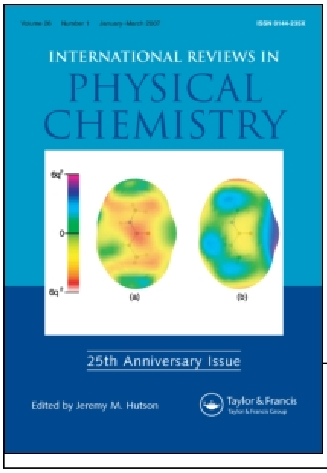

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

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To cite this Article: Wheatley, Richard J., Tulegenov, Akyl S. and Bichoutskaia, Elena (2004) 'Intermolecular potentials from supermolecule and monomer calculations', International Reviews in Physical Chemistry, 23:1, 151 — 185

To link to this article: DOI: 10.1080/01442350420020772
URL: http://dx.doi.org/10.1080/01442350420020772

INT. REVIEWS IN PHYSICAL CHEMISTRY, 2004
VOL. 23, NO. 1, 151–185

Intermolecular potentials from supermolecule and monomer calculations

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The use of monomer properties to improve supermolecule calculations of intermolecular potentials is reviewed. For Van der Waals dimers, the MP2 supermolecule method is too inaccurate for most purposes, and the CCSD(T) supermolecule method requires too much computer time for large molecules. Using perturbation theory to analyse the MP2 supermolecule energy shows that the second-order dispersion energy is the main source of the inaccuracy. It is shown that the dispersion energy can be improved by using more accurate dispersion energy coefficients which can be obtained from monomer frequency-dependent polarizabilities. The supermolecule MP2 electrostatic and exchange-repulsion interaction energies can also be recalculated or scaled to a higher level of theory, using monomer charge densities. Applying these corrections to the MP2 supermolecule energy does not require much additional computer time, and gives potential energy surfaces with comparable accuracy to supermolecule CCSD(T) calculations. Possible extensions of the method to different supermolecule methods and to larger molecules are discussed.

Contents

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International Reviews in Physical Chemistry ISSN 0144–235X print/ISSN 1366–591X online © 2004 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/01442350420020772

1. Background

Hydrogen bonds and Van der Waals bonds hold collections of molecules together to form macroscopic molecular assemblies such as liquids, solutions and molecular solids, and microscopic molecular assemblies such as dimers, trimers and clusters. The bonds between molecules are not formed primarily by sharing of electrons, and they are therefore quite different from the covalent bonds which hold atoms together to form the individual molecules. The relatively weak attraction between closed-shell molecules means that intermolecular bonds are not rigid, and can be easily deformed or broken at room temperature. The structural, thermal and dynamical behaviour of molecular assemblies depend on the intermolecular potential which describes the strength and direction of the intermolecular bonds. Calculating or measuring the intermolecular potential is the most important step in understanding these properties.

Intermolecular potentials have been obtained from experimental properties including gas non-ideality, collision cross-sections [1] and Van der Waals spectra [2, 3], and from theoretical calculations [4, 5] based on quantum chemistry. Experimental and theoretical methods are complementary, with experiments typically giving a smaller number of relatively accurate results, and calculations giving a larger number of less accurate results which can be refined and improved by comparison with experiment. Recently, the increase in computer power has seen theory play a more dominant role, and this review concentrates on theoretical calculations of intermolecular potentials.

Calculating intermolecular potentials is notoriously difficult. For covalent bonds, it is often adequate to know the equilibrium bond length and bond energy, but this is not the case for the highly non-rigid bonds between molecules, which can sample geometries far from equilibrium as a result of zero-point and thermal effects. Even for the simplest case of two molecules, the intermolecular potential energy surface is a function of up to six coordinates. Obtaining this surface computationally usually involves interpolation between individual calculations of the intermolecular potential at different geometries, and for a six-dimensional potential energy surface, thousands of separate calculations may be required to make the interpolation sufficiently accurate.

The nature of the bonding in Van der Waals molecules also complicates theoretical calculations of the intermolecular potential. The Hartree–Fock (HF) method describes covalent bonding reasonably well as a first approximation, and it can be improved by calculating the electron correlation using either density functional theory (DFT) or more expensive and more accurate post-Hartree–Fock methods. However, Van der Waals bonding is entirely the result of electron correlation, and the Hartree–Fock method predicts no Van der Waals attraction between molecules. Density functional theory gives 'local' correlation, but the correlation in Van der Waals bonds is 'non-local', so density functional theory also predicts no Van der Waals attraction. It is therefore necessary to use post-Hartree–Fock methods to obtain the electron correlation. These are often prohibitively demanding of computer resources, especially considering the number of different calculations required to cover the potential energy surface, and the accuracy of each calculation converges slowly with the size and expense of the method, because a percentage error in the intermolecular correlation energy gives a similar percentage error in the intermolecular potential.

Since high-accuracy theoretical calculations may not always be feasible, this review addresses the possibility of modifying relatively low-cost calculations of intermolecular potentials to improve their accuracy. The low-cost theoretical method chosen as the starting point may depend on the circumstances, but the method considered in most detail here is second-order Møller–Plesset perturbation theory (MP2). This method gives reasonable accuracy relative to the amount of computer time that it uses. MP2 calculations take longer than HF or DFT calculations, but give much better accuracy, whereas coupled-cluster (CCSD) calculations take longer than MP2 calculations, but usually do not give better accuracy. The best accuracy is obtained from CCSD(T) calculations, but these are very time-consuming, even for small molecules. It is therefore reasonable to use MP2 to obtain a first approximation to the intermolecular potential. However, MP2 calculations can still give errors of up to 50% in weak Van der Waals bond energies.

To improve the results of MP2 calculations, the intermolecular potential is divided into components (including electrostatic, induction, dispersion and exchange-repulsion energies) using perturbation theory. This is described in section 2.1. The results provide a link between supermolecule methods, where the intermolecular potential is calculated as a difference between the energy of the molecular assembly and the energies of its constituent molecules, and perturbation methods, where the intermolecular potential is calculated as a sum of different components. Perturbation methods are reviewed briefly in section 2.2.

Both supermolecule and perturbation methods can be time-consuming, and they have complementary strengths and weaknesses. Perturbation methods can be used to obtain accurate low-order contributions to the intermolecular potential; this is discussed in section 3.1. However, high-order contributions cannot be calculated efficiently. Supermolecule methods produce a sum of low-order and high-order contributions, but the accuracy of the low-order contributions to the energy is generally less than can be obtained using perturbation theory. In the main part of this review, section 3.2, strategies for combining supermolecule and perturbation methods are discussed. The most recent contributions made to this area by our research group are the SPT and SIMPER methods. These are reviewed in detail in section 3.2.2. Results obtained from these methods are presented in section 4, and it is shown that the SIMPER method, which takes not much more computer time than MP2 supermolecule calculations, improves the accuracy of MP2 intermolecular potentials substantially, making them comparable with the accuracy of CCSD(T) supermolecule calculations.

2. Components of the intermolecular potential

The general principles underlying the division of supermolecule calculations of the intermolecular potential into Coulomb and exchange-repulsion parts are introduced in this section. A Rayleigh–Schrödinger perturbation expansion gives the familiar components of the Coulomb energy, which can be related to properties of the interacting molecules. Full details are given for the Hartree–Fock and second-order Møller–Plesset methods. Methods for calculating individual components of the intermolecular potential are reviewed, and some common problems are identified.

A supermolecule method involves calculating the energies $E_A, E_B, \ldots$ of the individual molecules $A, B, \ldots$, and the energy E of the 'supermolecule' $AB\ldots$, and deducing the intermolecular potential ΔE. For a dimer,

$$\Delta E = E - E_A^{\{AB\}} - E_B^{\{AB\}} \tag{1}$$

where $E_A^{\{AB\}}$ is the energy of molecule A calculated in the dimer-centred basis set, to correct for basis set superposition error. If the energies are calculated using an expansion of the wave function in basis functions centred on the nuclei of A and B, it is possible to define a Coulomb interaction energy,

$$\Delta E_{\mathrm{Coul}} = E_{\mathrm{Coul}} - E_A - E_B. \tag{2}$$

The exchange-repulsion interaction energy is then obtained from

$$\Delta E_{\mathrm{exch}} = \Delta E - \Delta E_{\mathrm{Coul}}. \tag{3}$$

The Coulomb interaction energy defined in equation (2) is not affected by basis set superposition error, unlike the total interaction energy defined in equation (1). It is therefore necessary to calculate the energies E_A and E_B in the dimer-centred basis set in equation (1), and in the monomer-centred basis set in equation (2). If the energies E_A and E_B are defined in the same way in the two equations, then the exchange-repulsion energy as defined by equation (3) contains basis set superposition error, and is generally found to be unphysically negative at medium-to-large intermolecular distances.

In equation (2), the dimer 'Coulomb' energy, E_{Coul}, is calculated in the same way as the supermolecule energy E, but the Coulomb calculation 'distinguishes' the electrons of A from the electrons of B (that is, the Pauli principle is not applied between them), and the electrons of A are restricted to orbitals defined by basis functions on A, and similarly for B. In practice, this can be achieved by ignoring all integrals which involve products of basis functions on A and B. This includes intermolecular overlap, kinetic energy and nuclear attraction integrals. Electron repulsion integrals $(\alpha\beta|\gamma\delta)$ are ignored unless the orbital α is on the same molecule as β, and γ is on the same molecule as δ. In post-Hartree–Fock methods based on substitution of occupied by virtual orbitals, each occupied/virtual orbital pair must belong to a single molecule.

At the Hartree–Fock level, the dimer Coulomb energy is variational, and is calculated by minimizing the energy of a dimer Coulomb wave function of the form

$$\psi_{\mathrm{Coul,HF}} = \psi_{A,\mathrm{Coul}}(1, \ldots, n_A)\psi_{B,\mathrm{Coul}}(n_A + 1, \ldots, n_A + n_B), \tag{4}$$

where n_A is the number of electrons of A, n_B is the number of electrons of B, $\psi_{A,\mathrm{Coul}}$ and $\psi_{B,\mathrm{Coul}}$ are determinants of molecular orbitals of A and B, and these molecular orbitals are linear combinations of basis functions of A and B respectively. The exact dimer Hamiltonian is used in the calculation, and the molecular orbitals of each molecule therefore include the response to the Coulomb potential of the other molecule. In perturbation theory, this response is correct to all orders of the intermolecular interaction.

At the MP2 level, the Coulomb wave function is written as a sum of the Coulomb Hartree–Fock wave function from equation (4), plus three different types of double excitation: double excitations on A, double excitations on B, and simultaneous single excitations on both A and B. Like the Coulomb Hartree–Fock wave function, these are all direct products of two determinants, one for each molecule, and they are constructed from the Coulomb Hartree–Fock molecular orbitals. The usual MP2 equations are used to obtain the amplitudes and the resulting energy.

Coulomb and exchange-repulsion interaction energies can be calculated in a similar way for other post-Hartree–Fock methods, but no results have yet been reported in the literature.

2.1. *Analysing supermolecule calculations using perturbation theory*

In the Coulomb approximation, it is possible to define the unperturbed system and the perturbation uniquely, and to obtain contributions to the Coulomb interaction energy at different orders of perturbation theory. The unperturbed Hamiltonian, $H^{(0)}$, is the sum of the monomer Hamiltonians of A and B, and the perturbation, $V = H - H^{(0)}$, is the sum of all the intermolecular Coulomb interactions between electrons and nuclei. The zero-order energy is then $E_A + E_B$, calculated in the monomer-centred basis sets, and the Coulomb interaction energy, ΔE_{Coul}, can be expanded using Rayleigh–Schrödinger perturbation theory as a sum of first-order, second-order and higher-order terms in V. The first-order term, $\Delta E^{(1)}_{\mathrm{Coul}}$, is the classical electrostatic interaction energy, and the second-order term, $\Delta E^{(2)}_{\mathrm{Coul}}$, is a sum of induction and dispersion components, $\Delta E^{(2)}_{\mathrm{ind}}$ and $\Delta E^{(2)}_{\mathrm{disp}}$. Explicit expressions for these and higher-order components of the Coulomb energy can be obtained for variational supermolecule methods such as Hartree–Fock (HF) and configuration interaction (CI), and also for non-variational methods such as Møller–Plesset (MP) and coupled-cluster (CC), using a Lagrangian formalism. Details for the Hartree–Fock and MP2 methods are given here.

