non-relativistic Born–Oppenheimer calculation [30].

Even though MP2 is a better starting point for these dimers, the SIMPER methods still improve the MP2 potentials. For Ar₂ (see table 1), SIMPER-1P shows a good agreement with the reference potential of Aziz [13], within about 2%, and for the SIMPER-1K method, the difference is less than 6%. Next, the two SIMPER methods are compared with the most accurate (and computationally expensive) supermolecule method currently available, CCSD(T). The SIMPER-1K binding energy agrees with the CCSD(T)

binding energy within 0.5%, whereas the SIMPER-1P result differs by about 3%. Note that the MP2 approach, using an amount of computational time similar to SIMPER, gives a 15% difference from the CCSD(T) method.

Table 2 shows the calculated interaction energies for the Ar–H₂ dimer. For this system, both SIMPER-1K and SIMPER-1P improve the accuracy of the potential equally well for linear and T-shaped geometries, to about 5% compared to the XC (fit) potential of Bissonnette [14] and to about 2% compared to the CCSD(T) results.

The main source of binding in the Ar₂ and Ar–H₂ dimers is the dispersion energy, while for the Ar–HF dimer the situation is more complicated. It can be seen from table 4 that in the $\theta = 0^\circ$ linear geometry, Ar–F–H, dispersion forces still dominate, but in the $\theta = 180^\circ$ linear geometry, Ar–H–F, the induction energy makes a large contribution to the interaction energy. In general, the more the induction energy contributes to the interaction energy, the more discrepancy between the SIMPER results and experiment one can expect. The

Table 1. Interaction energies E_{int} for Ar₂ dimer, obtained with the SP-AV5Z basis set using different methods. The Ar–Ar separation R is in atomic units.

R	$E_{\text{int}}/\text{cm}^{-1}$					Ref. [13]
	MP2	CCSD(T)	SIMPER-1K	SIMPER-1P-2	SIMPER-1P-3	
5.00	3320.09	3465.77	3594.55	3561.78	3303.11	3053.91
6.00	192.65	236.15	252.18	246.27	231.23	188.19
7.00	−108.09	−92.37	−91.49	−94.59	−95.15	−98.69
7.11	−108.74	−94.49	−94.00	−97.03	−97.43	−99.55
7.25	−106.65	−94.20	−93.97	−96.81	−97.07	−97.99
8.00	−76.56	−69.58	−70.06	−72.06	−72.09	−70.07
9.00	−40.25	−36.63	−36.55	−37.92	−37.92	−36.24
10.00	−20.90	−18.87	−18.86	−19.47	−19.47	−18.52

Table 2. Interaction energies E_{int} for Ar–H₂ dimer, obtained with the SP-AV5Z basis set using different methods. The angle θ is given in degrees; R is in atomic units.

R	θ	$E_{\text{int}}/\text{cm}^{-1}$					Ref. [14]
		MP2	CCSD(T)	SIMPER-1K	SIMPER-1P-2	SIMPER-1P-3	
5.00	0.0	933.07	950.73	1015.47	992.42	988.11	916.04
6.00	0.0	20.88	22.65	26.73	25.01	23.71	10.73
6.70	0.0	−51.71	−51.81	−52.76	−52.92	−53.25	−55.81
7.00	0.0	−52.56	−52.86	−54.17	−54.24	−54.40	−55.36
9.00	0.0	−16.77	−16.83	−17.24	−17.35	−17.35	−17.09
5.00	90.0	685.86	673.99	699.57	719.39	717.43	630.02
6.00	90.0	9.80	4.71	5.96	9.03	8.37	−3.31
6.70	90.0	−41.86	−44.71	−45.42	−44.83	−44.99	−47.68
7.00	90.0	−41.88	−44.11	−44.90	−44.70	−44.78	−46.14
9.00	90.0	−13.36	−13.76	−14.89	−14.12	−14.12	−14.06

Table 3. Interaction energies E_{int} for the Ar–HF dimer, obtained with the SP-AV5Z basis set using different methods. The angle θ is given in degrees and R is in atomic units. The angle $\theta=0^\circ$ corresponds to the Ar–F–H linear geometry and $\theta=180^\circ$ to the Ar–H–F linear geometry.

R	θ	$E_{\text{int}}/\text{cm}^{-1}$					Ref. [15]
		MP2	CCSD(T)	SIMPER-1K	SIMPER-1P-2	SIMPER-1P-3	
5.00	0.0	596.46	600.86	586.18	580.82	558.85	872.95
5.50	0.0	57.99	56.15	46.19	44.60	39.79	92.98
6.00	0.0	-77.06	-79.71	-85.47	-85.97	-86.97	-89.58
6.32	0.0	-91.33	-93.64	-97.63	-97.94	-98.34	-107.47
7.00	0.0	-72.55	-73.80	-75.67	-75.89	-75.98	-83.35
9.00	0.0	-18.72	-18.74	-18.98	-19.06	-19.08	-20.10
5.00	90.0	1074.81	1035.09	1003.49	983.97	888.51	1022.42
6.00	90.0	0.94	-19.38	-27.84	-30.12	-35.94	-34.34
6.53	90.0	-62.26	-74.98	-84.32	-79.97	-81.29	-82.90
7.00	90.0	-62.98	-71.19	-73.44	-73.88	-74.23	-75.74
9.00	90.0	-18.62	-19.89	-20.10	-20.15	-20.15	-20.70
5.00	180.0	2780.85	2831.70	2648.63	2638.77	2387.65	2685.63
6.00	180.0	-67.35	-76.29	-127.35	-124.67	-147.06	-116.69
6.40	180.0	-186.32	-196.65	-224.73	-223.47	-232.32	-216.23
7.00	180.0	-174.52	-182.34	-193.71	-193.68	-196.13	-190.64
9.00	180.0	-41.21	-42.35	-43.25	-43.50	-43.53	-45.72

