Perturbation Theory Approach to Intermolecular Potential Energy Surfaces of van der Waals Complexes

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I. Introduction

As the experimental and theoretical investigations of the structure and energetics of isolated molecules are entering a mature stage of development, the interactions between molecules are becoming the next frontier of molecular science. Such interactions, although weak compared to the forces bonding molecules internally, are responsible for an extensive range of physical, chemical, and biological phenomena: from bulk properties of rare gases to the signal induction in neurotransmitters. There are too many fields where intermolecular potentials are needed to list them here. A few important examples are Monte Carlo and molecular dynamics simulations of biological systems,[1] drug design,[2] studies of processes in the earth's atmosphere,[3] and interstellar chemistry.[4] Investigations of intermolecular forces not only enlarge our knowledge of nature but may lead to significant technological advances. One may hope
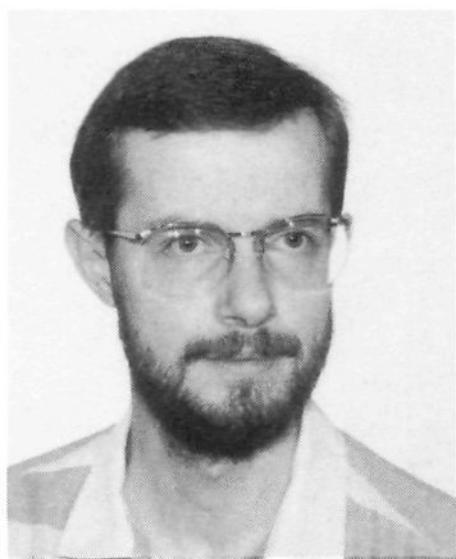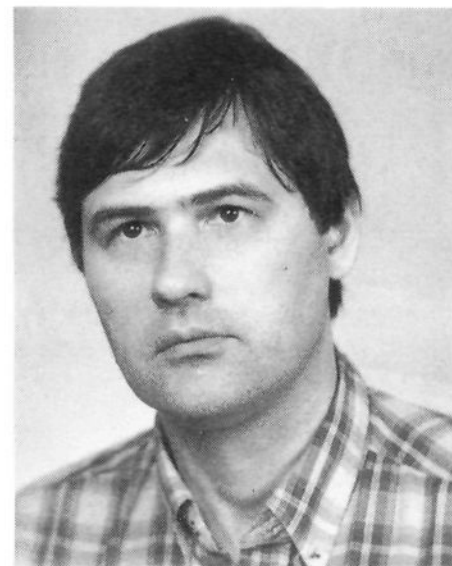
Bogumil Jeziorski received his M.S. degree in chemistry from the University of Warsaw in 1969. He conducted his graduate work also in Warsaw under the supervision of W. Kolos and in 1975 he received his Ph.D. for a thesis on the pairwise nonadditivity of overlap and exchange effects in interactions of small atoms and molecules. After a postdoctoral position at the University of Utah, he was a Visiting Professor at the University of Florida, University of Waterloo, University of Delaware, and University of Nijmegen. Since 1990 he has been a Professor of Chemistry at the University of Warsaw. His research has been mainly on the many-body and coupled-cluster theory of electronic correlation and on the perturbation theory of intermolecular interactions. His other research interests include chemical effects in nuclear β decay, theory of muonic molecules, and relativistic and radiative effects in molecules.

Krzysztof Szalewicz was born in Poland in 1950. He earned his M.S. degree in chemistry from the University of Warsaw in 1973. He received his Ph.D. degree in theoretical chemistry in 1977 for work in ab initio perturbation theory of intermolecular interactions. He was an Adjunct Professor at the University of Warsaw from 1978 to 1985 and then a research scientist at the University of Florida from 1985 to 1988. Since 1988 he has been at the University of Delaware where now he is a Professor of Physics and Chemistry. His research interests are in the theory of intermolecular forces, in high-accuracy quantum mechanical calculations for small atoms and molecules, and in the theory of muon-catalyzed fusion.

Robert Moszynski was born in Warsaw, Poland, in 1964. He received his M.S. degree in chemistry from the University of Warsaw in 1986. In 1987 he joined the Quantum Chemistry Laboratory at the University of Warsaw. He earned his Ph.D. degree in quantum chemistry from the University of Warsaw on intramonomer correlation effects in intermolecular interactions. In his research on perturbation theory of intermolecular forces he collaborated closely with Bogumil Jeziorski and Krzysztof Szalewicz. Recently, he joined the group of Ad van der Avoird at the Department of Chemistry, University of Nijmegen in the Netherlands. His research interests include ab initio studies of intermolecular forces and spectra and dynamics of van der Waals molecules.

that a proper manipulation of the energetical and stereochemical features of intermolecular forces might allow design of artificial receptor molecules capable of binding substrate species strongly and selectively, just as biological enzymes do, leading to construction of new materials.

The purpose of this article is to review a significant progress made during the 1980s and early 1990s in the perturbation theory of intermolecular interactions. The last major reviews in this field[5-8] were published in late 1970s and early 1980s. The monograph by Kaplan,[9] containing a broad discussion of the perturbation theory approach, is a translation (with minor extensions) of the 1982 Russian edition

and includes complete literature until 1979. A concise and very readable section on perturbation theory approach in the book by Hobza and Zahradnik[10] covers literature until 1984. It appears, then, that a review presenting the current state of the theory is now in order. In our view, the perturbation theory approach to intermolecular interactions serves three main purposes: (i) it provides the basic conceptual framework within which the intermolecular interactions are discussed, (ii) it provides asymptotic constraints on any potential energy surface obtained either from experiment or from theory, and (iii) it can accurately predict the complete intermolecular potential energy surfaces for weakly bound molecular complexes. We intend to cover significant developments in all the three areas but we will especially focus on the last point where recent advances were most rapid. The complete intermolecular potential could not be obtained in a perturbation approach until the notorious electron exchange problem was solved. This solution has been achieved by the development[8] and many-body implementation[11,12] of the symmetry-adapted perturbation theory (SAPT) so the discussion of the point (iii) is naturally limited to the field of SAPT. The polarization theory and the multipole expansion theory are limits of SAPT corresponding to the neglect of the exchange and of the overlap effects. The progress in these fields is relevant for applications of SAPT and is also reviewed.

By intermolecular interactions we will understand all interactions between molecules which are significantly weaker than the chemical bond. We will moreover restrict the scope of this review to interactions of closed-shell systems in the nonrelativistic quantum mechanics. Relativistic effects become important only for distances much larger than those of van der Waals minima[13-15] and therefore have a negligible effect on most observables. (See, however, ref 16 for an example of importance of relativistic effects for He_2.) The restriction to closed-shell sys-

tems also means that we will not discuss the resonance interactions appearing when at least one monomer is in an excited state. Also, we will not discuss interactions of more than two monomers, *i.e.*, we will not consider here the nonadditive many-body effects. (In this review the phrase "many-body" will always refer to the many-electron problem.) The depths of minima on intermolecular potential energy surfaces are typically from a few hundredths of kilocalories per mole to several kilocalories per mole, in contrast to chemical bonds which are of the order of one hundred kilocalories per mole. Some authors introduce a further division of intermolecular interactions into subtypes such as van der Waals interactions or the hydrogen-bonding interactions. However, from the point of view of perturbation theory such division is not necessary. All the intermolecular interactions contain the four fundamental physical contributions: electrostatic, induction, dispersion, and exchange—and differ only by proportions of these ingredients. The strongest of those interactions involve a large negative contribution from the electrostatic forces as in hydrogen bonded systems. If the electrostatic contribution is small, like in interactions of rare gas atoms with molecules, the minima depths are often below 1 kcal/mol. Nevertheless, in all cases the basic physics of the process is the same. Thus, from this point of view, a molecule such as the water dimer is also a van der Waals complex.[10,17]

The concept of intermolecular interaction energy appears in the Born—Oppenheimer approximation. The energy of interaction between molecules A and B is defined as the difference between the energy of the dimer E_{AB} and the energies of the monomers E_A and E_B

$$E_{\text{int}} = E_{AB} - E_A - E_B$$

It is assumed that the internal coordinates of the monomers used in computing E_A and E_B are the same as within the dimer AB. Thus, the interaction energy depends on the separation R between the centers of mass of the monomers, on the Euler angles characterizing their mutual orientation, and on monomer's internal coordinates. One may mention that published values of the intermolecular energy are sometimes obtained without keeping the internal coordinates of monomers the same in computing E_{AB}, E_A, and E_B (often when applying a global geometry optimization). The meaning of such a definition of the interaction energy is unclear and its usefulness for interpretation of experimental data is disputable.