The general expression for the Hartree–Fock Coulomb energy is

$$E_{\mathrm{Coul,\,HF}} = \langle 0|J|0\rangle, \tag{5}$$

where $|0\rangle = |\psi_A(1,\ldots,n_A)\psi_B(n_A+1,\ldots,n_A+n_B)\rangle$ is the product of the unperturbed monomer Hartree–Fock wave functions, and the effective Hamiltonian J is defined as [6]

$$J = \exp(-\kappa)H\exp(\kappa), \tag{6}$$

where κ is the orbital rotation operator resulting from the intermolecular perturbation. It is obtained from the condition

$$\frac{\partial E_{\mathrm{Coul,\,HF}}}{\partial\kappa} = 0 \tag{7}$$

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

$$\langle 0|[X,[\kappa^{(1)},H^{(0)}]]|0\rangle + \langle 0|[X,V]|0\rangle = 0, \tag{8}$$

where X is a general single (de-)excitation operator. The occupied–occupied and virtual–virtual blocks of κ are zero, and in the Coulomb approximation, κ is a sum of operators κ_A and κ_B restricted to the monomer subspaces of A and B, respectively.

The effective Hamiltonian in equation (6) is expanded in powers of the perturbation V [6], and the Coulomb interaction energy in the Hartree–Fock approximation is then obtained by substituting this expansion into equation (5). The zero-order Coulomb energy, $E^{(0)}_{\mathrm{Coul,\,HF}}$, is the sum of the Hartree–Fock monomer energies, $E_{A,\mathrm{HF}}$ and $E_{B,\mathrm{HF}}$, so the Hartree–Fock Coulomb interaction energy is the sum of all higher-order terms.

The first-order Hartree–Fock Coulomb interaction energy is

$$\Delta E^{(1)}_{\mathrm{Coul,\,HF}} = \langle 0|V|0\rangle. \tag{9}$$

This is the electrostatic interaction between the unperturbed Hartree–Fock charge densities of the molecules, $\rho_{A,\mathrm{HF}}$ and $\rho_{B,\mathrm{HF}}$. It is most important for ions and hydrogen-bonding interactions, but it cannot be neglected for any molecular dimer.

At second order,

$$\Delta E^{(2)}_{\mathrm{Coul,\,HF}} = \frac{1}{2}\langle 0|[\kappa^{(1)}, V]|0\rangle. \tag{10}$$

This is the induction energy produced by the coupled Hartree–Fock response of A to the Hartree–Fock density of B and vice versa. There is no dispersion energy at the Hartree–Fock supermolecule level. The induction energy is important for interactions involving at least one ion or polar molecule.

At third order,

$$\Delta E^{(3)}_{\mathrm{Coul,\,HF}} = \frac{1}{6}\langle 0|[\kappa^{(1)}, [\kappa^{(1)}, [\kappa^{(1)}, H^{(0)}]]]|0\rangle + \frac{1}{2}\langle 0|[\kappa^{(1)}, [\kappa^{(1)}, V]]|0\rangle. \tag{11}$$

This corresponds to hyperpolarization of A by B, and vice versa, and to the electrostatic interaction between polarized densities of A and B.

Using the same notation as in equation (5), the MP2 Coulomb energy is written as

$$E_{\mathrm{Coul,\,MP2}} = \langle 0|J|0\rangle + \langle t|J|0\rangle, \tag{12}$$

where $|t\rangle$ is a linear combination of doubly excited determinants,

$$|t\rangle = \sum_{\mu} t_{\mu}|\mu\rangle, \tag{13}$$

with the restriction that all excitations of individual electrons are restricted to monomer subspaces. The amplitudes satisfy the equation

$$\langle 0|J|\mu\rangle = -\sum_{\nu} t_{\nu}\langle \mu|F^{i}\{J\} - E_{\mathrm{Coul,\,HF}}|\nu\rangle, \tag{14}$$

where $F^{i}\{J\}$ is the inactive Fock operator [7] of operator J. The general expression for the MP2 Coulomb energy Lagrangian is therefore [6, 8]

$$E_{\mathrm{Coul,\,MP2}} = \langle 0|J|0\rangle + 2\langle t|J|0\rangle + \langle t|F^{i}\{J\} - E_{\mathrm{Coul,\,HF}}|t\rangle + \langle 0|[\zeta, J]|0\rangle, \tag{15}$$

where the last term is required to fulfil the Brillouin condition. The operator ζ is a sum of single (de-)excitations with amplitudes defined by Lagrange multipliers, and it is a sum of separate operators ζ_A, ζ_B for each molecule.

Computationally efficient expressions for the MP2 Coulomb energy can then be obtained by treating equation (15) as variational in all its parameters. The response equation (8) for $\kappa^{(1)}$ is obtained by making the Lagrangian stationary with respect to ζ. Making the Lagrangian stationary with respect to t_{μ} gives equation (14), from which expressions are obtained for the zero-order amplitudes

$$\sum_{\nu} t^{(0)}_{\nu}\langle \mu|F^{i}\{H^{(0)}\} - E^{(0)}_{\mathrm{Coul,\,HF}}|\nu\rangle = -\langle 0|H^{(0)}|\mu\rangle \tag{16}$$

and the first-order amplitudes

$$\sum_{\nu} t_{\nu}^{(1)} \langle \mu | F^{i}\{H^{(0)}\} - E^{(0)}_{\mathrm{Coul,\,HF}} | \nu \rangle = -\langle 0 | J^{(1)} | \mu \rangle - \langle \mu | F^{i}\{J^{(1)}\} - \Delta E^{(1)}_{\mathrm{Coul,\,HF}} | t^{(0)} \rangle. \quad (17)$$

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 of the intermolecular interaction are then obtained by expanding the Lagrangian in powers of V. At first order,

$$\Delta E^{(1)}_{\mathrm{Coul,\,MP2}} = \Delta E^{(1)}_{\mathrm{Coul,\,HF}} + \langle t^{(0)} | F^{i}\{J^{(1)}\} - \Delta E^{(1)}_{\mathrm{Coul,\,HF}} | t^{(0)} \rangle + \langle 0 | [\zeta^{(0)}, J^{(1)}] | 0 \rangle. \quad (18)$$

If the MP2 charge density is separated into the Hartree–Fock density and the MP2 correction,

$$\rho_{A,\,\mathrm{MP2}} = \rho_{A,\,\mathrm{HF}} + \delta\rho_{A,\,\mathrm{MP2}} \quad (19)$$

the first-order MP2 Coulomb energy includes the interaction of $\rho_{A,\,\mathrm{HF}}$ with $\delta\rho_{B,\,\mathrm{MP2}}$ and $\delta\rho_{A,\,\mathrm{MP2}}$ with $\rho_{B,\,\mathrm{HF}}$, but does not include the interaction of the MP2 corrections with each other.

At second order,

$$\begin{aligned}\Delta E^{(2)}_{\mathrm{Coul,\,MP2}} = {} & \Delta E^{(2)}_{\mathrm{Coul,\,HF}} + 2\langle t^{(0)} | J^{(2)} | 0 \rangle + \langle t^{(1)} | J^{(1)} | 0 \rangle \\ & + \langle t^{(1)} | F^{i}\{J^{(1)}\} - \Delta E^{(1)}_{\mathrm{Coul,\,HF}} | t^{(0)} \rangle \\ & + \langle t^{(0)} | F^{i}\{J^{(2)}\} - \Delta E^{(2)}_{\mathrm{Coul,\,HF}} | t^{(0)} \rangle \\ & + \langle 0 | [\zeta^{(0)}, J^{(2)}] | 0 \rangle. \end{aligned} \quad (20)$$

This expression includes an induction energy component, which can be expressed in terms of the molecular charge densities ρ and the molecular 'susceptibilities' P [9]. The susceptibility is the response of the density to a change in the external electrostatic potential. If the MP2 susceptibility of molecule A is separated into the coupled Hartree–Fock susceptibility $P_{A,\,\mathrm{HF}}$ and the MP2 correction $\delta P_{A,\,\mathrm{MP2}}$, the second-order MP2 Coulomb interaction energy includes contributions from $P_{A,\,\mathrm{HF}}\rho_{B,\,\mathrm{HF}}\delta\rho_{B,\,\mathrm{MP2}}$ and $\delta P_{A,\,\mathrm{MP2}}\rho_{B,\,\mathrm{HF}}\rho_{B,\,\mathrm{HF}}$, but has no terms involving more than one MP2 correction.

The second-order MP2 energy also includes a dispersion energy component, which is the contribution to $\langle t^{(1)} | J^{(1)} | 0 \rangle$ in equation (20) from single excitations on A and B. This term is classified as dispersion, rather than induction, because it has a long-range component even for spherical interacting atoms. That is, it does not depend on κ or $F^{i}\{V\}$.

At third order,

$$\begin{aligned}\Delta E^{(3)}_{\mathrm{Coul,\,MP2}} = {} & \Delta E^{(3)}_{\mathrm{Coul,\,HF}} + 2\langle t^{(0)} | J^{(3)} | 0 \rangle + 2\langle t^{(1)} | J^{(2)} | 0 \rangle \\ & + 2\langle t^{(0)} | F^{i}\{J^{(2)}\} - \Delta E^{(2)}_{\mathrm{Coul,\,HF}} | t^{(1)} \rangle \\ & + \langle t^{(0)} | F^{i}\{J^{(3)}\} - \Delta E^{(3)}_{\mathrm{Coul,\,HF}} | t^{(0)} \rangle \\ & + \langle t^{(1)} | F^{i}\{J^{(1)}\} - \Delta E^{(1)}_{\mathrm{Coul,\,HF}} | t^{(1)} \rangle \\ & + \langle 0 | [\zeta^{(0)}, J^{(3)}] | 0 \rangle + \langle 0 | [\zeta^{(1)}, J^{(2)}] | 0 \rangle. \end{aligned} \quad (21)$$

There is no dispersion energy contribution to the MP2 supermolecule energy at third order in V, because all the terms in this equation involve κ or $F^i\{V\}$ explicitly or implicitly. Induction and 'mixed' induction/dispersion terms can be identified, but they will not be considered separately in this review.

2.2. *Direct calculation of intermolecular potentials using perturbation theory*

Methods based on perturbation theory do not usually correspond exactly to the perturbation expansion of supermolecule energies discussed in section 2.1. Instead, perturbation theory is applied to the wave function of the dimer, giving formally exact expressions for the intermolecular potential to different orders of the interaction operator V. In order to make the calculations tractable, the first-order, second-order and higher-order energies are evaluated by making approximations to the wave functions appearing in the perturbation expressions. Depending on the nature of these approximations, the interaction energy at each order of V may contain different terms than expanded supermolecule energies.

The most highly developed and widely used perturbation theory for intermolecular potentials is symmetry-adapted perturbation theory (SAPT) [10]. This is based on the symmetrized Rayleigh–Schrödinger (SRS) perturbation theory [11], which differs from the Coulomb perturbation theory described in section 2.1 in that SAPT calculates the energies at different orders in the perturbation using antisymmetrized Coulomb wave functions [12]. (Note that 'Coulomb' in this review means the same as 'polarization' in the SAPT papers.) Antisymmetrizing the wave functions enables the exchange-repulsion interaction energy to be obtained from SAPT. The first-order SAPT interaction energy includes the first-order Coulomb energy, together with a first-order exchange-repulsion energy which is obtained by antisymmetrizing the zero-order dimer Coulomb wave function over all electron coordinates. The second-order interaction energy includes induction and dispersion, and also exchange-induction and exchange-dispersion interaction energies [13, 14].

The convergence of the perturbation expansion of the Coulomb interaction energy, and of the SAPT/SRS perturbation theory, has been investigated for several Van der Waals dimers [15, 16]. The main problem with the Coulomb perturbation theory is that the formal definition of the Coulomb interaction energy, equation (2), cannot be used at short range for some interactions, because even at the Hartree–Fock level the Coulomb wave function is unphysical. The electrons of molecule A are not constrained to be in orbitals orthogonal to the orbitals of B, and since the Pauli principle does not apply between them, the electrons of A can be unphysically transferred to the occupied orbitals of B, and vice versa. This produces a Pauli-forbidden state with lower energy than the Pauli-allowed states. For example, in a complex between a two-electron molecule A with one occupied molecular orbital A_1, and a four-electron molecule B with two occupied molecular orbitals B_1 and B_2, the 'physical' Pauli-allowed Coulomb wave function is $|A_{1\alpha}A_{1\beta}| \times |B_{1\alpha}B_{1\beta}B_{2\alpha}B_{2\beta}|$, and the 'unphysical' Pauli-forbidden states include $|A_{1\alpha}A_{1\beta}| \times |B_{1\alpha}B_{1\beta}A_{1\alpha}A_{1\beta}|$, where the electrons in the first determinant, which belong to A, are distinguished from the electrons in the second determinant, which belong to B. This state could be reached in a Coulomb energy calculation, if the basis set of B were large enough to describe the molecular orbitals of A.