 Table 4. Coulomb interaction energies and associated data at intermolecular separations R near the equilibrium values R_e . All energies are given in cm^{-1} , distances R and R_e are in atomic units. The SIMPER-1K data are denoted by (1K) and the SIMPER-1P data by (1P). The calculations, and the ‘low’ and ‘high’ levels of theory, are described in the text.

	Ar–H ₂			Ar–HF		
	Ar ₂	$\theta=0.0^\circ$	$\theta=90.0^\circ$	$\theta=0.0^\circ$	$\theta=90.0^\circ$	$\theta=180.0^\circ$
R_e [reference]	7.10 [13]	6.7 [14]	6.7 [14]	6.32 [29]	6.53 [29]	6.406 [29]
R	7.11	6.70	6.70	6.32	6.53	6.40
$E_{\text{Coul,low}}^{(1)}$	-44.70	-29.10	-20.64	-43.76	-51.18	-99.51
$E_{\text{Coul,high}}^{(1)}$	-42.19	-28.45	-19.44	-40.87	-46.45	-93.21
$E_{\text{Coul,low}}^{(1)+(2)}$ (1P)	-272.96	-176.54	-128.45	-239.29	-238.44	-812.28
$E_{\text{Coul,low}}^{(1)+(2)+(3)}$ (1P)	-280.94	-193.89	-136.91	-246.39	-254.80	-994.23
$E_{\text{Coul,low}}$ (1K)	-277.91	-189.89	-136.09	-232.95	-227.48	-856.31
$E_{\text{disp,low}}^{(2)}$	-215.92	-132.70	-101.65	-175.46	-159.09	-330.98
$E_{\text{disp,high}}^{(2)}$	-195.24	-131.76	-102.64	-176.82	-172.83	-343.62
$S_{\rho,\text{high}}/S_{\rho,\text{low}}$	0.95	0.98	0.96	0.94	0.92	0.95

reason is that in the SIMPER-1 approach the induction energy is not improved, although it is believed that a higher-level treatment may change the value of the induction energy significantly; efficient methods for doing this are currently being investigated. In the T-shaped geometry of the Ar–HF dimer, the SIMPER well depth differs from the H6(4,3,2) potential of Hutson [15] by about 2%, which increases to 4% for SIMPER-1K for the linear Ar–H–F geometry (table 3). In the case of the linear Ar–F–H geometry, both SIMPER methods differ by 9% from the H6(4,3,2) potential.

For the three systems, the SIMPER approach performs well at long and intermediate distances, which is an argument in favour of the dispersion energy model chosen in the current version of SIMPER. At short distances, the induction component of the interaction energy becomes significant and, therefore, the correction of this component is more important. In the SIMPER-1P approach, the contribution of higher-order energies in the perturbation expansion of the Coulomb energy may be another source for the discrepancies in the resulting interaction energies. This might be important

when going beyond the first-order response of the wavefunction (the third-order interaction energy), but as tables 1–3 show, truncation at second order in the Coulomb energy does not change the results of the extrapolation procedure significantly, compared to truncation at third order. The largest difference is for the linear Ar–H–F geometry, where the extrapolated SIMPER-1P-3 potential is 4% lower than the SIMPER-1P-2 potential at the minimum. This difference is due to the fact that the Coulomb contribution is the largest for this geometry and the exchange-repulsion energy, obtained as the difference between the total supermolecule energy and the finite-order Coulomb energy, is ‘contaminated’ by higher-order induction contributions. This ‘contamination’ is greater for SIMPER-1P-2 and it is surprising, therefore, that it gives better agreement with experiment than SIMPER-1P-3. This fact will need further investigation.

4. Summary

Two methods, SIMPER-1K and SIMPER-1P, for improving supermolecule calculations of the intermolecular potential energy are described. Both methods successfully resolve the issue of ‘Coulomb collapse’ occurring in the Coulomb approximation. The methods are applied to Ar–Ar, Ar–H₂ and Ar–HF complexes, and show excellent agreement with experimentally derived intermolecular potentials for the three systems. The cost of both methods is approximately equal to MP2, but the agreement with experiment is similar to, or better than, CCSD(T). There are some further improvements to SIMPER which can be considered. Scaling of the second-order induction component of the interaction energy is required for interactions involving ions or polar molecules; here, the knowledge of high-level non-expanded induction energies and accurate charge densities is important. It may also be useful to investigate the possibility of a complete basis set extrapolation of the SIMPER interaction energy. Finally, it is emphasized that the SIMPER theories produce a useful decomposition of the interaction energy into different contributions, and that the extrapolation methods used are general and can be applied to a wide variety of ‘low-level’ calculation methods.

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