A complete potential energy surface (containing a dependence on internal coordinates) can be utilized to obtain a solution of the Schrödinger equation for the nuclear motion. This solution provides information which can be directly compared with experiment. Clearly, the inclusion of the dependence on the internal coordinates adds significantly to the time of calculations of potential energy surfaces. Often a reasonable approximation is to decouple the internal and external motion of monomers and use in nuclear dynamics calculations an intermolecular interaction potential computed for fixed internal coordinates. The internal coordinates should then be obtained by averaging intramonomer geometries over the appropriate rovibrational wave function for a given monomer.

Experimental investigations of intermolecular forces have undergone a significant development in the past two decades. Not long ago only very fragmentary information, mainly from bulk measurements and scattering experiments, was available.[18,19] At the present time experiments, in particular the infrared spectroscopy,[20-23] can provide data enabling construction of quantitatively correct multidimensional empirical potential energy surfaces for small van der Waals molecules.[24,25] Since there exist no direct experimental method of measuring the intermolecular potential, a significant amount of theoretical effort is needed to fit a surface to a set of experimental data.[24,25] Until recently theoretical intermolecular potentials could not match the accuracy of the empirical ones, except for the simplest systems. (See refs 7-10, and 26-30 for recent reviews of theory.)

Since intermolecular forces are so much weaker than the intramolecular ones, standard computational methods of electronic structure theory are not very well suited for applications to intermolecular interactions. The standard methods are always applied in the so-called *supermolecular approach*,[31] *i.e.*, the interaction energy is computed by subtracting the sum of monomer's energies from the energy of the dimer. However, in practical calculations, due to the use of incomplete basis sets, these methods always contain the basis set superposition error resulting from nonphysical lowering of monomer's energy in dimer's calculation due to "borrowing" of the basis set from the interacting partner.[32] There is no general consensus on how to compute the supermolecular interaction energies such that the effects of basis set superposition are minimized.[33-37] Since for all many-electron systems except for very small ones the errors in total energies are much larger than the interaction energy itself, accuracy of the computed potential depends on a cancellation of these large errors. Moreover, a supermolecular calculation does not allow any physical insight into the nature of intermolecular interactions. Methods taking into account specific nature of intermolecular interactions, *i.e.*, the perturbation methods which are the subject of this review, have actually been useful in providing an interpretation and an estimation of reliability of potential energy surfaces obtained by the supermolecular approach.[31]

The first quantum mechanical theory of intermolecular interactions was developed in the 1930s by London and co-workers[38-40] (an even earlier development was due to Wang[41]). This theory is based on the standard low-order Rayleigh—Schrödinger (RS) perturbation expansion with the unperturbed Hamiltonian describing noninteracting monomers. The difference between the total and the unperturbed Hamiltonians is the intermolecular interaction operator V. In London's method the exact interaction operator is replaced by its multipole expansion.[42,43] Since such expansion of V is convergent only in a small part of the configuration space (corresponding to electrons localized on the monomers), the London method is valid only asymptotically for large intermolecular separations.[44] At finite internuclear separations the resulting multipole expansion of the interaction energy is divergent.[45-47] London's theory became a classical tool for investigating intermolecu-

lar interactions at large separations and it is still actively developed as better methods for calculating the asymptotic expansion constants are devised.[6,48]

The London theory can be improved by using the exact, nonexpanded form of V. The resulting perturbation expansion is referred to as the *polarization* approximation or polarization theory.[49] The interaction energy components which are missing in London's theory but are included by the polarization theory are called the charge overlap or penetration effects. By inclusion of the charge overlap effects the problem of the divergent nature of the multipole expansion is circumvented and all interaction energy components appearing in the polarization theory have well-defined values for finite intermolecular separations (see sections II, IV, and V for a further discussion of these issues).

The neglect of the overlap is not the only defect of London's theory. Even if the intermolecular interaction operator were not expanded, *i.e.*, in the polarization approach, the computed intermolecular potential energy surface would be qualitatively incorrect and in particular would not exhibit the van der Waals minima nor would it give the repulsive wall for small intermolecular separations. The reason is that the polarization method, as shown in refs 50−52, is not able in a finite order to account for the exchange effects resulting from tunneling of electrons between interacting systems.[53] This difficulty is removed by combining a perturbation expansion with imposition of the correct permutational symmetry of the wave function. The resulting symmetry-adapted perturbation theory (SAPT)[39,54−64] is an *ab initio* method which takes care of both defects of London's theory and enables investigations of the complete potential energy surface. The method provides a conceptual framework for understanding the complete phenomenon of intermolecular interactions. Similarly as in London's theory the starting point are the unperturbed monomers. Since both the overlap and exchange effects vanish exponentially for large intermolecular separations, SAPT is asymptotically equivalent to London's theory. Each of the interaction energy corrections computed in the SAPT approach can be classified as describing one of the four fundamental interactions: electrostatic, induction, dispersion, or exchange. Thus, the SAPT approach represents the interaction energy as a sum of terms with well-defined physical interpretation which allows a better insight into the nature of intermolecular interaction mechanism. Such insight is helpful in understanding of trends in spectroscopic and scattering experiments and relations between the strength of intermolecular interaction and the properties of monomers. It will also provide guidance in constructing semiempirical methods to be applied for larger systems. Since all the terms computed by SAPT contribute directly to the interaction energy, the method is free from the basis set superposition error.

Although the first formulation of SAPT dates back to 1930 and properties of SAPT have been extensively investigated in the late 1960s and in 1970s, all this work has been restricted to the simplest systems such as H_2^+ and H_2. Application of SAPT to many-electron systems required development of a double-perturbation theory which was done in the late 1970s.[65] In

such theory, referred to as the *many-body* SAPT, the Møller−Plesset fluctuation potentials[66] for monomers (intramolecular correlation operators) are considered together with the standard intermolecular interaction operator V. This theory has been initially applied to interactions of two helium atoms.[65,67,68] More recently general formulas of the many-body SAPT in terms of one- and two-electron integrals and orbital energies have been derived and coded making practical calculations on arbitrary systems possible.[11,12,69−74]

We start in section II from a presentation of the polarization expansion, including an analysis of its convergence properties. The exchange effects and the SAPT approach are described in section III. This section contains also a discussion of the convergence properties of the SAPT expansions for model systems (H_2^+, H_2, and He_2). Section IV is devoted to the London's theory which can now be treated as a limit of SAPT for very large intermolecular separations. The use of the multipole expansion in London's theory provides a division of the interaction energy into components related to "partial waves" on each center. It is possible to keep this division in the polarization theory replacing the (approximate) multipole expansion of the interaction operator V by the exact *bipolar* expansion, and section V will review the present status of theory in this field. In section VI the many-body implementation of SAPT is outlined. Applications of many-body SAPT to several weakly interacting systems are surveyed in section VII, and section VIII contains conclusions.

II. Polarization Theory

The conceptually simplest perturbation approach to intermolecular interactions is provided by the *polarization theory*. This is a standard application of the Rayleigh−Schrödinger perturbation method to the eigenvalue problem for the electronic (Born−Oppenheimer) Hamiltonian H for the dimer AB

$$(H_0 + \zeta V)\Phi_{AB} = E_{AB}\Phi_{AB} \qquad (1)$$

with the unperturbed operator $H_0 = H_A + H_B$ chosen as the sum of the monomer electronic Hamiltonians H_A and H_B. The perturbation operator V, defined as the difference between the total Hamiltonian H and H_0, collects all Coulombic potentials corresponding to interactions between electrons and nuclei associated with monomer A on one side and those associated with monomer B on the other. Usually, one assumes that the Hamiltonians H_A and H_B act on the coordinates of electrons $1, ..., N_A$ and $N_A + 1, ..., N_A + N_B$, respectively. This means that the electrons $1, ..., N_A$ are assigned to monomer A and the electrons $N_A + 1, ..., N_A + N_B$ to monomer B. The total dimer energy $E_{AB} = E_{AB}(\zeta)$ and the wave function $\Phi_{AB} = \Phi_{AB}(\zeta)$, satisfying eq 1, depend implicitly on the parameter ζ introduced to define the orders of perturbation expansion.

The Hamiltonian partitioning used in eq 1 is very natural from the physical point of view. When $\zeta = 0$ the intermolecular interaction terms in the Hamiltonian are switched off and the dimer energy becomes equal to the sum of the energies of the unperturbed monomers $E_{AB}(0) = E_A + E_B \equiv E_0$. At the same time

the dimer wave function becomes the product of the monomer wave functions $\Phi_{AB}(0) = \Phi_A\Phi_B \equiv \Phi_0$ (in this review we shall be concerned with the situations when Φ_A and Φ_B correspond to nondegenerate ground states only). When $\zeta = 1$, the intermolecular interaction terms in the Hamiltonian (given by V) are completely included and the corresponding wave function $\Phi_{AB}(1)$ and energy $E_{AB}(1)$ become the exact, physical wave function and energy of the dimer. The operator V is thus fully responsible for the intermolecular interaction phenomenon and is usually referred to as the *intermolecular interaction operator*.