This unphysical behaviour can occur around the Van der Waals equilibrium separation for interactions between molecules involving first-row and second-row atoms which are described using very large basis sets. Equation (2) is not useful under these circumstances, and Coulomb perturbation theory cannot be used to high order, because the energy either diverges or converges to the Pauli-forbidden value. In the SRS perturbation theory the wave functions are calculated within the Coulomb approximation, so they also either diverge or converge to a Pauli-forbidden state, which affects the convergence of the energies calculated from them [17]. The use of either Coulomb or SRS perturbation theory therefore relies on rapid convergence to a physical state, so that the perturbation series can be truncated at second or third order in the energy, and slow approach to the unphysical state (that is, weak coupling between the physical and unphysical states), so that the second-order and third-order energies, which are retained in the perturbation expansion, are not significantly affected by mixing with the unphysical states. This is certainly true for Van der Waals interactions of small atoms at reasonably large separations [16], but more work on the behaviour of the perturbation series for larger systems is required.

To second order in V, the SAPT expansion of the intermolecular potential includes four Hartree–Fock terms: $E^{(10)}_{\mathrm{pol}}$, $E^{(10)}_{\mathrm{exch}}$, $E^{(20)}_{\mathrm{ind}}$ and $E^{(20)}_{\mathrm{exch\text{-}ind}}$. The $E^{(10)}_{\mathrm{pol}}$ and $E^{(20)}_{\mathrm{ind}}$ terms are identical to $\Delta E^{(1)}_{\mathrm{Coul,\,HF}}$ and $\Delta E^{(2)}_{\mathrm{Coul,\,HF}}$ from equations (9) and (10). The sum of all four Hartree–Fock terms gives a second-order perturbation expansion of the Hartree–Fock supermolecule interaction energy. The difference between the perturbation expansion and the supermolecule energy is a measure of the importance of higher-order Hartree–Fock energy contributions, and it has been calculated to be between 3 and 17% of the Hartree–Fock interaction energy for several molecular dimers [18]. This is a significant difference, and potential energy surfaces derived from SAPT usually incorporate higher-order Hartree–Fock energy contributions by replacing these four terms by the Hartree–Fock supermolecule interaction energy.

In addition, SAPT gives energy contributions arising from intramolecular and intermolecular electron correlation, of which the lowest-order and most frequently used terms are $E^{(1,\,2\leq l\leq 3)}_{\mathrm{pol}}$, $E^{(1,\,1\leq l\leq 2)}_{\mathrm{exch}}$, $E^{(2,\,0\leq l\leq 2)}_{\mathrm{disp}}$ and $E^{(2,0)}_{\mathrm{exch\text{-}disp}}$. The $E^{(1,2)}_{\mathrm{pol}}$ term is the same as the MP2 supermolecule correction to the first-order Coulomb energy in equation (18), and $E^{(2,0)}_{\mathrm{disp}}$ is the dispersion energy contribution to $\Delta E^{(2)}_{\mathrm{Coul,\,MP2}}$ in equation (20). The other E_{pol} and E_{disp} terms correspond to higher levels of electron correlation than supermolecule MP2. For Van der Waals interactions, it is particularly important to correct the MP2 dispersion energy using the $E^{(2,1)}_{\mathrm{disp}}$ and $E^{(2,2)}_{\mathrm{disp}}$ terms. A more complete discussion of the perturbation expansion of the MP2 supermolecule energy was given by Cybulski *et al.* [19], who also reported the basis set dependence of the different contributions.

The intermolecular perturbation theory (IMPT) of Hayes and Stone [20] also gives first-order exchange-repulsion and Coulomb interaction energies, and second-order induction, dispersion and exchange-dispersion energies. The sum of the first-order exchange-repulsion and Coulomb interaction energies is the Heitler–London interaction energy,

$$\Delta E_{\mathrm{HL}} = \frac{\langle\psi_0|H|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} - E_{A,\,\mathrm{HF}} - E_{B,\,\mathrm{HF}} = \Delta E^{(1)}_{\mathrm{Coul,\,HF}} + \Delta E^{(1)}_{\mathrm{exch,\,HF}} \tag{22}$$

where $|\psi_0\rangle$ is obtained by antisymmetrizing the zero-order Hartree–Fock Coulomb wave function $|0\rangle$ over all electronic coordinates, and the first-order Coulomb interaction energy is defined by equation (9). IMPT differs from SAPT in having a separate charge transfer interaction energy. Charge transfer occurs because the orbitals of A and B are treated differently in IMPT, and it corresponds to the transfer of one or more electrons from orbitals of A to B, or vice versa. The charge transfer energy is difficult to define uniquely, and estimates of its importance for hydrogen bonds range from 18% [21] to 4% [22]; most definitions are very sensitive to the basis set. When IMPT was used to produce a potential energy surface for the water dimer [23], the charge transfer was originally not included, as it was believed to be dominated by basis set superposition error. More recent IMPT potential energy surfaces for the water dimer [24], and for the hydrogen fluoride dimer [25], have included charge transfer contributions.

Perturbation theory and supermolecule calculations can therefore be compared to fixed orders in V, but they have the fundamental difference that the supermolecule calculations include terms to infinite order in V. The higher-order terms may be important, especially at short intermolecular separations where the interaction is strong. It is therefore useful to consider whether methods can be devised where high-order terms in V are obtained from supermolecule calculations, and low-order terms in V are obtained from perturbation theory. This is the main subject of the next section.

3. The use of monomer calculations

Perturbation theory gives expressions for some components of the intermolecular potential in terms of properties of the separated monomer molecules. The use of monomer calculations to obtain components of the intermolecular potential, where possible, is greatly preferable to supermolecule calculations. Monomers are smaller than dimers, and often have higher spatial symmetry; calculations on monomers are free of basis set superposition error, and do not need to be repeated at every intermolecular geometry for which the intermolecular potential is required. Approximate techniques, such as linear-scaling *ab initio* methods, can be used to improve the speed of monomer calculations, but they may introduce larger errors in supermolecule calculations [26], and in general the same level of *ab initio* theory gives better results in monomer calculations than in dimer calculations. For example, Hartree–Fock and density functional methods give reasonable dispersion energy coefficients when they are used in monomer calculations, but give no long-range dispersion energy in supermolecule calculations. Methods for calculating intermolecular potentials based mostly or entirely on monomer properties are reviewed in section 3.1, followed by more recent developments in using monomer properties to improve supermolecule calculations.

3.1. *Estimating intermolecular potentials from monomer properties*

Different components of the Coulomb interaction energy can be expressed exactly in terms of properties of the interacting molecules, and intermolecular Coulomb integrals. The first-order Coulomb energy can be written in terms of the charge densities (in atomic units) as

$$\Delta E^{(1)}_{\mathrm{Coul}} = \iint \rho_A(1)\rho_B(2)r_{12}^{-1}\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2, \tag{23}$$

or it can be expanded in a basis set,

$$\Delta E^{(1)}_{\mathrm{Coul}} = \rho_{A,pq}\rho_{B,rs}(pq|rs) \tag{24}$$

plus nuclear density contributions, where p, q, r and s are (atomic or molecular) orbitals, ρ_A and ρ_B are density matrices, $(pq|rs)$ is a two-electron integral, and the summation convention is used.

The second-order induction energy is

$$\Delta E^{(2)}_{\text{ind}} = -\frac{1}{2}\rho_{A,pq}\rho_{A,rs}P_{B,tuvw}(pq|tu)(rs|vw) + A \leftrightarrow B, \tag{25}$$

plus nuclear density contributions, where P_B is a polarization propagator [27, 28], which is essentially a basis set expansion of the susceptibility introduced in section 2.1. Similarly, the second-order dispersion energy can be written as an integral over imaginary frequency, using frequency-dependent polarization propagators of the monomers.

The two main problems with this approach are the computational cost of calculating and storing the densities and particularly the propagators, and the absence of similar relationships for the exchange-repulsion energy.

The dependence of the energy on the density and propagator matrices can be removed by using a multipole expansion, which expresses the intermolecular potential as a power series in R^{-1}, that is,

$$\Delta E_{\text{mult}} = -\sum_{n=1}^{\infty} C_n R^{-n}, \tag{26}$$

where R is some intermolecular separation, and C_n is a multipole coefficient which depends only on the molecular orientations, and not on the separation R. The multipolar interaction energy between two molecules can be formally defined by

$$\Delta E_{\text{mult}} = E_{\text{mult}} - E_A - E_B, \tag{27}$$

where E_{mult} is obtained by performing a supermolecule calculation, replacing all intermolecular electron repulsion and nuclear attraction integrals by their multipolar equivalents. The integrals neglected in the Coulomb interaction energy are also neglected in the multipolar interaction energy, so both calculations are free of basis set superposition error, exchange-repulsion is absent from ΔE_{mult}, and the monomer energies in equation (27) should be calculated in the monomer-centred basis sets.

Equation (27) is not useful by itself because ΔE_{mult} diverges as the basis set is enlarged, but in combination with a perturbation expansion, it can be used to give simplified expressions for the different components of the Coulomb interaction energy.

The multipolar first-order Coulomb interaction energy has been widely studied. Using the multipole expansion, the summation over orbital indices in equation (24) reduces to a (usually) much smaller sum over angular momentum indices l_A, l_B, m_A and m_B; the density matrices reduce to multipoles $Q_{A,lm}$ and $Q_{B,lm}$, and the two-electron integrals reduce to multipole integrals with a well-known dependence [29, 30] on the angular momentum indices and on the intermolecular geometry. For a Gaussian basis set, it is easy to show that the multipolar first-order Coulomb interaction energy can be approximated to any desired accuracy as a sum of interactions between atom-centred multipoles. The multipolar Coulomb interaction energy then takes the form of a sum of interatomic terms:

$$\Delta E_{\text{mult}} = -\sum_{a,b}\sum_{n=1}^{\infty} C_{n,ab} R_{ab}^{-n}, \tag{28}$$

where a and b are atoms of A and B, respectively, and R_{ab} is their internuclear distance. This atomic multipole expansion [31] converges when the intermolecular separation is larger than the intramolecular bond lengths, which is usually the case.

The multipolar first-order interaction energy can also be expressed as an interaction between molecule-centred multipoles, giving a very simple multipole expansion for the energy in the form of equation (26). However, this expansion only converges when the intermolecular distance is more than the sum of the radii of the interacting molecules, so it is useful only for very small molecules. Of course, the multipolar first-order interaction energy does not equal the 'non-expanded' first-order Coulomb interaction energy obtained from equation (24). The first-order Coulomb energy contains a non-multipolar component, called the penetration energy, which falls off approximately exponentially with separation. For typical Van der Waals complexes, the penetration energy is negative, and it cannot be neglected in calculating the intermolecular potential. For example, it provides about 40% of the binding energy of both the Van der Waals dimer Ar_2 [32] and the hydrogen-bonded dimer $(H_2O)_2$ [33].