A. Polarization Series for the Wave Functions and Energy

The polarization series for the wave function and the interaction energy $E_{\mathrm{int}} \equiv E_{AB} - E_0$ are defined as power series in ζ for $\Phi_{AB}(\zeta)$ and $E_{AB}(\zeta) - E_0$:

$$\Phi_{AB}(\zeta) = \sum_{n=0}^{\infty} \zeta^n \Phi_{\mathrm{pol}}^{(n)} \qquad (2)$$

$$E_{\mathrm{int}}(\zeta) = \sum_{n=1}^{\infty} \zeta^n E_{\mathrm{pol}}^{(n)} \qquad (3)$$

The individual corrections $\Phi_{\mathrm{pol}}^{(n)}$ and $E_{\mathrm{pol}}^{(n)}$ are referred to as the *n*th-order *polarization wave functions* and *polarization energies*. As observed by Ahlrichs,[75] it follows from the mathematical work of Kato[76] that $\Phi_{AB}(\zeta)$ and $E_{\mathrm{int}}(\zeta)$ are analytic functions of the complex variable ζ for ζ belonging to a certain circle $|\zeta| < \varrho$ of radius $\varrho > 0$. This means that the series of eqs 2 and 3 do converge for sufficiently small values of ζ. Since only for $\zeta = 1$ the Hamiltonian $H_0 + \zeta V$ corresponds to physical reality, the practically relevant question is whether these series converge at $\zeta = 1$ or, equivalently, whether the convergence radius ϱ is greater than unity. Considerable effort has been devoted to answer this question.[50–52,75,77–78] Irrespective of the controversies surrounding this problem[52,87] and of the definite answer to the convergence question (which as we know now depends on the considered system, see section II.C), the polarization theory still provides the basis for most of our understanding of the physical nature of the weak intermolecular interaction phenomenon.

The expression for the interaction energy $E_{\mathrm{int}}(\zeta)$ takes a particularly simple form

$$E_{\mathrm{int}}(\zeta) = \langle \Phi_0 | \zeta V \Phi_{AB}(\zeta) \rangle \qquad (4)$$

when the arbitrary phase and normalization of the wave function $\Phi_{AB}(\zeta)$ are fixed by the so-called intermediate normalization condition[89]

$$\langle \Phi_0 | \Phi_{AB}(\zeta) \rangle = 1 \qquad (5)$$

Consequently, the polarization energy of the *n*th-order is given by

$$E_{\mathrm{pol}}^{(n)} = \langle \Phi_0 | V \Phi_{\mathrm{pol}}^{(n-1)} \rangle \qquad (6)$$

The polarization functions are obtained from the recurrence relationships[89]

$$\Phi_{\mathrm{pol}}^{(n)} = -\hat{R}_0 V \Phi_{\mathrm{pol}}^{(n-1)} + \sum_{k=1}^{n-1} E_{\mathrm{pol}}^{(k)} \hat{R}_0 \Phi_{\mathrm{pol}}^{(n-k)} \qquad (7)$$

The zeroth-order polarization function $\Phi_{\mathrm{pol}}^{(0)}$ needed to start the recurrence procedure is equal to the unperturbed wave function $\Phi_0 = \Phi_A\Phi_B$. The operator $\hat{R}_0$ is the reduced resolvent of H_0, defined, *e.g.*, as[90]

$$\hat{R}_0 = (H_0 - E_0 + P_0)^{-1}Q_0 \qquad (8)$$

where $P_0 = |\Phi_0\rangle\langle\Phi_0|$ and $Q_0 = 1 - P_0$. The operator $\hat{R}_0$, commonly used in perturbation theory considerations, may be viewed as an "inverse" of the singular operator $H_0 - E_0$ in the space orthogonal to Φ_0. It has the following spectral (sum-over-states) representation

$$\hat{R}_0 = \sum_{m \neq 0} \frac{|\Phi_m\rangle\langle\Phi_m|}{E_m - E_0} \qquad (9)$$

in terms of excited eigenfunctions Φ_m and eigenvalues E_m of H_0. The sum-over-states formulas characteristic of the early development of perturbation theory do not have practical utility since they necessarily involve continuum wave functions. In practice, the action of $\hat{R}_0$ on an arbitrary function f is calculated by solving the partial differential equation $(H_0 - E_0)\chi = Q_0 f$ (usually using the Hylleraas variational principle[89]) and orthogonalizing a solution to Φ_0 so that $\hat{R}_0 f = Q_0 \chi$.

B. Physical Interpretation of Low-Order Polarization Energies

The polarization energies through third order have an appealing, partly classical, physical interpretation. They can also be rigorously related to monomer properties, which considerably facilitates their estimation and practical evaluation.

1. Electrostatic Interaction

The first-order polarization energy is given by

$$E_{\mathrm{pol}}^{(1)} = \langle \Phi_A\Phi_B | V \Phi_A\Phi_B \rangle \qquad (10)$$

Using the explicit form of the intermolecular interaction operator and performing the integration over the coordinates of all electrons except for one electron on the monomer A and/or one electron on the monomer B, one can express $E_{\mathrm{pol}}^{(1)}$ in terms of the total charge distribution $\varrho_A^{\mathrm{tot}}(r)$ and $\varrho_B^{\mathrm{tot}}(r)$ of the monomers[5,17]

$$E_{\mathrm{pol}}^{(1)} = \int\int \varrho_A^{\mathrm{tot}}(r_1)\frac{1}{r_{12}}\varrho_B^{\mathrm{tot}}(r_2)\, d^3r_1\, d^3r_2 \qquad (11)$$

where $r_{12} = |r_1 - r_2|$. The total electric charge distribution for the monomer A is given (in atomic units) by

$$\varrho_A^{\mathrm{tot}}(r) = \sum_\alpha Z_\alpha \delta(r - R_\alpha) - \varrho_A(r) \qquad (12)$$

where the term containing Dirac's delta $Z_\alpha\delta(r - R_\alpha)$ represents the contribution from the positive point charge Z_α at the position of nucleus α and $-\varrho_A(r)$ is

the electronic charge distribution, given by the diagonal element of the first-order density matrix (normalized to the number of electrons in monomer A).

Equations 11 and 12 show that the first-order polarization energy has a very transparent physical interpretation. It simply represents the energy of the electrostatic (Coulombic) interaction of the monomers' charge distributions. For this reason it is referred to as the *electrostatic energy*. At large intermonomer distances R the electrostatic energy can be represented as a sum of classical electrical interactions between the permanent multipole moments of unperturbed monomers (see section IV). However, one should emphasize that the electrostatic energy contains also important short-range terms due to the mutual penetration (charge overlap) of monomers' electron clouds (see section V). This short-range part of the electrostatic energy makes significant contributions to the stabilization energy of atom−diatom van der Waals complexes[72,91−94] and cannot be neglected in any accurate calculations of potential energy surfaces for such systems. The electrostatic interaction plays a major role in determining the structure of dimers consisting of polar molecules, in particular hydrogen-bonded systems.[29,95−98] The evaluation of the electrostatic interaction energy for such systems is often performed by approximating the electrostatic potential of a molecule by that resulting from a set of point charges[5] or from a multicenter distribution of multipole moments.[99−105] Evaluation of the electrostatic part of the interaction energy for polyatomic molecules, often very large ones, is presently an actively developing subfield of the theory of intermolecular forces. It has been recently reviewed for this journal by Dykstra.[106]

2. Induction Interaction

The second-order polarization energy $E_{pol}^{(2)}$ is given by

$$E_{pol}^{(2)} = -\langle \Phi_0 | V \hat{R}_0 V | \Phi_0 \rangle = -\sum_{m \neq 0} \frac{|\langle \Phi_0 | V \Phi_m \rangle|^2}{E_m - E_0} \quad (13)$$

The induction energy is obtained when the sum-over-states in definition 13 is restricted to "singly excited" (in the molecular sense) eigenfunctions of H_0, i.e., to the functions of the form $\Phi_A \Phi_B^{exc}$ and $\Phi_A^{exc} \Phi_B$, where the superscript exc is used to denote an excited state. The corresponding part of $E_{pol}^{(2)}$, denoted by $E_{ind}^{(2)}$, is given by

$$E_{ind}^{(2)} = E_{ind}^{(2)}(A) + E_{ind}^{(2)}(B) \quad (14)$$

where

$$E_{ind}^{(2)}(A) = -\langle \Phi_A | \Omega_B \hat{R}_0^A \Omega_B | \Phi_A \rangle \quad (15)$$

and similarly for $E_{ind}^{(2)}(B)$. Ω_B denotes here the operator of the electrostatic potential generated by the unperturbed monomer B

$$\Omega_B = \sum_{i \in A} \omega_B(r_i) \quad (16)$$

$$\omega_B(r_i) = \int \frac{1}{r_{ij}} \varrho_B^{tot}(r_j) \, d^3 r_j \quad (17)$$

and $\hat{R}_0^A = (H_A - E_A + P_A)^{-1} Q_A$, where $P_A = |\Phi_A\rangle\langle\Phi_A|$ and $Q_A = 1 - P_A$, is the ground-state reduced resolvent of H_A, which can also be expressed in terms of the excited eigenfunctions and eigenvalues of the monomer A using sum-over-states formula similar to eq 9.

Equation 15 has the form of the second-order energy correction arising when monomer A is perturbed by the static electric field generated by the (unperturbed) monomer B. This field, corresponding to the potential ω_B, induces a modification $\Phi_{ind}^{(1)}(A) = -\hat{R}_0^A \Omega_B \Phi_A$ in the wave function of monomer A and the energetic effect of this modification, given by $\langle \Phi_A | \Omega_B \Phi_{ind}^{(1)} \rangle$, is equal exactly to $E_{ind}^{(2)}(A)$. The second-order induction energy results, thus, from the mutual polarization of the monomers by the static electric fields of unperturbed partners. Asymptotically, at large R, this effect is fully determined by the permanent multipole moments and static multipole polarizabilities of the monomers (see section IV for further details). At finite R additional monomer information is needed to account for the short-range, penetration part of $E_{ind}^{(2)}$. This information is contained in the short-range part of the electrostatic potentials $\omega_X(r)$, $X = A$ or B, and in the polarization propagators of the monomers. The polarization propagator is a molecular property, which fully describes the linear response of a molecule to an arbitrary external perturbation.[107,108] It is defined for an arbitrary frequency ω by

$$\Pi_{\kappa\kappa'}^{\lambda\lambda'}(\omega) = -\langle \Phi_A | a_\kappa^\lambda \hat{R}^A(-\omega) a_{\kappa'}^{\lambda'} \Phi_A \rangle - \langle \Phi_A | a_{\kappa'}^{\lambda'} \hat{R}^A(\omega) a_\kappa^\lambda \Phi_A \rangle \quad (18)$$

where $a_\kappa^\lambda = a^\lambda a_\kappa$ is a product of ordinary creation (a^λ) and annihilation (a_κ) operators and $\hat{R}^A(\omega)$ is the frequency dependent resolvent defined as $\hat{R}_A(\omega) = (H_A - E_0^A + \omega)^{-1} Q_A$, for $\omega \neq 0$ and by $\hat{R}^A(0) = \hat{R}_0^A$ for $\omega = 0$. The induction energy $E_{ind}^{(2)}(A)$ is related to the static part (at $\omega = 0$) of the polarization propagator via[17,74]

$$E_{ind}^{(2)}(A) = (-1/2)(\omega_B)_\lambda^\kappa (\omega_B)_{\lambda'}^{\kappa'} \Pi_{\kappa\kappa'}^{\lambda\lambda'}(0) \quad (19)$$

where $(\omega_B)_\lambda^\kappa$ is the matrix element of the electrostatic potential $\omega_B(r)$ calculated with the one-particle functions (spinorbitals) ψ_λ used to define the second quantization operators a_λ, i.e., $(\omega_B)_\lambda^\kappa = \langle \psi_\lambda | \omega_B | \psi_\kappa \rangle$. The Einstein summation convention over repeated lower and upper indices is used in eq 19 and further on in this article. Since the electron densities (needed to calculate ω_B) and the static propagators can be calculated as the first and second derivatives of the monomer energy with respect to appropriate perturbations, the existing quantum chemical technology[109−115] of calculating analytic first and second derivatives can be directly utilized to study induction interactions in the region where charge overlap effects play an important role, i.e., in the region of van der Waals minima and at shorter distances.

In studies of larger molecules one can approximate the induction component of the interaction energy

using distributed multipole moments and polarizabilities.[101,116,117] It should be noted, however, that the distributed polarizabilities (defined usually using basis set partitioning techniques) are highly nonunique and do not always lead to stable expressions for the induction energy.[117] Very recently a basis set independent definition of distributed multipole polarizabilities has been introduced and successfully applied.[118]

In calculating the induction energy $E_{ind}^{(2)}(A)$ the motion of the electrons in monomer A is not correlated with the motion of electrons in monomer B since the effect of the latter is represented only by the averaged electrostatic potential $\omega_B(r)$. This means that by considering only the induction interaction we completely neglect the *intermonomer* electron correlation. (The *intramonomer* correlation does affect the induction interaction, see section VI.) This property of the induction interaction is the basis for the generalization of the induction energy concept to higher orders in V. Specifically, the third-order induction energy $E_{ind}^{(3)}$ represents that part of $E_{pol}^{(3)}$ which can be obtained when the intermonomer electron correlation is completely neglected. In general, the infinite-order induction energy $E_{ind}(\zeta)$ is defined via the variational principle as the minimum of the expectation value of the Hamiltonian $H_0 + \zeta V$ with the (normalized) trial function $\tilde{\Phi}$ of the form $\tilde{\Phi}_A\tilde{\Phi}_B$, where the functions $\tilde{\Phi}_A$ and $\tilde{\Phi}_B$ depend on the coordinates of electrons assigned to monomers A and B, respectively. Expanding $E_{ind}(\zeta)$ as a power series in ζ one obtains definitions of the induction energies of specific order in V.[119] In second order one recovers the expression given by eqs 14 and 15 and in third order one obtains

$$E_{ind}^{(3)} = \langle \hat{I}_A\Phi_0|[\Omega_B,\hat{I}_A]\Phi_0\rangle + \langle \hat{I}_B\Phi_0|[\Omega_A,\hat{I}_B]\Phi_0\rangle +$$
$$2Re\langle \hat{I}_A\Phi_0|V\hat{I}_B\Phi_0\rangle + 2Re\langle \Phi_0|V\hat{I}_A\hat{I}_B\Phi_0\rangle \quad (20)$$

where the operators $\hat{I}_A = -\hat{R}_0^A\Omega_B P_A$ and $\hat{I}_B = -\hat{R}_0^B\Omega_A P_B$ generate the first-order induction functions $\Phi_{ind}^{(1)}(A) = -\hat{R}_0^A\Omega_B\Phi_A$ and $\Phi_{ind}^{(1)}(B) = -\hat{R}_0^B\Omega_A\Phi_B$ when acting on Φ_A and Φ_B, respectively, e.g., $\hat{I}_A\Phi_A = \Phi_{ind}^{(1)}(A)$. The square brackets in eq 20 denote the commutator of two operators, $[X,Y] = XY - YX$. Note that the third-order induction energy cannot be represented as a sum of two terms describing the (second-order) polarization of the monomer A by the fields of the monomer B and *vice versa* but contains also mixed terms (the last two terms in eq 20), which correspond to simultaneous polarization of both monomers by the field of their partners. Recently, it has been shown[74] that the third-order induction energy (including the charge-overlap contribution) can be expressed through the static polarization propagators of monomers

$$E_{ind}^{(3)} = \frac{1}{6}(\omega_B)_\lambda^\kappa(\omega_B)_{\lambda'}^{\kappa'}(\omega_B)_{\lambda''}^{\kappa''}\Pi_{\kappa\kappa'\kappa''}^{\lambda\lambda'\lambda''}(0,0) +$$
$$\frac{1}{6}(\omega_A)_\nu^\mu(\omega_A)_{\nu'}^{\mu'}(\omega_A)_{\nu''}^{\mu''}\Pi_{\mu\mu'\mu''}^{\nu\nu'\nu''}(0,0) +$$
$$(\omega_B)_\lambda^\kappa(\omega_A)_\nu^\mu v_{\lambda'\nu'}^{\kappa'\mu'}\Pi_{\kappa\kappa'}^{\lambda\lambda'}(0)\Pi_{\mu\mu'}^{\nu\nu'}(0) \quad (21)$$

where $\Pi_{\kappa\kappa_1\kappa_2}^{\lambda\lambda_1\lambda_2}(\omega_1,\omega_2)$ denotes the quadratic polarization propagator (quadratic response function[108,109,120])

(in ref 120 the propagator $\Pi_{\kappa\kappa_1\kappa_2}^{\lambda\lambda_1\lambda_2}(\omega_1,\omega_2)$ is denoted by $\ll a_\kappa^\lambda; a_{\kappa_1}^{\lambda_1}; a_{\kappa_2}^{\lambda_2}\gg_{\omega_1,\omega_2}$). In eq 21 we use the convention that the indices λ and κ label spin orbitals of monomer A while μ and ν label spin orbitals of monomer B. The symbol $v_{\kappa\mu}^{\lambda\nu}$ denotes the standard Coulomb integral $\langle \psi_\kappa(1)\psi_\mu(2)| r_{12}^{-1}|\psi_\lambda(1)\psi_\nu(2)\rangle$. The third-order induction effects have thus far been considered in the literature only in the multipole approximation.[121-125] In this approximation the first two terms in eq 21 can be related to the multipole hyperpolarizabilities of the monomers and the third one can be expressed through the polarizabilities only. However, it cannot be expected that the multipole approximation can be used to estimate the contribution of the third-order induction effects to the stabilization of van der Waals complexes. This is due to the fact that the importance of the charge-overlap effects, which already dominate the second-order induction effect at the distances of van der Waals minima, increases with the increasing order of perturbation theory.