The multipolar second-order interaction energy diverges at all intermolecular geometries for a complete basis set. This is illustrated in figure 1 for the helium dimer; note the behaviour of the upper dashed line compared to the upper solid line. The figure also shows the difficulty of calculating second-order Coulomb energies, whether using the multipole approximation or not. The lower solid and dashed lines show results obtained using the standard augmented correlation-consistent basis sets [34] which are widely used in quantum chemistry. The convergence to the basis set limit is very slow, and even for the aug-cc-pV6Z basis set the basis set incompleteness error is probably more than 10%. Calculations on larger molecules are not feasible using such large basis sets. Instead, it has been shown [35] that it is

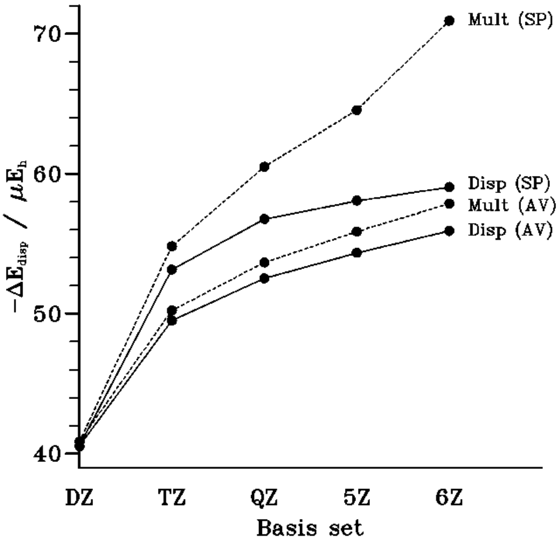

Figure 1. The second-order dispersion energy for the He_2 dimer, at a separation of $R = 5.5\,a_0$, calculated at supermolecule MP2 (monomer uncoupled Hartree–Fock) level. Dashed lines labelled 'Mult' use the multipole approximation, solid lines labelled 'Disp' do not. The lower solid and dashed lines labelled 'AV' are obtained using aug-cc-pVnZ basis sets, and the upper solid and dashed lines labelled 'SP' using the SP-aug-cc-pVnZ basis sets defined in the text.

possible to modify the aug-cc-pVnZ basis sets to improve the description of the dispersion energy without resorting to dimer-centred or midbond basis functions. For hydrogen and helium, the exponents of the n_l Gaussian basis functions for angular momenta $l \geq 2$ (d and higher functions) are changed to the n_l lowest exponents for angular momentum $l=1$ (p functions). For first-row and second-row atoms, Gaussian exponents with $l \geq 3$ are changed to the lowest d-function exponents. This simple modification makes the Gaussians with higher angular momentum more diffuse, and gives a better (although presumably still not optimal) basis set for calculating the dispersion energy. The new basis sets are called SP-aug-cc-pVnZ (SP for Shifted Polarization exponents). The upper solid line in figure 1 shows that the convergence to the basis set limit of the dispersion energy calculated with the SP basis sets is faster than with the standard basis sets, and in practice the saving in computer time achieved with the SP basis sets, for the same accuracy, is usually about a factor of 10.

Although the multipolar second-order energy always diverges in the complete basis set limit, for reasonably well-separated small molecules the multipole expansion follows the pattern of an asymptotically divergent series, and useful results can be obtained by summing the first few powers of R^{-1}. Using the multipole expansion, the summation over orbital indices in equation (25) again reduces to a sum over angular momentum indices, the density matrices reduce to multipoles, the two-electron integrals reduce to multipole integrals, and the polarization propagator reduces to a polarizability $\alpha_{B,lm,l'm'}$. The multipolar dispersion energy can similarly be calculated using frequency-dependent polarizabilities. In the multipolar dispersion energy, the coefficients C_n in equation (26) are called dispersion energy coefficients, and the minimum value of n is 6.

For small molecules, it is reasonable to calculate the multipolar second-order induction and dispersion energies using multipoles and polarizabilities located at the centres of the molecules, giving a single expression of the form of equation (26). For larger molecules, it is clearly necessary (as for the multipolar first-order energy) to use atom-centred multipoles and polarizabilities. Obtaining atom-centred polarizabilities has proved to be a difficult task [9], although there has been some promising progress in this area [36–40].

Given that the multipolar second-order energy diverges, it is not meaningful to define a second-order analogue of the penetration energy as the difference between the multipolar energy and the non-expanded energy. Instead, several 'damping' schemes have been considered (see below), in which each term $-C_nR^{-n}$ of the divergent multipole series is multiplied by a damping function $f_n(R)$ to make the series converge, ideally to the correct non-expanded energy. Damping functions have been published for several small atoms and ions [41–45], but accurate calculations are very time-consuming for larger systems.

The Coulomb energy at higher orders of V can be expanded as a multipole series in the same way as the second-order Coulomb energy. However, higher-order contributions are rarely considered explicitly. They suffer from the same divergence problems as the second-order energy, it is much more time-consuming to calculate even the leading multipole coefficients, less is known about the damping of higher-order interaction energies, and the contribution of higher-order terms to the intermolecular potential is usually relatively small.

Intermolecular potential energy surfaces based entirely on monomer calculations therefore usually include the first-order Coulomb interaction energy, the second-order multipolar dispersion (and induction) energy, damping of the dispersion (and induction) multipole series, and the exchange-repulsion interaction energy. The exchange-repulsion cannot be defined rigorously in terms of monomer properties, but several empirical models based on monomer properties have been devised. The simplest is the overlap model [46–48], which assumes that the exchange-repulsion interaction energy is proportional to the electron density overlap integral:

$$\Delta E_{\text{exch}} = KS_{\rho}, \tag{29}$$

where K is a parameter, and the electron density overlap integral S_{ρ} is defined by

$$S_{\rho} = \int \rho^{e}_{A}(\mathbf{r})\rho^{e}_{B}(\mathbf{r})\,\mathrm{d}\mathbf{r}, \tag{30}$$

where ρ^{e}_{A} is the unperturbed electron density of monomer A. The quantities $(S_{\rho})^{x}$ [49, 50] and $(S_{\rho}/R^{2})^{x}$ [51] have also been used in equation (29) instead of S_{ρ}, where x is a parameter and R is the intermolecular separation.

A linear relationship between the exchange-repulsion interaction energy and the first-order penetration energy has also been proposed [52, 53],

$$\Delta E_{\text{exch}} = -\gamma(1 + aR)(\Delta E^{(1)}_{\text{Coul}} - \Delta E^{(1)}_{\text{mult}}), \tag{31}$$

and calculating the exchange-repulsion energy from this equation also requires only monomer charge densities and the parameters γ and a. The parameter a is usually taken to be 0.1 atomic units. Long-range multipolar $1/R$ terms are not present in the exchange-repulsion energy or the penetration energy. However, short-range $1/R$ terms are present in the penetration energy, and for equation (31) to be applied to non-spherical molecules, these $1/R$ terms should be removed, which is difficult to do properly [54].

The parameters in equations (29) and (31) are often fitted to make the complete potential energy surface reproduce experimental or supermolecule data. This fitting procedure corrects for deficiencies elsewhere in the potentials, so the fitted exchange-repulsion is not necessarily an individually meaningful term in the total intermolecular potential. Methods for estimating the exchange-repulsion interaction energy with no empirical parameters have also been devised, including the surface integral model [55–57] and the spherical Gaussian overlap model [58–61]. The lack of parameters makes these methods preferable in principle to using equations (29) or (31), but in practice they currently seem to be too approximate to be capable of generating accurate intermolecular potential energy surfaces.

The monomer-based models for the exchange-repulsion interaction energy defined by equations (29) and (31) have been incorporated into methods for calculating complete intermolecular potentials, based entirely on monomer properties. The XC model, devised by Meath and co-workers, is based on equation (31) for the exchange-repulsion energy, and a damped multipole series for the dispersion energy [52, 53]. It is, in principle, completely based on monomer properties, namely charge densities and dispersion energy coefficients. Dispersion energy coefficients up to C_{10} are used, and the multipolar dispersion energy is damped as follows:

$$\Delta E_{\text{disp}} = -G(R)\sum_{n} C_{n} f_{n}(R) R^{-n}. \tag{32}$$

The 'individual damping functions' f_{n}, and the 'overall corrector function' G, are both based on near-exact calculations [41, 52] on the model Van der Waals dimer H_2

in its $^3\Sigma_u^+$ electronic state. The damping functions f_n correct each individual multipolar term C_nR^{-n} to the corresponding non-expanded term obtained from basis functions with angular momentum L_A on atom A and angular momentum L_B on atom B, where $n = 2L_A + 2L_B + 2$. The corrector function G accounts for the neglect of coefficients above $n = 10$, and for the spherical dispersion energy, which is obtained from states with $L_A = 0$ or $L_B = 0$ and has no multipole expansion. For other Van der Waals molecules, the damping functions and corrector function are assumed to differ only by a linear scaling of the length coordinate. Therefore, for a general dimer AB, damping functions are obtained using

$$f_n(R; AB) = f_n((X_{\mathrm{HH}} R/X_{AB}); \mathrm{HH}) \tag{33}$$

and similarly for G, where X_{AB} is some property of AB which increases with the 'sizes' of the interacting molecules. Different properties have been used in this context (see [42]); one simple property based on the dispersion energy coefficients is

$$X_{AB} = \sqrt{C_8(AB)/C_6(AB)}. \tag{34}$$

Using this property requires no additional data, since the C_6 and C_8 dispersion energy coefficients are already used in the XC model.

The XC model was originally used for calculating spherically symmetrical intermolecular potentials [62], but more recently the Heitler–London first-order interaction energy, given by equation (22), has been used in the XC model instead of the penetration energy, and potential energy surfaces have been calculated for Ar-N_2 [63], Kr-N_2 [64], Ar-H_2 [65] and Ne-N_2 [66].

The systematic potential method (SPM) is related to the XC method, but the exchange-repulsion energy is obtained from the overlap model, equation (29), rather than from the first-order Coulomb energy, equation (31). The use of the overlap model has the advantage that the charge density overlap is free from short-range $1/R$ terms, so equation (29) can be used without modification for any interacting molecules. Intermolecular potentials for Li^+-H_2O [67], Na^+-H_2O [33] and the water dimer [33] have been calculated using this method, with separate damped multipole series for the dispersion and induction energies.

The XC and SPM methods are often more accurate and faster to use than MP2 supermolecule calculations, but they are not as accurate or reliable as CCSD(T) supermolecule calculations. For example, they lack explicit exchange-induction terms, and the assumption that damping functions can be scaled from the triplet-H_2 intermolecular potential is sometimes not valid [42]. Since parameters in the exchange-repulsion energy need to be fitted to experimental data, XC and SPM are not true *ab initio* methods. To improve their accuracy, the monomer properties used to construct the XC and SPM potentials can be combined with supermolecule calculations, as described in the next section.

3.2. *Improving supermolecule calculations using monomer properties*

When the Coulomb and exchange-repulsion contributions to the supermolecule interaction energy are considered separately, both can be shown to depend strongly on the level of theory used to calculate them. Deficiencies in the low-level Coulomb interaction energy can be demonstrated using perturbation theory, as will be described in this section. In addition, calculations have shown that the exchange-repulsion interaction energy differs by up to 30% between Hartree–Fock and correlated calculations [68–70]. Given that some of their deficiencies are known, it is important to investigate whether it is possible to improve the results of low-level supermolecule calculations, without resorting to higher-level supermolecule calculations which may not be affordable.

3.2.1. *Methods based on Hartree–Fock and density functional theories*

The most obvious deficiency of low-level supermolecule calculations is the lack of a dispersion interaction energy in Hartree–Fock theory. This can be remedied by calculating the dispersion energy separately, and adding it to the Hartree–Fock interaction energy. A popular method for doing this is the Hartree–Fock plus damped dispersion (HFD) method.

In the HFD method, the dispersion energy is calculated using a damped multipole series of the form of equation (32). The individual damping functions $f_n(R)$ are defined in the same way as in the XC model, although a different functional form is used to represent them. However, the HFD corrector function $G(R)$ is intended [71] to account for the exchange-dispersion, which is missing from the Hartree–Fock supermolecule calculation, so it is different from the XC corrector function. The property X_{AB} used to scale the length coordinate of the damping functions in equation (33) is based on the ionization energies of the monomers. The HFD method was first used to calculate potential energy surfaces for rare gas atoms and hydrogen [72]. Related methods have more recently been described with Heitler–London instead of Hartree–Fock calculations, and used to calculate intermolecular potentials for a number of interactions including the nitrogen [73] and carbon monoxide [74] dimers.

Like the HFD model, the Tang–Toennies (TT) model was originally based on Hartree–Fock supermolecule calculations and a damped multipole series for the dispersion energy. More dispersion energy coefficients are included in the TT model than in the HFD or XC models, by estimating the higher dispersion energy coefficients from the lower ones based on a reasonable empirical relationship. The TT dispersion damping does not, therefore, need to take account of missing higher terms in the multipole series. No corrector function $G(R)$ is present in the TT model. The TT damping functions $f_n(R)$ used to damp the C_n multipolar term are incomplete gamma functions of order $n+1$ [68]:

$$f_n(R) = 1 - \sum_{k=0}^{n} \frac{(bR)^k}{k!}\,\mathrm{e}^{-bR}, \qquad (35)$$

where b is a constant. These behave differently, as a function of n, from the XC individual damping functions. It is reasonable for the two to be different, because a correction for the spherical dispersion must be included in the TT individual damping functions, but not in the XC individual damping functions. However, the TT damping functions are more empirical, because the XC and HFD damping functions are based on exact calculations, whereas the TT damping functions are simply physically reasonable functions of R. Unlike the HFD model, the exchange-dispersion energy is not included in the TT model through the damped multipole series. (In this context, it is ironic that the TT damping functions appear to represent the dispersion plus exchange-dispersion energy of Ar_2 better than the dispersion energy alone [75].) Instead, the exchange-repulsion energy contributions missing from the Hartree–Fock supermolecule calculation, including the exchange-dispersion energy, are included in the TT model by scaling the

Hartree–Fock interaction energy by a constant factor, originally obtained from experiment [68]. The Hartree–Fock interaction energy was scaled by between 1.14 and 1.17 for rare gases interacting with nitrogen [76]. The Heitler–London interaction energy has also been used in the TT model instead of the Hartree–Fock interaction energy. The Heitler–London interaction energy was scaled by 1.31 to obtain potential energy surfaces in agreement with experiment for rare gases interacting with halide and alkali ions [77].

The main computational cost of the HFD and TT methods is the Hartree–Fock supermolecule calculations. They are therefore computationally efficient methods, and the computer time needed to use them scales with system size as N^4S, where N is the size of the basis set and S is the number of points on the potential energy surface. The XC model scales in the same way. However, their accuracy is not competitive with more modern methods unless empirical parameters are used and fitted to experimental data (see for example [65]). In particular, the use of Hartree–Fock supermolecule calculations for the first-order Coulomb, induction and exchange-repulsion energies causes significant errors. In hydrogen-bonded dimers, the Hartree–Fock method overestimates the monomer dipoles by about 10%, and hence the first-order Coulomb and induction energies may be overestimated by as much as 20%.

Density functional calculations have recently been used instead of Hartree–Fock supermolecule calculations in methods based on the HFD model [78–80]. If a suitable density functional is chosen, then the properties of the monomers can be more accurate than at Hartree–Fock level, and this method therefore has conceptual advantages over the HFD and TT models, and the scaling of computational effort with system size is the same. However, one disadvantage is that although density functional theory gives no long-range dispersion interaction energy, it does give some intermolecular correlation, and hence a short-range dispersion interaction, when the charge densities overlap. It is therefore not correct to add to the DFT interaction energy the same damped dispersion series that is used in the HFD method, because this would count some of the short-range dispersion energy twice [78]. Furthermore, the exchange-repulsion interaction energy may be less reliable in density functional calculations than in Hartree–Fock calculations, as the exchange functional used in DFT is not usually exact.

3.2.2. *The SIMPER and SPT methods*

Instead of starting from the low level of a Hartree–Fock supermolecule calculation, it is now reasonable, for molecules which are not very large, to use the correlated MP2 supermolecule method to generate a potential energy surface. The computer time used by MP2 supermolecule calculations scales as nN^4S, where n is the number of electrons. MP2 supermolecule calculations give a non-zero dispersion interaction energy, and predict some binding for all Van der Waals complexes; they are therefore a significant improvement on Hartree–Fock supermolecule calculations. However, the first-order Coulomb energy and induction energy in MP2 supermolecule calculations correspond to using equations (24) and (25) with a mixture of relatively low-level MP2 and coupled Hartree–Fock monomer properties, as discussed in section 2.1. The dispersion energy in MP2 supermolecule calculations corresponds to using uncoupled Hartree–Fock monomer polarization propagators, which is an even lower level of theory than the coupled Hartree–Fock polarization propagators in the induction energy. This generally means that MP2 supermolecule calculations underestimate the strength of weak Van der Waals bonds, often by 30–50% (see also [81]). The systematic intermolecular potential extrapolation routine (SIMPER) has been developed with the aim of replacing parts of the supermolecule MP2 intermolecular potential by more high-level calculations using monomer properties, in a way which involves no significant extra computational expense.

The MP2 intermolecular potential ΔE_{MP2} is partitioned as

$$\Delta E_{\mathrm{MP2}} = \Delta E^{(1)}_{\mathrm{Coul,\,MP2}} + \Delta E^{(2)}_{\mathrm{disp,\,MP2}} + \Delta E^{(2)}_{\mathrm{ind,\,MP2}} + \Delta E^{(n>2)}_{\mathrm{Coul,\,MP2}} + \Delta E_{\mathrm{exch,\,MP2}}, \quad (36)$$

where the first-order Coulomb energy is defined by equation (18), and the dispersion and induction interaction energies are defined by separating equation (20) into two parts as explained in the text following that equation. The last two terms in equation (36) are more difficult to separate; they will be discussed later.

A high-level first-order Coulomb interaction energy is then calculated from equation (24). The only properties required are high-level density matrices, and the computer time required to apply equation (24) scales as N^4S, independent of the level of theory used to obtain the densities. Using MP2 densities in equation (24) is theoretically preferable to using the first-order MP2 supermolecule energy from equation (18), but the two differ only by the interaction between the MP2 density corrections, which is usually negligible. Better results have been obtained by using quadratic CI (QCISD) and coupled-cluster (CCSD) densities [82] in equation (24). The computer time required to obtain these densities scales as n^2N^4, which is small relative to the MP2 supermolecule calculations, since the number of points on the potential energy surface is usually much larger than the number of electrons. The MP2 intermolecular potential is therefore modified by replacing the ‘low-level’ MP2 first-order Coulomb energy in equation (36) by the high-level first-order Coulomb energy from equation (24), calculated using QCISD or CCSD densities. The difference between these ‘low-level’ and ‘high-level’ first-order Coulomb interaction energies is usually about 5–10%.

For atoms and non-polar molecules, the induction energy is smaller than the dispersion energy, and in MP2 supermolecule calculations the dispersion energy is present at a lower level of (monomer) theory and is expected to have a larger relative error than the induction energy. Therefore, it is more important to improve the dispersion energy than the induction energy, and this is reflected by the greater emphasis on the former in the literature. The most obvious way to improve the dispersion energy (and the induction energy) is to calculate the monomer polarization propagators at a higher level of theory. However, for any level higher than coupled Hartree–Fock, this requires significant computational effort in calculating, storing and using the propagators. This would probably make the method uncompetitive with higher-level supermolecule calculations in terms of computer resources. Coupled Hartree–Fock propagators are better than uncoupled Hartree–Fock ones, and could be used to improve the MP2 dispersion energy, but since the level of theory would still be quite low, this method would be of limited use.

Instead of recalculating the propagators at a higher level, and hence improving the non-expanded second-order energy, high-level polarizabilities can be obtained with relatively little effort. In the SIMPER method, TD-CISD polarizabilities are used. (The TD-CISD method has not been published; it is a CISD analogue of the TD-MP2 method [83].) The computer time used to obtain the TD-CISD polarizabilities scales as n^2N^4. The multipolar dispersion energy coefficients, and hence the multipole expansion of the second-order energy, are obtained from the frequency-dependent polarizabilities. The 'low-level' MP2 dispersion energy in equation (36) is then replaced by a damped multipole expansion using the high-level multipole coefficients. The main difficulty is finding suitable damping functions. For induction, this is currently an unsolved problem, because the electric field experienced by molecule A is a balance between opposing nuclear and electronic contributions from molecule B, and this can exceed the multipolar value, giving individual damping functions greater than 1 [43]. Indeed, the non-expanded induction energy can be non-zero even when the multipolar induction energy is zero. The dispersion energy is simpler, because it involves only electron repulsion, so there is no cancellation of opposing effects, and the individual damping functions are always found to have values between 0 and 1 (although this is an empirical observation confirmed by the known data, rather than a proven fact).

Damping functions for dispersion can be estimated if no information is available other than the dispersion energy coefficients, using equations (33) and (34). These equations are based on scaling the damping functions of triplet-H_2, which may not always give reliable results [42]. In the SIMPER method, the MP2 supermolecule dispersion energy is known, so this can be used instead of triplet-H_2 as the starting point of the scaling procedure. The 'low-level' MP2 supermolecule dispersion energy is written as

$$\Delta E^{(2)}_{\text{disp, MP2}} = -\sum_n C_{n,\text{low}} f_{n,\text{low}}(R) R^{-n}, \tag{37}$$

and the dispersion energy coefficients $C_{n,\text{low}}$ corresponding to the multipolar MP2 supermolecule dispersion energy are obtained from uncoupled Hartree–Fock polarizabilities. Damping functions for the MP2 dispersion energy are assumed to have the TT form,

$$f_{n,\text{low}}(R) = 1 - \sum_{k=0}^{n} \frac{(b_{\text{low}}R)^k}{k!} \,\mathrm{e}^{-b_{\text{low}}R}. \tag{38}$$

The quantities $\Delta E^{(2)}_{\text{disp, MP2}}$ and $C_{n,\text{low}}$ are calculated at each point on the potential energy surface, and b_{low} is then obtained at each point by substituting equation (38) into equation (37) and solving the resulting equation, in which b_{low} is the only unknown quantity. The value of b_{low} is therefore allowed to depend on the intermolecular geometry. This procedure does not require any fitting, unlike the method used by Moszynski *et al.* [84]. In practice, the dispersion energy coefficients C_n must be calculated up to quite large values of n, at least $n = 14$, otherwise the truncated multipolar dispersion energy may be less negative than the non-expanded energy at fairly long range, and b_{low} cannot be found.

Having obtained b_{low} at each point on the potential energy surface, a 'high-level' value of b is estimated at each point, using

$$b_{\text{high}} = b_{\text{low}} \left(\frac{C_{6,\text{high}} C_{8,\text{low}}}{C_{6,\text{low}} C_{8,\text{high}}} \right)^{1/2}, \tag{39}$$

which is based on equations (33) and (34). The 'high-level' damped dispersion energy is then calculated at each point using

$$\Delta E^{(2)}_{\text{disp, high}} = -\sum_n C_{n,\text{high}} f_{n,\text{high}}(R) R^{-n}, \tag{40}$$

where $C_{n,\text{high}}$ are the 'high-level' TD-CISD dispersion energy coefficients and

$$f_{n,\text{high}}(R) = 1 - \sum_{k=0}^{n} \frac{(b_{\text{high}} R)^k}{k!} \mathrm{e}^{-b_{\text{high}} R}. \tag{41}$$

This recalculation of the dispersion energy is usually the most important modification made to the MP2 supermolecule energy. For example, the dispersion energy is reduced by about 10% for the argon dimer, and increased by about 25% for the neon dimer. Since the dispersion energy is larger than the total intermolecular potential for Van der Waals dimers at the equilibrium separation, the corresponding percentage changes in the intermolecular potential are even larger: about 20% for Ar_2, and 50% for Ne_2.

For weak Van der Waals interactions, these modifications to the first-order Coulomb interaction energy and the second-order dispersion energy are expected to be the only significant corrections that need to be made to the Coulomb interaction energy. The second-order induction energy and higher-order Coulomb interaction energy terms are smaller at medium and long range, and they are not modified by the SIMPER procedure; their MP2 values from equation (36) are retained in the total intermolecular potential.

The exchange-repulsion interaction energy is important at the equilibrium separation and at short range, and the exchange-repulsion component of the MP2 supermolecule calculation may not be sufficiently accurate. For interactions between non-polar molecules, the percentage error in the first-order exchange-repulsion energy is likely to be similar to the percentage error in the first-order Coulomb energy, since both depend on the electron density overlap. This means that the MP2 exchange-repulsion energy may be in error by up to 10%, and since the exchange-repulsion energy is similar in size to the total intermolecular potential around the minimum, this equates to an error of up to 10% in the well depth.

To improve the MP2 exchange-repulsion energy, the overlap model is used. It is assumed that the proportionality parameter K in equation (29), which relates the exchange-repulsion interaction energy to the electron density overlap, is independent of the level of theory. The correction applied to the 'low-level' MP2 supermolecule exchange-repulsion energy is therefore

$$\Delta E_{\text{exch, high}} = \Delta E_{\text{exch, low}} S_{\rho,\text{high}} / S_{\rho,\text{low}}. \tag{42}$$

This assumption has been tested for the helium dimer, for which accurate calculations of the exchange-repulsion are available. Here, 'high' level was full CI and 'low' level was Hartree–Fock. The difference between the Hartree–Fock and full-CI exchange-repulsion interaction energies is about 10% around the potential energy minimum, but when the Hartree–Fock exchange-repulsion interaction energy was scaled by the ratio of the full-CI and Hartree–Fock charge density overlaps, the agreement improved by about an order of magnitude over a wide range of separations [35]. The same method improved the accuracy of the exchange-repulsion energy of the water dimer by a factor of about 6, at 2500 different points on the potential energy surface [85].