One should emphasize that although the individual induction energies of arbitrarily high order can be easily defined, the total, infinite-order induction energy is not a well-defined concept, except for small one- or two-electron monomers. For larger systems the induction series, similar to the polarization series (see section II.C), must diverge. This divergence shows up already in low orders so that an evaluation of the third- and higher-order induction energies without appropriate exchange corrections leads at finite distances to substantial overestimation of the total interaction energy.[126,127]

3. Dispersion Interaction

The second-order dispersion energy $E_{disp}^{(2)}$ is defined as the difference between the second-order polarization and induction energies, $E_{disp}^{(2)} = E_{pol}^{(2)} - E_{ind}^{(2)}$. Equivalently, in view of eqs 13–15, one can use the following direct definition

$$E_{disp}^{(2)} = -\langle \Phi_0|V\hat{R}_0^{AB}V|\Phi_0\rangle \quad (22)$$

where $\hat{R}_0^{AB} = \hat{R}_0 - \hat{R}_0^A P_B - P_A\hat{R}_0^B$ is the "dispersion part" of the resolvent $\hat{R}_0$, i.e., that part of $\hat{R}_0$, which involves only "doubly excited" states $\Phi_m = \Phi_A^{exc}\Phi_B^{exc}$ in the sum-over-states formula of eq 13. Alternatively, one may write $E_{disp}^{(2)} = \langle \Phi_0|V\Phi_{disp}^{(1)}\rangle$, where $\Phi_{disp}^{(1)} = -\hat{R}_0^{AB}V\Phi_0$ is the "dispersion function" representing the leading intermolecular correlation contribution to the dimer wave function. By the very definition the dispersion interaction represents a pure intermolecular correlation effect. It may be viewed as the stabilizing energetic effect of the correlations of instantaneous multipole moments of the monomers. Since the classic work of Casimir and Polder[128] we know that, asymptotically at large R, the energy of the dispersion interaction can be expressed in terms of dynamic multipole polarizabilities of monomers. A powerful generalization of Casimir and Polder's result has been found recently by Dmitriev and Peinel[129] and by McWeeny.[17,130] (See also a closely related work by Claverie.[131]) These authors have shown that the complete dispersion energy, including the charge-overlap effects, can be

expressed, via Casimir−Polder-type integral, in terms of the polarization propagators of monomers

$$E_{\text{disp}}^{(2)} = -\frac{1}{4\pi} v_{\lambda_1\nu_1}^{\kappa_1\mu_1} v_{\lambda_2\nu_2}^{\kappa_2\mu_2} \int_{-\infty}^{+\infty} \Pi_{\kappa_1\kappa_2}^{\lambda_1\lambda_2}(i\omega)\Pi_{\mu_1\mu_2}^{\nu_1\nu_2}(-i\omega)\ d\omega \tag{23}$$

Equation 23 is very important since at physically most relevant distances of the van der Waals minima the charge-overlap contribution to the dispersion energy is always substantial. Additionally, the powerful computational techniques, developed in the 1980s to obtain accurate polarization propagators,[108,109] can be utilized via eq 23 in calculations of dispersion energies at finite distances. One should note, however, that in practice for an accurate calculation of the dispersion energy at intermediate and short distances the polarization propagators must be calculated using the so called *dimer-centered basis set*.[71] This reduces somewhat the advantage of formula 23 relative to a direct variational calculation of the dispersion function $\Phi_{\text{disp}}^{(1)}$ [67,132] since the expensive step of calculating the propagators must be repeated at each dimer's geometry.

In the third order of polarization theory the intermolecular correlation contribution $E_{\text{pol}}^{(3)} - E_{\text{ind}}^{(3)}$ separates into two parts: the induction−dispersion energy $E_{\text{ind−disp}}^{(3)}$ and the third-order dispersion energy $E_{\text{disp}}^{(3)}$. The induction−dispersion effect results from the coupling of the induction and dispersion interactions and gives the following contribution to the interaction energy

$$E_{\text{ind−disp}}^{(3)} = E_{\text{ind−disp}}^{(3)}(A) + E_{\text{ind−disp}}^{(3)}(B) \tag{24}$$

where

$$E_{\text{ind−disp}}^{(3)}(A) =$$
$$2Re\langle \hat{D}\Phi_0|[V,\hat{I}_A]\Phi_0\rangle + \langle \hat{D}\Phi_0|[\Omega_B,\hat{D}]\Phi_0\rangle \tag{25}$$

and $\hat{D} = -\hat{R}_0^{AB}VP_0 = |\Phi_{\text{disp}}^{(1)}\rangle\langle\Phi_0|$ is the operator which produces the dispersion function when acting on Φ_0 (the definition of $E_{\text{ind−disp}}^{(3)}(B)$ is obtained by interchanging A and B). The induction−dispersion energy can be expressed through monomer properties (electron densities and polarization propagators) using the formula[74]

$$E_{\text{ind−disp}}^{(3)}(A) =$$
$$-\frac{1}{4\pi}(\omega_B)_\lambda^\kappa v_{\lambda_1\nu_1}^{\kappa_1\mu_1} v_{\lambda_2\nu_2}^{\kappa_2\mu_2} \int_{-\infty}^{+\infty} \Pi_{\kappa\kappa_1\kappa_2}^{\lambda\lambda_1\lambda_2}(i\omega, -i\omega)\Pi_{\mu_1\mu_2}^{\nu_1\nu_2}(-i\omega)\ d\omega \tag{26}$$

where the symbols have the same meaning as in eqs 21 and 23.

The third-order dispersion energy $E_{\text{disp}}^{(3)}$ is defined by

$$E_{\text{disp}}^{(3)} = \langle \hat{D}\Phi_0|[V-\Omega_A-\Omega_B,\hat{D}]\Phi_0\rangle \tag{27}$$

Despite some efforts,[133] this energy could not be expressed, even asymptotically, through monomer properties. One may add here that the third-order dispersion energy is a true third-order intermolecular correlation effect while the induction−dispersion contribution can be obtained in a second-order per-

turbation treatment if in zeroth order the monomers are fully deformed by the induction effects.[134] The two-body third-order dispersion interaction has been considered in the literature almost exclusively in the multipole approximation.[122,135,136] For atom−atom and atom−molecule interactions this energy contribution behaves like R^{-11} and R^{-10}, respectively, and can be expected to be small at the distances of van der Waals minima. One can expect a larger contribution for interactions of polar molecules when $E_{\text{disp}}^{(3)}$ vanishes like R^{-9}. The calculations for the water dimer and the HF dimer[11] have shown, however, that even for these polar systems the contribution of the third-order dispersion energy is small (1−2% of the total interaction energy at the equilibrium configurations). It remains to be seen if this optimistic result holds also for other complexes.

C. Large-Order Convergence Properties

As discussed in section II.B, the polarization theory in low orders provides the basis for most of our understanding of the physical nature of the weak intermolecular interaction phenomenon and gives important relations connecting the strength of the intermolecular interaction with static and dynamic monomer properties. It is not surprising then that the question of the convergence of the polarization expansion has been studied quite extensively.[50−52,75,77−82,84−88] We know[75,76] that expansion 3 must converge for sufficiently small ζ and the question is whether the convergence radius ϱ is large enough so that the physical value of the expansion parameter $\zeta = 1$ lies within the convergence circle.