In the SIMPER method, the 'low-level' overlap, $S_{\rho,\,\mathrm{low}}$, is defined at the MP2 supermolecule level in a similar way to the MP2 first-order Coulomb energy, by using equation (30) to calculate the overlap between the Hartree–Fock electron densities ($\rho^e_{A,\,\mathrm{HF}}$ with $\rho^e_{B,\,\mathrm{HF}}$) and between the Hartree–Fock densities and the MP2 density corrections ($\rho^e_{A,\,\mathrm{HF}}$ with $\delta\rho^e_{B,\,\mathrm{MP2}}$ and $\rho^e_{B,\,\mathrm{HF}}$ with $\delta\rho^e_{A,\,\mathrm{MP2}}$), but the overlap between the two MP2 density corrections is not included. The 'high-level' overlap, $S_{\rho,\,\mathrm{high}}$, is the overlap between the QCISD or CCSD electron densities. The computer time needed to calculate the charge density overlap scales in the same way with system size as the calculation of the first-order Coulomb energy, so it does not add significantly to the cost of the calculation. The scaling factor $S_{\rho,\,\mathrm{high}}/S_{\rho,\,\mathrm{low}}$ applied to the exchange-repulsion energy is usually found to be less than 1. It can be as low as 0.9, so the exchange-repulsion energy can be reduced by up to 10%, and this increases the total intermolecular potential by up to 10%. However, for the helium dimer this scaling factor is greater than 1, and in this case the SIMPER method increases the calculated exchange-repulsion energy.

The main difficulty with using equation (42) to scale the exchange-repulsion energy is the definition of $\Delta E_{\mathrm{exch,\,low}}$, which is $\Delta E_{\mathrm{exch,\,MP2}}$ in equation (36). As discussed in section 2.2, the use of equation (3) to obtain the exchange-repulsion interaction energy relies on a calculation of the Coulomb interaction energy which is not stable, and which collapses to an unphysical state for small intermolecular separations and large basis sets. Therefore, two alternative methods for calculating the exchange-repulsion energy, SIMPER-P and SIMPER-K, have recently been investigated.

The SIMPER-P method is based on perturbation theory. The first few terms of a truncated perturbation expansion of the Coulomb interaction energy are calculated, and the exchange-repulsion interaction energy is defined by replacing the Coulomb interaction energy in equation (3) by the truncated perturbation expansion. This is a straightforward procedure, as the Coulomb perturbation theory is unambiguously defined, but it would also be interesting to investigate the possibility of using a perturbation expansion of the exchange-repulsion energy. This method makes the assumption discussed for SAPT, that the truncated perturbation expansion of the Coulomb energy recovers most of the 'physical' Coulomb interaction energy and a negligible amount of the 'unphysical' Coulomb interaction energy. It is expected that this is most likely to be true at second or third order in the energy, which is first order in the wave function.

The SIMPER-P method requires MP2 and high-level charge densities for each monomer, and MP2 and high-level dispersion energy coefficients for each relative orientation of the interacting molecules in the dimer. At each point on the potential energy surface, an MP2 supermolecule calculation is performed, and the MP2 Coulomb interaction energy is calculated to second or third order using equations (18), (20) and (21). This allows the MP2 exchange-repulsion interaction energy to be obtained. The MP2 exchange-repulsion interaction energy is then scaled by the ratio of the high-level to MP2 electron density overlap, and the MP2 first-order Coulomb interaction energy is replaced by the high-level first-order Coulomb interaction energy. The MP2 dispersion interaction energy is expressed as a damped multipole series, the MP2 damping parameter b_{low} is obtained, from which b_{high} is calculated using equation (39), and the MP2 dispersion energy is then replaced by the high-level dispersion energy calculated from equation (40), using $b_{\rm high}$ and the high-level dispersion energy coefficients.

The SIMPER-K method is based on using a pseudopotential to prevent the unphysical charge transfer between molecules. The Coulomb interaction energy is calculated using the method described after equation (2), but an additional charge-overlap operator $K'V'$ is added to the dimer Hamiltonian, where K' is a positive constant, and

$$V' = \sum_{i_A, i_B} \delta(\mathbf{r}_{i_A} - \mathbf{r}_{i_B}), \tag{43}$$

δ is a delta-function and i_A and i_B are electrons of A and B. The expectation value of the operator V' over the zero-order Coulomb wave function is the electron density overlap S_ρ. In effect, the charge-overlap operator increases the intermolecular electron repulsion at small intermolecular separations, and therefore increases the energy of the 'unphysical' charge-transfer states, relative to the energy of the 'physical' state. This is because the charge-transfer states have a large overlap between orbitals of A and B, which are spread over both molecules, whereas in the 'physical' state the orbitals of A and B are located on their own molecules.

Even if the SIMPER-K calculation converges to a 'physical' state, the calculated Hartree–Fock Coulomb interaction energy $\Delta E_{\rm Coul,\,HF}(K')$ is not correct, because it is affected by the use of the charge-overlap operator. Perturbation theory is therefore used to remove the effect of this operator, to second order in the energy. This is achieved at Hartree–Fock level using

$$\Delta E_{\rm Coul,\,HF} = \Delta E_{\rm Coul,\,HF}(K') + \Delta E^{(1)}_{\rm Coul,\,HF}(K') + \Delta E^{(2)}_{\rm Coul,\,HF}(K'), \tag{44}$$

where the superscripts here denote powers of K', not V;

$$\Delta E^{(1)}_{\rm Coul,\,HF}(K') = -\langle 0(K')|K'V'|0(K')\rangle, \tag{45}$$

where $|0(K')\rangle$ is the Coulomb Hartree–Fock wave function, calculated with the additional $K'V'$ term in the Hamiltonian, and

$$\Delta E^{(2)}_{\rm Coul,\,HF}(K') = \frac{1}{2}\langle 0(K')|[\kappa^{(1)}(K'), K'V']|0(K')\rangle, \tag{46}$$

where

$$\langle 0(K')|[X, [\kappa^{(1)}(K'), H + K'V']]|0(K')\rangle + \langle 0(K')|[X, K'V']|0(K')\rangle = 0. \tag{47}$$

The assumption is that a value of K' can be found which is small enough not to perturb the 'physical' Coulomb wave function excessively (so that the second-order correction for the use of the charge-overlap operator is adequate), but which is also large enough to raise the energy of the 'unphysical' states above the energy of the 'physical' state.

The SIMPER-K method uses the same charge densities and dispersion energy coefficients as SIMPER-P. The MP2 Coulomb interaction energy is obtained from a Coulomb supermolecule calculation using the modified Hamiltonian $H + K'V'$, and the corrections $\Delta E^{(1)}_{\rm Coul,\,HF}(K')$ and $\Delta E^{(2)}_{\rm Coul,\,HF}(K')$ are calculated using equations (45)–(47) and added to it. The MP2 exchange-repulsion interaction energy is then defined as the difference between the MP2 supermolecule and Coulomb interaction energies as usual, and the rest of the calculation proceeds in the same way as the SIMPER-P method.

The SIMPER-P and SIMPER-K methods are quite general, because the definition of 'low-level' and 'high-level' (see for example equations (39) and (42)) can be changed as required. The specific use of MP2 supermolecule calculations, CCSD charge densities, and TD-CISD dispersion energy coefficients is denoted by SIMPER-1P and SIMPER-1K. In the SIMPER-1P method, truncation of the perturbation expansion of the Coulomb interaction energy at the second or third order is denoted by SIMPER-1P-2 or SIMPER-1P-3.

The Scaled Perturbation Theory (SPT) method, which preceded SIMPER, also uses high-level dispersion energy coefficients and charge densities to improve low-level calculations of a potential energy surface. However, the number of different potential energy contributions which are separated and scaled in SPT is different from SIMPER, and the scaling methods are not always the same.

In the SPT method [35], the MP2 supermolecule interaction energy is divided into six contributions:

$$\begin{aligned}\Delta E_{\mathrm{MP2}} = \Delta E^{(1)}_{\mathrm{Coul,\,MP2}} + \Delta E^{(2)}_{\mathrm{disp,\,MP2}} + \Delta E_{\mathrm{ind,\,MP2}} \\ + \Delta E^{(1)}_{\mathrm{exch,\,MP2}} + \Delta E_{\mathrm{exch\text{-}ind,\,MP2}} + \Delta E_{\mathrm{exch\text{-}disp,\,MP2}},\end{aligned} \tag{48}$$

where the first-order Coulomb interaction energy and second-order dispersion energy are the same as in equation (36). The induction energy is calculated using finite-field methods [35]. The first-order MP2 exchange-repulsion interaction energy is calculated by multiplying the first-order Hartree–Fock exchange-repulsion energy, defined by equation (22), by the ratio of MP2 and Hartree–Fock electron density overlap integrals. The MP2 exchange-induction interaction energy is calculated by multiplying the Hartree–Fock exchange-induction interaction energy by the ratio of MP2 and Hartree–Fock electron density overlap integrals. The Hartree–Fock exchange-induction interaction energy is calculated by dividing the Hartree–Fock supermolecule interaction energy into three contributions.

$$\Delta E_{\mathrm{HF}} = \Delta E_{\mathrm{HL}} + \Delta E^{(2)}_{\mathrm{Coul,\,HF}} + \Delta E_{\mathrm{exch\text{-}ind,\,HF}}. \tag{49}$$

The first two contributions are calculated directly, giving the Hartree–Fock exchange-induction energy by subtraction. The MP2 exchange-dispersion interaction energy is then obtained from the other six quantities in equation (48).

The energy contributions defined in equation (48) are then replaced by higher-level terms. The first-order Coulomb interaction energy is replaced by the interaction between high-level charge densities. The dispersion and induction interaction energies are scaled by the ratio of the leading, spherically averaged, multipole coefficients at high level and low (MP2) level, so for the dispersion energy,

$$\Delta E^{(2)}_{\mathrm{disp,\,high}} = \Delta E^{(2)}_{\mathrm{disp,\,MP2}} C_{6,\,\mathrm{high}}/C_{6,\,\mathrm{MP2}}. \tag{50}$$

The first-order exchange-repulsion interaction energy is scaled by the ratio of the high-level and low-level electron density overlap integrals, as in the SIMPER method, but the exchange-induction and exchange-dispersion energies are not scaled. SPT therefore resembles SIMPER-P, with the perturbation expansion in SIMPER-P truncated at second order. However, the two methods have significant differences: the dispersion energies are scaled differently, the induction energy is scaled in SPT but not in SIMPER-P, and the first-order exchange-repulsion energy is scaled in SPT, whereas the total exchange-repulsion energy is scaled in SIMPER-P.

4. Results

In this section, the MP2 supermolecule energies and monomer properties which form the input to the SPT and SIMPER methods are discussed. The collapse of the Coulomb interaction energy to unphysical values is demonstrated, and methods by which this is prevented in SIMPER-P and SIMPER-K are compared. Intermolecular potential energy surfaces obtained using SPT and SIMPER are reviewed. The agreement with potential energy surfaces derived from experiment, and the agreement between spectroscopic constants obtained from SIMPER and experiment, are shown to be comparable with potential energy surfaces calculated using the best *ab initio* methods, and much better than results obtained from the MP2 supermolecule method, which requires a similar amount of computer time to SIMPER and SPT.

4.1. *A case study for weak interactions: the neon dimer*

Table 1 shows the components of the MP2 intermolecular potential for the neon dimer as a function of the intermolecular separation R, calculated using the SP-aug-cc-pV5Z basis set. The MP2 Coulomb interaction energy is calculated without making any correction for possible collapse of the Coulomb wave function to the Pauli-forbidden state. The high-level first-order Coulomb interaction energy is calculating using CCSD monomer charge densities. The first three dispersion energy coefficients corresponding to the long-range limit of the MP2 intermolecular potential, obtained from uncoupled Hartree–Fock frequency-dependent monomer polarizabilities, are $C_6 = 5.294$, $C_8 = 61.84$ and $C_{10} = 866.4$, and the high-level (TD-CISD) dispersion energy coefficients are $C_6 = 6.207$, $C_8 = 82.97$ and $C_{10} = 1234.8$. The best literature value of C_6 is 6.383, obtained from constrained dipole oscillator strength distributions [86]. This differs by 21% from the MP2 value, but by only 3% from the TD-CISD value. The high-level Coulomb interaction energy is defined as $\Delta E_{\text{Coul, high}} = \Delta E_{\text{Coul, MP2}} - \Delta E^{(1)}_{\text{Coul, MP2}} - \Delta E^{(2)}_{\text{disp, MP2}} + \Delta E^{(1)}_{\text{Coul, high}} + \Delta E^{(2)}_{\text{disp, high}}$. The high-level exchange-repulsion interaction energy is obtained by multiplying the MP2 exchange-repulsion energy by the ratio of CCSD and MP2 charge density overlaps, and the total SIMPER intermolecular potential is defined as $\Delta E_{\text{high}} = \Delta E_{\text{Coul, high}} + \Delta E_{\text{exch, high}}$.