1. H_2^+

The first studies of the convergence properties of the polarization series were carried out for the interaction of a hydrogen atom with a proton, *i.e.*, for the H_2^+ system. Initial investigations performed using very simple, physically rather unrealistic models of $H_2^{+\ 78,79}$ suggested that the convergence radius ϱ is greater than unity and that the polarization series converges at $\zeta = 1$. Later Whitton and Byers Brown[80] discovered that the convergence radius ϱ for the realistic hydrogen atom−proton interaction is determined by a pair of complex branch points ζ_b of the function $E_{\text{int}}(\zeta)$

$$\zeta_b = 1 + \delta \pm i\eta \tag{28}$$

where δ and η are real parameters and $\varrho = |\zeta_b|$. These authors also found that η vanishes at large R like $2K$, and that δ is of the order K^2, where $K \approx 2Re^{-R-1}$ is the so-called exchange energy defined as half of the energy difference between the $1s\sigma_g$ and $2p\sigma_u$ states. They incorrectly concluded, however, without estimating the sign and the magnitude of δ, that $\varrho \approx 1 + \delta + \eta^2/2$ is greater than unity, *i.e.*, that the polarization series is convergent in this case. Somewhat later the convergence radius for this system was computed numerically using quadratic Padé approximants[51] and shown to be greater than unity for internuclear distances corresponding to both the chemical and the van der Waals minima. This work has resolved the question of the convergence of the polarization series for H_2^+. Very recently

Table 1. Interatomic Distance Dependence of the Branch Points $\zeta_b = 1 + \delta \pm i\eta$ and of the Convergence Radius ϱ of the Polarization Expansion for the Interaction Energy in the Ground $X^1\Sigma_g^+$ state of H_2 (Ref 52)[a]

R	δ	η	ϱ
1.4	1.717(−1)	5.054(−1)	1.276
2.0	6.715(−2)	2.442(−1)	1.094 7
4.0	7.898(−4)	1.577(−2)	1.000 914
6.0	1.957(−6)	6.134(−4)	1.000 002 15
8.0	2.897(−9)	2.012(−5)	1.000 000 0031

[a] The expression $(-N)$ denotes the factor of 10^{-N}.

Kutzelnigg[88] has found that δ behaves asymptotically at large R as $2RK^2$, which proves that ϱ must be greater than unity for sufficiently large R, in agreement with the findings of ref 51. Since at large R the convergence radius ϱ is only marginally greater than unity (at the distance of van der Waals minimum $\varrho = 1.000\ 000\ 02$) one can expect that the polarization series converges very slowly in this case. This agrees with the results of an early numerical study of Chalasinski et al.[50] who showed that the sum of the polarization series initially approaches very fast the so-called *Coulomb energy* Q, defined as the average value of the energies of the $1s\sigma_g$ and $2p\sigma_u$ states, and then converges, although extremely slowly, to the energy of the ground $1s\sigma_g$ state.

2. H_2

Since the symmetry groups of H_2^+ and H_2 are so similar, one could expect that for the interactions of two hydrogen atoms the convergence properties of the polarization expansion will be qualitatively similar to those for the hydrogen atom−proton system. Very recently, however, Tang and Toennies[87] conjectured that the polarization expansion for the H_2 molecule "converges to the Coulomb energy at $R \to \infty$ and to a value between the Coulomb energy and the singlet ground state energy at smaller distances". (For H_2 the Coulomb energy is defined as the average value of the energies of the asymptotically degenerate $X^1\Sigma_g^+$ and $b^3\Sigma_u^+$ states.) This would be in a striking disagreement with the results obtained earlier for H_2^+, and would contradict the conventional wisdom that the Rayleigh−Schrödinger perturbation series either converges to the right answer (*i.e.*, to an eigenvalue) or diverges. Tang and Toennies were motivated by an observation[137,138] that the polarization expansion for the wave function, when inserted into the Herring−Holstein[53] surface integral formula, gives the correct asymptotic expression for the energy of the singlet−triplet splitting in H_2, the result which is in apparent contradiction with the convergence of the polarization expansion to the fully symmetric ground-state wave function. To clarify this controversy Cwiok et al.[52] performed highly accurate numerical calculations of the convergence radius and the high-order polarization corrections for the interaction between two ground-state hydrogen atoms. The results of this study are summarized in Tables 1 and 2. Similarly as for H_2^+, the convergence circle of the polarization series is determined by a pair of complex branch points $\zeta_b = 1 + \delta \pm i\eta$ in the closest vicinity of the point $\zeta = 1$, where $\delta > 0$ for the interatomic distances studied ($1.4 \leq R \leq 8.0$ bohr)

Table 2. Convergence of the Polarization Series at the Distance R_e Corresponding to the Bottom of the van der Waals Minimum for H_2^+ ($R_e = 12.5$ bohr), for H_2 ($R_e = 8.0$ bohr), and for He_2 ($R_e = 5.6$ bohr)[a]

n	H_2^+	H_2	He_2
1	−1.0000	−0.9676	−0.9656
2	−0.2781	−0.3057	−0.5693
3	−0.2684	−0.3296	−0.5677
4	−0.2672	−0.3194	−0.5629
5	−0.2671	−0.3203	−0.5602
6	−0.2671	−0.3193	−0.5582
7	−0.2671	−0.3190	−0.5567
8	−0.2671	−0.3187	−0.5555
9	−0.2671	−0.3186	−0.5546
10	−0.2670	−0.3185	−0.5539
15	−0.2670	−0.3183	−0.5521
20	−0.2669	−0.3182	−0.5516
25	−0.2669	−0.3182	−0.5514

[a] The numbers quoted are relative errors defined as $(\Sigma_{k=1}^n E^{(k)} - E_{int})/E_{int}$, where E_{int} is the interaction energy in the fully symmetric state to which the polarization series converge. The exchange energy K represents -26.725% of the interaction energy for H_2^+, -31.833% for H_2, and -55.15% for He_2.

(see Table 1). At the same time Kutzelnigg[88] has rigorously shown that at large R the complex part of ζ_b approaches the exchange energy K (defined in this case as half of the singlet-triplet splitting energy), *i.e.*,

$$\eta = K[1 + R^{-1} + O(R^{-2})] \tag{29}$$

No similar rigorous large-R estimate has been found for the real part of ζ_b, although the arguments of Kutzelnigg[88] make it highly probable that δ is positive asymptotically at large R. The convergence radius $\varrho \approx 1 + \delta + \eta^2/2$ is, thus, greater than unity for the distances studied in ref 52 and, most likely,[88] also at arbitrarily large finite values of R. Consequently, the polarization expansion is convergent for $1.4 \leq R \leq 8.0$ and most likely also at $R > 8$. The results of Table 2 (computed at the van der Waals minimum distances) show that the convergence properties of the polarization expansion for H_2 are very similar to those observed for H_2^+.[50] Initially the sum of the series approaches very fast the Coulomb energy Q. After the value of the Coulomb energy is reached with a very good accuracy, the convergence deteriorates dramatically and becomes extremely slow, in accord with the computed convergence radius of $1.000\ 000\ 003\ 1$. Although the series does converge in mathematical sense, a certain part of the interaction energy is not recovered in any practically reasonable order. Asymptotically, at large R, this part of the interaction energy turns out to be equal to the negative of the exchange energy K. This result, illustrated in Figure 1, can be rationalized in the following way. The polarization series is a sum of two series: one converging quickly to the Coulomb energy Q and another converging extremely slowly to $-K$; the total series converges, also extremely slowly, to the interaction energy $E_{int} = Q - K$ in the ground $X^1\Sigma_g^+$ state. Although the exchange part of the interaction energy, defined as $E_{int} - Q$, cannot be obtained in practice by a direct summation of the perturbation series, the information about the accurate value of K is contained in the polarization corrections and can be recovered using appropriate analytic continuation procedures[51] or large-order
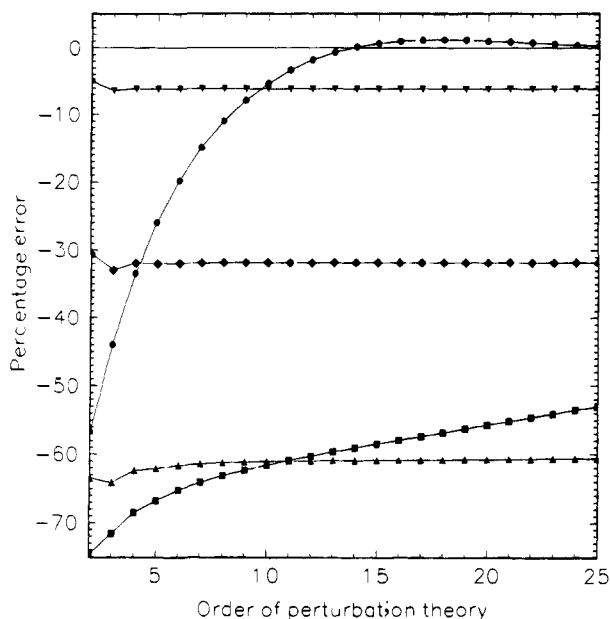
Figure 1. Percentage error of the nth-order polarization expansion for H_2. The error is given with respect to the variational energy for the singlet state of H_2 computed using the same basis set. The distances are marked as follows: $R = 2$, dots; 4, squares; 6, triangles up; 8, diamonds; and 10 bohr, triangles down.

perturbation theory techniques. Specifically, using the large-order representation for $E_{pol}^{(n)}$ it has been shown[52] that the exchange energy K can be very accurately calculated (with five digit accuracy) from three consecutive polarization corrections of sufficiently large order.