Table 1. Contributions to the Ne-Ne intermolecular potential. Distances R are in Bohr, energies are in microHartree.

R	5.5	6.0	6.5	7.0
ΔE_{MP2}	−17.11	−83.20	−73.24	−52.71
$\Delta E^{(1)}_{\text{Coul, MP2}}$	−84.57	−24.38	−7.57	−2.52
$\Delta E^{(2)}_{\text{disp, MP2}}$	−306.48	−169.33	−98.37	−59.86
$\Delta E_{\text{Coul, MP2}}$	−395.60	−194.25	−105.94	−62.30
$\Delta E_{\text{exch, MP2}}$	378.49	111.05	32.70	9.59
$\Delta E^{(1)}_{\text{Coul, high}}$	−76.74	−21.84	−6.73	−2.23
$\Delta E^{(2)}_{\text{disp, high}}$	−372.29	−206.90	−120.18	−72.89
$\Delta E_{\text{Coul, high}}$	−453.58	−229.28	−126.91	−75.04
$\Delta E_{\text{exch, high}}$	346.71	100.29	29.13	8.46
ΔE_{high}	−106.87	−128.99	−97.78	−66.58
$\Delta E_{\text{CCSD(T)}}$	−92.34	−125.94	−98.06	−67.50

The results are typical of those obtained using SIMPER for dimers involving helium, neon and small molecules. The MP2 intermolecular potential is about 50% too small, compared to higher-level supermolecule calculations and to experiment [87]. At the separations shown, there is no evidence of the expected divergence of the Coulomb interaction energy. The Coulomb interaction energy is dominated by the sum of the first-order Coulomb energy and the second-order dispersion energy. The dispersion energy damping parameter b is found to be fairly independent of separation, with values between 2.66 and 2.77 atomic units over the range of separations shown. The modification of the dispersion energy is the most important change to the MP2 intermolecular potential, but the exchange-repulsion also decreases by a significant amount when it is scaled using the ratio of charge density overlaps. The SIMPER potential energy surface is in much better agreement with CCSD(T) supermolecule calculations, and with experiment, than is the MP2 potential energy surface. The cost of the calculations is dominated by the MP2 supermolecule and Coulomb interaction energies. The high-level frequency-dependent polarizabilities of neon take a significant amount of time to calculate, but they can be stored and re-used to produce potential energy surfaces for any neon-containing dimer, without additional effort.

4.2. *The collapse of the Coulomb interaction energy*

The intermolecular potential calculated using SIMPER-K depends on the value chosen for the parameter K'. This is not an adjustable parameter of the method, and it would not be appropriate to fit it to experimental data because the method is designed so that the dependence of the intermolecular potential on K' is weak, except at geometries where a Coulomb calculation with $K' = 0$ gives an unphysical state. At these geometries, the Coulomb energy is unphysically negative when $K' = 0$, but as K' is increased, the stability of the unphysical state decreases, and when K' passes a critical value there is a sharp rise in the Coulomb interaction energy. Above this critical value of K', the physical state is obtained from the Coulomb energy calculation, and the dependence of the calculated energy on K' is fairly weak. Evidently it is necessary to choose a value of K' larger than the critical value, but not so large that the calculation is spoiled by higher-order terms in K'.

It is difficult to calculate critical values of K', because the unphysical behaviour of the Coulomb energy only occurs for large basis sets, and the calculations are difficult to converge for lower values of K'. Based on results for argon-containing dimers [88], for which the critical value of K' at geometries high on the repulsive wall is about 2 atomic units, it was suggested that a value of $K' = 3$ atomic units is reasonable, and this value has been used in all subsequent work.

Figure 2 shows the unphysical collapse of the Coulomb interaction energy for the argon dimer. These results are obtained using the aug-cc-pV5Z basis set. For the SIMPER (dashed) curve, the exchange-repulsion interaction energy is defined by equation (3). In general, the exchange-repulsion interaction energy is expected to be approximately an exponentially decreasing function of separation, and strong deviation of the plot from linearity at short distances indicates that the calculated Coulomb energy is unphysical. Slight deviation from linearity at larger distances arises mainly from the use of a finite basis set, but this is unimportant, because the exchange-repulsion energy is small at these separations. The SIMPER-K method described in section 3.2.2, using $K' = 3$ atomic units, corrects the unphysical

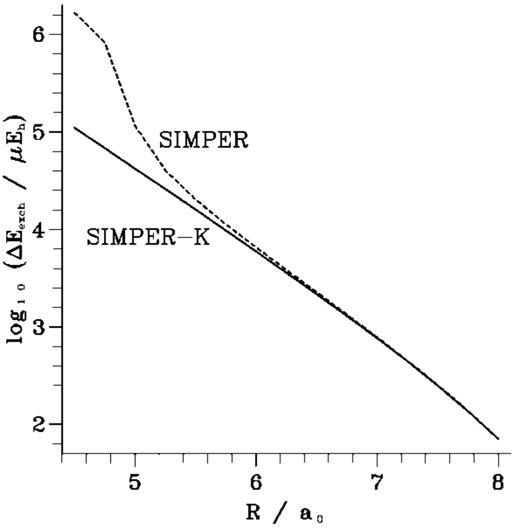

Figure 2. The exchange-repulsion interaction energy for the argon dimer calculated using SIMPER (upper dashed curve) and SIMPER-K (lower solid curve).

behaviour of the energy at all the separations shown, and gives an exchange-repulsion interaction energy which is very close to exponential at short range.

4.3. *Calculated potential energy surfaces*

An early version of the SPT method was used to calculate a potential energy surface for the interaction of helium with ammonia as a function of the three intermolecular coordinates and the ammonia inversion coordinate [89]. The method described in section 3.2.2 was used, but the exchange-induction and exchange-dispersion energies were not included. The equilibrium geometry of the ammonia-helium dimer was predicted to have C_s symmetry, with the helium atom about 6.1 a_0 from the nitrogen atom, halfway between two N–H bonds. A first-order saddle point occurs when the helium atom passes over an N–H bond, and second-order saddle points are found when the helium atom is at either end of the molecule. The well depth was predicted to be about 150 microHartree. This prediction was shown to be within 2% of the results of high-level supermolecule calculations performed at the MP4 and CCSD(T) levels. In contrast, the CCSD and CCSD(T) predictions differed by over 20%. The main difference between the SPT and CCSD(T) results was found to occur at the second-order stationary points, where the difference was up to 14%.

A similar method was used to calculate the potential energy surface for the water–helium dimer [90]. An empirical correction factor of k^{n-6} was applied to each dispersion energy coefficient C_n, since the errors in the low-level dispersion energy coefficients are expected to increase with increasing n (see, for example, the coefficients given in section 4.1 for the neon dimer). Without this correction, the potential energy surface was found to be about 10% too shallow, but qualitatively correct. The equilibrium geometry is planar, with the O→He vector nearly perpendicular to the water symmetry axis. First-order saddle points occur when the helium atom is at either end of the molecule, and there is a second-order saddle point at a symmetrical non-planar geometry, with the helium atom directly over the plane of the water molecule. To make the potential energy surface deeper, a value of

$k = 1.07$ was chosen, to give agreement with a complete basis set extrapolation of the CCSD(T) intermolecular potential near the equilibrium geometry, with the helium atom 5.9 a_0 from the oxygen atom. With this value of k, agreement within 3% was found between the SPT and CCSD(T) potential energy surfaces at the other planar stationary points, but at the non-planar stationary point the SPT surface was 20% too shallow.

Intermolecular potential energy surfaces for the water–neon and water–argon dimers were calculated using the SPT method, with explicit exchange-induction and exchange-dispersion terms [91]. As the size of the rare-gas atom increases from helium to argon, the calculated potential energy surface for the rare-gas–water interaction becomes more strongly bound and flatter around the minimum, and the equilibrium separation increases. With one fitted parameter, the agreement with CCSD(T) calculations for water–neon and water–argon was much better than for the water–helium interaction. The energies of all four stationary points of neon–water agreed with CCSD(T) calculations to within 7%, and for argon–water the maximum difference was 14%, but the SPT surface for argon–water is more strongly bound than the CCSD(T) surface, and some of the 14% difference is expected to be the result of using a finite basis set in the CCSD(T) calculations. The better agreement between SPT and CCSD(T) potential energy surfaces for these dimers than for the helium–water dimer is likely to be the result of treating the exchange-induction and exchange-dispersion explicitly in the SPT method. Similarly, in recent work on the water–hydrogen interaction [92], good agreement between SPT and CCSD(T) calculations was obtained. The difference between the SPT intermolecular potential and CCSD(T) supermolecule calculations extrapolated to the complete basis set limit was only 2%, whereas literature potential energy surfaces differed by up to 40% from each other and from the CCSD(T) calculations.

The most recent version of the SPT method, as described in section 3.2.2, was first applied to the helium dimer [35]. For this interaction, the 'high-level' CCSD and TD-CISD monomer properties are exact, within the limitations of the basis set. The difference between SPT and exact calculations therefore tests the approximations made in the scaling of the different terms, mainly the exchange-repulsion and dispersion damping. The agreement with near-exact *ab initio* calculations was found to be better than 1%, provided that the SPT calculations were performed with a basis set close to the basis set limit. These results therefore give considerable support to the use of the overlap model for improving the calculation of the exchange-repulsion interaction energy of Van der Waals dimers.

An early version of the SIMPER method was used to calculate intermolecular potential energy surfaces for all six Van der Waals dimers of the rare-gas atoms He, Ne and Ar [32]. This was the first time that the exchange-repulsion energy had been calculated using equations (2) and (3). The exchange-repulsion energy was scaled using the ratio of QCISD to MP2 electron density overlap integrals using equations (42) and (30). High-level first-order Coulomb interaction energies were calculated using QCISD charge densities. The dispersion energy was not expanded as a damped multipole series. Instead, the SPT scaling shown in equation (50) was used. The resulting well depths for He_2, HeNe and Ne_2 agreed with accurate literature values within 2.3%, whereas the maximum discrepancy between CCSD(T) calculations and literature values was 3.6%. However, for the dimers containing argon the agreement between SIMPER and literature values was worse, and the SIMPER intermolecular potential for the argon dimer was 36% too shallow. This discrepancy can easily be understood. For the argon dimer, the MP2 C_6 coefficient is 76.49 atomic units, which is higher than the TD-CISD value of 66.37, but all the higher C_n coefficients are too low. For example, the supermolecule MP2 value of C_8 is 1525 atomic units and the TD-CISD value is 1636 atomic units. Unlike the neon and helium dimers, the use of equation (50) for the argon dimer reduces the dispersion energy too much around the potential well region, where the higher dispersion energy coefficients are important.

It is therefore necessary to use the more detailed SIMPER scaling of the dispersion energy for the dimers containing argon, and the complete SIMPER method described in section 3.2.2 was later developed and applied [93] to the same six rare-gas dimers, and to the H_2–Ne and H_2–Ar dimers. Potential energy surfaces for these dimers were calculated using the SIMPER and SPT methods. The monomer charge densities were calculated using the QCISD method, and SP-aug-cc-pV5Z basis sets were used for all the calculations. Some results from these calculations are presented in table 2.

The SIMPER intermolecular potentials for the He–Ar, Ne–Ar and Ar_2 interactions were found to agree much better with literature potentials when the improved dispersion scaling method was used. For Ar_2, the difference in the well depths decreased from 36% to less than 6%. The He–Ar and Ne–Ar intermolecular potentials were in even closer agreement with literature potentials. The SPT potentials also gave reliable values for the well depths, with the largest discrepancy in well depths between SPT and literature values for the six rare-gas dimers being 5.5% for the Ne_2 and Ne–Ar dimers. The SIMPER calculations were also compared with supermolecule CCSD(T) calculations, and the largest difference in well depths was found to be 5.7%, for the helium dimer. The CCSD(T) intermolecular potential was less accurate than SIMPER for the helium dimer, as shown in table 2. The well depths for the other five dimers differed by less than 3.2% between the SIMPER

Table 2. Summary of intermolecular potential well depths calculated using the MP2, SIMPER and CCSD(T) methods, and reliable literature potentials obtained from fitting to spectroscopy and other experimental data for the dimers. All dimers are linear. Separations R are in Bohr, and refer to the Ar–F and Ne–F distances in the HF complexes, and the distance from the rare-gas atom to the H_2 bond centre in the H_2 complexes. When the separation is given as R_e, each potential energy surface is fitted, and the fitted well depth is quoted. When the separation is given an explicit value, all calculations are performed at this separation, which is close to the equilibrium separation. Energies are in microHartree.

Dimer	He_2	Ne_2	Ar_2	Ar–H_2	Ar–HF	Ar–FH	Ne–HF	Ne–FH
R	R_e	R_e	R_e	6.7	6.40	6.32	R_e	R_e
MP2	21.80	84.07	495.5	235.6	849	416	301	163
SIMPER [93]	35.60	133.1	430.1					
SIMPER-K			430.1 [88]	240.4 [88]	1024 [88]	445 [88]	427 [94]	241 [94]
SIMPER-P2 [88]			443.7	241.1	1018	446		
SIMPER-P3 [88]			445.0	242.6	1058	448		
CCSD(T)	33.67	130.3	441.9	236.0	895	427	388	212
Literature	34.77 [95]	133.9 [87]	453.6 [96]	254.3 [65]	1003 [97]	490 [97]	403 [98]	228 [98]

and CCSD(T) methods. In comparison, the MP2 supermolecule calculations, from which the SIMPER potentials were derived, differed from CCSD(T) by between 50% and 60% for He_2, He–Ne and Ne_2, and between 12 and 23% for the three argon-containing dimers. The SIMPER method of correcting MP2 supermolecule calculations therefore produced an improvement of about one order of magnitude in accuracy for these dimers, with very little extra expenditure of computer time.

For the H_2–Ne dimer, similarly close agreement between the SIMPER and CCSD(T) methods was obtained for both the linear and T-shaped geometries. Both methods agreed well with an experimentally derived intermolecular potential [72]. The SPT method gave stronger binding by around 10%, and the MP2 method gave about 40% less binding than the other methods. However, for the H_2–Ar dimer, the SIMPER method could not be used in the linear geometry, because the collapse of the Coulomb energy to unphysical values occurred outside the equilibrium separation. The SPT method gave a deeper potential well than the experimentally derived potential, but the CCSD(T) method gave a potential well which was shallower by a similar amount. For the H_2–Ar dimer, the MP2 and CCSD(T) intermolecular potentials were in good agreement.

The SIMPER-P and SIMPER-K methods, described in section 3.2.2, were used for the first time [88] to calculate intermolecular potential energy surfaces for Ar_2, Ar–H_2 and Ar–HF. The calculated well depths are shown in table 2. In each case, calculating the Coulomb interaction energy using the original SIMPER method gave unphysical results. This behaviour is shown in figure 2 for the argon dimer. For Ar_2, the 'collapse' of the Coulomb interaction energy occurred inside the equilibrium separation of about 7.1 Bohr, but for the other two dimers, an unphysical Coulomb state was reached close to the equilibrium separation.

The SIMPER-P and SIMPER-K calculations were performed using CCSD monomer charge densities, which are expected to be slightly more accurate than QCISD densities. For the argon dimer, the well depth calculated using the SIMPER-K and SIMPER-P methods was within 6% of the experimental potential, and within 3% of supermolecule CCSD(T) results. In addition, it was demonstrated that the Coulomb collapse was removed by both methods down to separations of 5 Bohr or less. The same encouraging results were found for the other two dimers. In fact, for the linear and T-shaped geometries of Ar–H_2 and Ar–HF, the SIMPER-P method gave well depths consistently closer to experiment than the CCSD(T) method, as shown in table 2.

The SIMPER-K, MP2 and CCSD(T) methods have recently been used to calculate complete two-dimensional potential energy surfaces for Ne–HF [94]. The Ne–HF dimer has two minima in the linear Ne–H–F and Ne–F–H geometries, at equilibrium Ne–F separations of about 6 a_0. Results of calculations at these geometries are shown in table 2. The MP2 well depth is about 30% less than the CCSD(T) well depth, but the difference between CCSD(T) and SIMPER-K is 14 and 10% in the two linear geometries, and the difference between SIMPER-K and the experimentally derived potential energy surface of Meuwly and Hutson [98] is about 6%. It is expected that the main source of error in the SIMPER-K potential for Ne–HF, as well as for Ar–HF, is in the induction energy, which is not improved from its MP2 value.

Using the calculated Ne–HF potential energy surfaces, the rotational and intermolecular vibrational bound states for the Ne–HF and Ne–DF dimers were obtained [94]. The theoretical spectra, calculated using differences between these bound-state energies, were compared with high-resolution experimental Ne–HF and

Ne–DF spectra by extracting 14 different spectroscopic constants [98] including rotational constants, centrifugal distortion constants, Van der Waals stretching and bending wavenumbers and Coriolis splittings. The overall accuracy of the SIMPER-K, MP2 and CCSD(T) potential energy surfaces were then assessed using two criteria. The first is the weighted RMS deviation σ_1, defined by

$$(\sigma_1)^2 = \frac{1}{n}\sum_{i=1}^{n}[(P_{i,\text{calc}} - P_{i,\text{expt}})/\delta_{i,\text{expt}}]^2, \tag{51}$$

where P_i are the $n = 14$ different spectroscopic constants, and $\delta_{i,\text{expt}}$ are their experimental uncertainties. This was the quantity used by Meuwly and Hutson to fit their potential energy surface. The second criterion is the percentage RMS deviation σ_2, defined by

$$(\sigma_2)^2 = \frac{1}{n}\sum_{i=1}^{n}[100(P_{i,\text{calc}} - P_{i,\text{expt}})/P_{i,\text{expt}}]^2. \tag{52}$$

The first quantity, σ_1, tends to penalize poor agreement with rotational constants, since the percentage experimental uncertainty is smallest for these, whereas σ_2 penalizes poor agreement with Coriolis splittings, which are most sensitive to the potential energy surface.

The results showed that the MP2 method is unsuitable to describe the bound states of Ne–HF. Six of the 14 spectroscopic constants could not be obtained from the MP2 intermolecular potential, because some of the bound states were missing. Using equations (51) and (52) with the remaining $n = 8$ constants gave a weighted deviation of $\sigma_1 = 300$ and a percentage deviation of $\sigma_2 = 32.1$.

In contrast to MP2, the SIMPER-K method predicted all the bound states, and the calculated spectroscopic constants were in much better agreement with experiment. The average deviations were $\sigma_1 = 47$ and $\sigma_2 = 11.8$. The worst agreement was found for the Coriolis splittings of the $J = 1$ e and f states, which are 0.020 58 cm^{-1} and 0.022 98 cm^{-1} for Ne–HF and Ne–DF, respectively, and were calculated to be 0.028 56 and 0.018 97 cm^{-1} from the SIMPER-K intermolecular potential. Even without correcting the induction energy, the SIMPER-K method gave results of similar accuracy to the much more time-consuming CCSD(T) method, for which $\sigma_1 = 71$ and $\sigma_2 = 8.3$. The high value of σ_1 for the CCSD(T) method was a result of the rotational constants tending to differ from experiment more than the SIMPER-K rotational constants, although the maximum difference between calculated and experimental rotational constants was found to be about 10% in each case.

5. Discussion and further work

For small molecules, intermolecular potentials can be calculated to an accuracy of a few percent by careful consideration of all the contributions up to second order in the intermolecular interaction, together with a more approximate representation of higher-order terms. The supermolecule CCSD(T), SAPT and SIMPER methods all fulfil these requirements. Supermolecule CCSD(T) calculations are the most general, as they can be used for any type of interaction, including covalent bonding, but they require the most computer time. SIMPER calculations are the quickest, but like SAPT they are restricted to non-covalent interactions where the molecular orbitals of the supermolecule are similar to the molecular orbitals of the individual molecules.

The SIMPER method involves dividing the supermolecule calculation of the intermolecular potential into electrostatic, induction, dispersion and exchange-repulsion contributions, then recalculating or scaling these contributions to a higher level of theory using monomer properties. The supermolecule MP2 method is currently used in the first step, but it would be possible to start from a higher level of theory such as supermolecule CCSD(T), and this could further improve the accuracy of the SIMPER method at the cost of significantly increased computational effort. For example, the bonding in the carbon monoxide dimer is sensitive to intramolecular correlation contributions to the first-order Coulomb interaction energy which are not present in supermolecule CCSD(T) calculations [99, 100]. These could easily be included in the SIMPER method.

The strong dependence of calculated intermolecular potentials on the basis set is well known. It is necessary to use basis sets which account for both the intramolecular and intermolecular correlation. This requires basis functions with high angular momentum and with a range of Gaussian exponents, because the intermolecular correlation is represented better by more diffuse Gaussians with lower exponents, whereas the intramolecular correlation requires Gaussians with higher exponents. The SP basis sets described in this review are more efficient than the standard augmented correlation-consistent basis sets for interactions dominated by dispersion, but they are also more prone to linear dependence, and for larger molecules it will not be possible to approach the basis set limit even using SP basis sets. Techniques used to accelerate the convergence to the basis set limit include using dimer-centred basis sets, basis functions in the middle of the Van der Waals bond, and complete basis set extrapolation. These techniques have not yet been applied to the SIMPER method, and it is not known whether they would be successful. It may also be possible to use small basis sets for the supermolecule calculations in SIMPER, and large basis sets to obtain the monomer properties, but this also needs more investigation.

The use of monomer properties to improve the electrostatic, dispersion and exchange-repulsion energies has been investigated. However, the induction energy is not modified in the SIMPER procedure. For interactions dominated by induction, when one or both of the molecules are polar, it will be important to improve the MP2 induction energy. This should not present any major problems. The MP2 supermolecule energy already includes the MP2 response of one molecule to the electrostatic potential generated by the Hartree–Fock charge density of the other. It is straightforward to replace the Hartree–Fock charge density by the CCSD charge density, for example, which should improve the induction energy significantly. A smaller improvement could be obtained by changing the polarization propagator from MP2 to higher level, but this would be considerably more difficult, and more expensive in computer time. One possible problem with improving the induction energy is that at very short range, the induction energy is affected by the 'collapse' of the Coulomb wave function to the unphysical state, and there is close cancellation between the induction and the exchange-induction energy in the supermolecule calculations. Improving the induction energy without considering the exchange-induction could make the situation worse in these extreme cases.

Since SIMPER calculations require relatively little computer time compared to other methods of similar accuracy, it is interesting to consider whether the SIMPER theory could be extended to larger molecules. The methods used to obtain the high-level electrostatic and exchange-repulsion energies could be applied to any interacting molecules, as could the method suggested for improving the induction energy. The only problem is the high-level dispersion energy, which depends on a damped multipole series involving the intermolecular separation. For large molecules, the intermolecular separation is not well-defined, and the damped multipole series does not converge. An alternative method for obtaining the high-order dispersion energy is therefore required. One possibility is to calculate it using time-dependent density functional theory, using the method described by Misquitta and coworkers [101, 102]. Alternatively, if the better reliability of post-Hartree–Fock methods is required, it will be necessary to expand the dispersion energy as a sum of damped multipolar interactions between atoms, by dividing the MP2 supermolecule dispersion energy into atom–atom contributions, and calculating the dispersion energy coefficients for each atom–atom interaction at low and high levels of theory. At present, there appears to be no completely satisfactory way of doing this.

The properties of larger clusters and condensed phases depend on non-additive interactions between more than two molecules. Intermolecular perturbation theory, such as SAPT, can be applied to non-additive interactions [103–105], and because the non-additive interactions are usually less important, the percentage accuracy required for non-additive interactions is lower. However, the non-additive potential energy surface depends on more coordinates, up to 12 for three molecules, and the effort required to calculate the complete surface and fit it to an analytic form can be overwhelming. It is almost always necessary to use a low level of theory to make the calculations feasible, even for small molecules. It is therefore likely that the use of methods like SIMPER to improve low-level calculations will become important in the future for first-principles simulations of condensed phases.

Acknowledgments

The authors are grateful to the EPSRC and the University of Nottingham for funding this work. RJW thanks Prof. K. Szalewicz for his recent hospitality and stimulating discussions, and is pleased to acknowledge the major influence that Dr. A. J. Stone and Prof. W. J. Meath have had on his approach to this subject.

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