Cwiok et al. have also shown[52] that the polarization series for the wave function converges to the wave function of the ground state of H_2. Although the individual polarization functions $\Phi_{pol}^{(n)}$ do not have a definite permutation symmetry, the sum of the series for $\zeta = 1$ is *symmetric* under the interchange P_{12} of the spatial electronic coordinates. This result was recently reconciled with the findings of Tang, Toennies, and Yiu[137,138] by Scott and collaborators.[139]

3. He₂ and Other Many-Electron Systems

Very little quantitative information is available about the convergence properties of the polarization expansion for the interaction of two many-electron systems. Recently Cwiok et al.[140] performed high-order polarization expansion calculations for the interaction energy of two ground-state helium atoms using full configuration interaction basis built from a small 5s3p1d set of orbitals. This investigation suggests that the convergence radius of the polarization series is greater than unity at least for small values of the interatomic distance R. Similar numerical results have been obtained independently by Adams.[141] For large interatomic distances the convergence radius is very close to unity, too close to infer that the convergence will persist in the limit of basis set saturation. As shown in Table 2, the convergence pattern observed for He₂ is very similar to that found for H_2^+ and H_2. There is one very significant difference, however. In the case of H_2^+ and H_2 the perturbation series converges to the wave function and energy of the ground, physical state of

the complex. For He₂ it converges to a Pauli forbidden "bosonic" solution of the Schrödinger equation, which is completely symmetric under the exchange of spatial electronic coordinates. At large R such a solution is quasidegenerate with the physical ground state ($^1\Sigma_g^+$) but at smaller distances it exhibits a strong chemical bond resulting from the 4-fold occupancy of the lowest energy orbital. This behavior of the polarization series was predicted by Claverie more than 20 years ago.[77] Claverie carried out an insightful analysis of the permutation symmetry of the He₂ wave functions and discovered that only the fully symmetric "bosonic" solution can correlate at $\zeta = 1$ [can be analytically connected via the function $E_{int}(\zeta)$] with the unperturbed solution at $\zeta = 0$ and, consequently, can be the limit of the perturbation series.

When one of the monomers has more than two electrons and, consequently, its Hamiltonian has a Pauli forbidden ground state, the situation is even more complicated. The Pauli forbidden state of the dimer, which could possibly represent the limit of the polarization series, is not asymptotically degenerate with the physical ground state of the complex.[81,82] In such a situation there must be an avoided crossing for $\zeta < 1$ of two solutions of eq 1 correlating to two different limits at $R = \infty$. Such an avoided crossing is always associated with a singularity in the complex plane (usually a first-order branch point) and this singularity will determine the convergence radius for the series. This reasoning shows that if a monomer has more than two electrons, the convergence radius of the polarization series must be smaller than unity and the polarization series must diverge for the physical value of the expansion parameter ζ.[81,82] The above theoretical considerations were recently confirmed in numerical calculations by Adams.[85,86,141] This author performed small basis set full configuration interaction calculations for the interaction energy of the ground-state lithium and hydrogen atoms and found[141] that indeed the convergence radius for this system is smaller than one for all interatomic distances studied ($\varrho = 0.78$, 0.77, and 0.78 for $R = 3.0$, 5.0, and 10.0 bohr, respectively).

There exists another reason for the divergence of the polarization expansion for many-electron systems discovered by Morgan and Simon[45] and elaborated on by Adams.[85,86] The relevant argument is based on the observation[45] that the energy corresponding to the physical ground state of the dimer AB lies above the ionization threshold in the Pauli forbidden, unphysical part of the spectrum. This means that physical states of the system are in fact bound states buried in the continuum of states violating the Pauli principle. Since the zeroth-order wave function in the polarization theory has an exclusion principle violating component, it will interact via V with unphysical continuum states of the same energy (the intermolecular interaction operator V is not invariant with respect to all permutations and can mix states of different permutation symmetry). Thus, there are an infinite number of perturbed states the energies of which are arbitrarily close to the unperturbed level E_0. The Rayleigh–Schrödinger perturbation theory cannot be expected to converge in such circumstances.

D. Significance of the Polarization Theory

The results of the preceding paragraph show that the polarization series must diverge when applied to interactions of many-electron systems. The nonsymmetric decomposition of the Hamiltonian used in eq 1, which enabled introduction of such useful and physically appealing concepts like the electrostatic, induction or dispersion interactions, violates the principle of indistinguishability of electrons. As a result, the corresponding zeroth-order wave function Φ_0 does not have the correct, Pauli-allowed permutation symmetry. Only for one- and two-electron systems can the perturbation theory cope with this defect, although very inefficiently at large interatomic distances R. For many-electron systems coupling to the unphysical continuum destroys the convergence of the perturbation series. One may ask then what is the significance of a finite-order polarization theory calculation.[85] The answer is that the polarization series for the energy provides the correct asymptotic expansion of the interaction energy in the following sense:[8]

$$E_{\text{int}} = \sum_{n=1}^{N} E_{\text{pol}}^{(n)} + O(R^{-\kappa(N+1)}) \qquad (30)$$

where $\kappa = 2$ if at least one of the interacting molecules has a net charge and $\kappa = 3$ if both molecules are neutral. After a proper symmetry projection, usually the antisymmetrization carried out using the antisymmetrization operator $\mathcal{A}$, the polarization expansion for the wave function gives the correct[8] asymptotic expansion for the exact (unnormalized) wave function Ψ

$$\Psi = \mathcal{A}\Phi_0 + \sum_{n=1}^{N} \mathcal{A}\Phi_{\text{pol}}^{(n)} + O(R^{-\kappa(N+1)}) \qquad (31)$$

Moreover, the symmetry-adapted perturbation theory provides so-called exchange corrections, which when added to the polarization energies lead to rapidly convergent perturbation expansions (see section III). Finally these exchange corrections can be calculated with a very good approximation, although not exactly, by employing the polarization wave functions in the evaluation of volume integrals of the symmetry-adapted perturbation theory[142] or the surface integrals of the Herring–Holstein theory.[137–139,143]

III. Exchange Effects

A. Electron Tunneling Problem

The origin of the failure of the polarization theory to correctly describe the intermolecular interaction phenomenon can be identified most easily by considering a hydrogen atom A interacting with a proton B at a large distance R.[8] The unperturbed function Φ_0 is then the $1s_A$ hydrogenic orbital located at the proton A. Since the exact wave function Ψ must be symmetric with respect to the reflection $\mathcal{R}$ in the plane perpendicular to the internuclear axis and passing through its midpoint, the correct form of Ψ at large R is

$$\Psi \approx 1s_A + 1s_B$$

It is clear that $\Phi_0 = 1s_A$ is not a good approximation to Ψ. The component $1s_B$, due to the perturbation $V = R^{-1} - r_B^{-1}$, is as large as the unperturbed function itself. Thus the perturbation operator V cannot be considered as a small perturbation. Actually the action of V has a double effect. The tail of V polarizes the electron cloud in the vicinity of nucleus A. This effect is small and vanishes at large R as R^{-2} (as R^{-3} for an interaction of neutral systems). The large negative part of V in the vicinity of nucleus B has another effect on Ψ. It causes a tunneling of the electron from the potential energy well at the nucleus A to that at nucleus B. The $1s_B$ component of Ψ is just the result of this tunneling. The polarization theory can recover this component but only in a very large order because all polarization wave functions for this system are localized at the nucleus A (i.e., decay exponentially with the distance from the nucleus A).

The situation is not much more complicated for the interaction of two hydrogen atoms. In this case both electrons can simultaneously tunnel in opposite directions between two potential energy wells in the six-dimensional configuration space. (See ref 143 for a recent discussion of this point.) Such a simultaneous tunneling of two electrons is called the electron exchange. Since the two wells are equivalent by symmetry, the tunneling leads to resonance splitting of the unperturbed energy level, the magnitude of this splitting decaying exponentially with R. Asymptotically at large R the exact wave function becomes a linear combination of two equally weighted "resonance structures" $\Phi_0 = 1s_A(1)1s_B(2)$ and $P_{12}\Phi_0 = 1s_A(2)1s_B(1)$, the second of which cannot be recovered by a low-order polarization theory.

When the interacting systems are larger, the situation is much more complicated since many electrons may simultaneously tunnel among many potential energy minima. For two nondegenerate systems with N_A and N_B electrons, respectively, there are $M = (N_A + N_B)!/(N_A!N_B!)$ equivalent minima and the same number of "resonance structures". The zeroth-order polarization function represents just one of these M equivalent "structures". As the result of the resonance tunneling between the equivalent wells, the zeroth-order energy is split into many energy levels. Since for the interaction of nondegenerate systems (see ref 144 for a discussion of more complicated cases) all of these levels except for one correspond to states violating the Pauli exclusion principle, the wave function approximating the Pauli-allowed state can be obtained by antisymmetrization of any of the M resonance structures, in particular by antisymmetrization of Φ_0.

B. Symmetry-Adapted Perturbation Theory

From the heuristic discussion given above it is clear that $\mathcal{A}\Phi_0$ rather than Φ_0 should be considered as the correct zeroth-order wave function in the theory of intermolecular interactions. We also see from eq 31 that it is $\mathcal{A}\Phi_0$ rather Φ_0 that is a good large R approximation to the exact function Ψ. Unfortunately, the function $\mathcal{A}\Phi_0$ cannot be used in a conventional RS perturbation treatment employing the sum of the monomer Hamiltonians as the unperturbed operator since it is not an eigenfunction of H_0

$= H_A + H_B$. There are two possible ways of overcoming this difficulty. We can either abandon the natural partitioning of the Hamiltonian and find an alternative zeroth-order operator $\tilde{H}_0$ and a perturbation $\tilde{V}$ such that $\mathcal{A}\Phi_0$ is an eigenfunction of $\tilde{H}_0$ and $\tilde{V}$ can be considered as a small perturbation or we can maintain $H_A + H_B$ as the unperturbed operator and reject the standard Rayleigh–Schrödinger perturbation scheme. The first, seemingly more attractive possibility has been exploited in the so-called "symmetric" perturbation treatments.[17,145–160] It appears that no really successful construction of $\tilde{H}_0$ and $\tilde{V}_0$ has been found thus far.[8,144] In fact, in all attempts the unperturbed operator has been defined, either explicitly or implicitly, by finite matrix manipulations, and consequently, the resulting perturbation corrections do not have a well-defined meaning in the limit of an infinite, complete basis set. For this reason the "symmetric" theories will not be further considered in this review.

The second possibility, *i.e.*, keeping $H_A + H_B$ as an unperturbed operator, requires a modification of the perturbation procedure such that the function $\mathcal{A}\Phi_0$ can be utilized in the perturbation development. Such a modification, usually referred to as symmetry adaptation, was first attempted in 1930 by Eisenschitz and London.[39] There was a surge of activity in this field in the late 1960s and in the 1970s triggered by the important works of Murrell, Randic, and Williams,[55] Hirschfelder and Silbey,[56] Hirschfelder,[49,58] van der Avoird,[59] Murrell, Shaw, Musher, and Amos,[57] and Kirtman.[161] (See, however, an initially overlooked work by Carr[54] containing an early presentation of the theory rediscovered later in ref 57). The work until 1980 was reviewed in ref 8 and in the monographs by Arrighini[7] and Kaplan.[9] (See also refs 90, 81, and 144 for a critical overview of earlier work.)

From a practical standpoint the proposed symmetry-adapted perturbation theories can be divided into two categories. In the first category, corresponding to the so called *weak symmetry forcing* (or *weak symmetry adaptation*),[64,90] the antisymmetrizer $\mathcal{A}$ is used only in the energy expressions. The perturbation equations do not contain the antisymmetrizer $\mathcal{A}$ or any other nonlocal symmetry operator. Only these types of theories have been applied thus far to interactions of many-electron systems. In the second class, corresponding to the *strong symmetry forcing* (or *strong symmetry adaptation*)[64,90] the symmetry operators enter the perturbation equations, significantly complicating their solution when the interacting monomers have more than two electrons.

1. Weak Symmetry Forcing

The simplest possible symmetry-adapted perturbation expansion, referred to as the *symmetrized Rayleigh–Schrödinger* or SRS theory,[64] can be obtained in a straightforward way if the antisymmetrizer $\mathcal{A}$ is used in eq 4 to project away all Pauli-forbidden components from the wave function $\Phi_{AB}(\zeta)$. The resulting expression for the SRS interaction energy is[142]

$$E_{\text{SRS}}(\zeta) = \frac{\langle \Phi_0 | \zeta V \mathcal{A} \Phi_{AB}(\zeta) \rangle}{\langle \Phi_0 | \mathcal{A} \Phi_{AB}(\zeta) \rangle} \qquad (32)$$

where the function $\Phi_{AB}(\zeta)$ is defined as in the polarization theory, *i.e.*, by eq 1. A renormalizing denominator was introduced here to guarantee that the intermediate normalization of the wave function, *cf.* eq 5, is preserved after the projection. The individual perturbation energies $E_{\text{SRS}}^{(n)}$ are defined by expanding $E_{\text{SRS}}(\zeta)$ in powers of ζ. The resulting recurrence relations for $E_{\text{SRS}}^{(n)}$ are[64,142]

$$E_{\text{SRS}}^{(n)} = N_0(\langle \Phi_0 | V \mathcal{A} \Phi_{\text{pol}}^{(n-1)} \rangle - \sum_{k=1}^{n-1} E_{\text{SRS}}^{(k)} \langle \Phi_0 | \mathcal{A} \Phi_{\text{pol}}^{(n-k)} \rangle) \qquad (33)$$

where $N_0 = \langle \Phi_0 | \mathcal{A} \Phi_0 \rangle^{-1}$ and $\Phi_{\text{pol}}^{(k)}$ are the usual polarization functions given by eq 7. By decomposing the antisymmetrizer into contributions from intra- and intermonomer permutations of electrons one can show (see section III.C for more details) that the nth-order SRS correction is a sum of the nth-order polarization energy $E_{\text{pol}}^{(n)}$ and the *short-range* correction involving this part of $\mathcal{A}$ which interchanges electrons between monomers

$$E_{\text{SRS}}^{(n)} = E_{\text{pol}}^{(n)} + E_{\text{exch}}^{(n)} \qquad (34)$$

The short-range corrections represent an exchange effect and are, accordingly, denoted by $E_{\text{exch}}^{(n)}$. The low-order exchange corrections have a simple physical interpretation (discussed in more detail in section III.C) resulting from their close relationship with the well understood polarization functions.

Recently Tang and Toennies[162] derived a perturbation expansion which also uses only the polarization functions to express the exchange contribution in each order of perturbation theory. These authors refer to their theory as the *generalized Heitler–London* method. When the energy expressions of the generalized Heitler–London theory are consistently expanded in powers of V, they can be shown[142] to be equivalent to the SRS series of ref 64.

The so-called MSMA theory discovered independently by Carr[54] and by Murrell, Shaw, Musher, and Amos[57] represents another example of a theory employing a weak symmetry forcing. Although this fact is not evident from the original formulations, it can be shown[90] that the perturbation energies of the MSMA theory can be obtained from the recurrence relationships of eqs 33 and 7 if the following substitutions are made: $E_{\text{pol}}^{(n)} \rightarrow E_{\text{MSMA}}^{(n)}$, $E_{\text{SRS}}^{(n)} \rightarrow E_{\text{MSMA}}^{(n)}$, and $\Phi_{\text{pol}}^{(n)} \rightarrow \Phi_{\text{MSMA}}^{(n)}$, where $\Phi_{\text{MSMA}}^{(n)}$ are auxiliary functions different from the original perturbed wave functions of the MSMA theory.[57] In second order the SRS and MSMA energies are identical. In higher orders there are differences due to the fact that the polarization energies $E_{\text{pol}}^{(k)}$ are replaced by the MSMA energies in eq 7 when this equation is used in MSMA calculations. Despite some additional complications the MSMA theory is not an improvement over the SRS theory. Actually, for the *ungerade* states of H_2^+ and H_2 the MSMA theory diverges,[51,64,163,164] while the SRS expansion remains convergent. For this reason we believe that the SRS theory is an optimal symmetry-adapted perturbation theory based on the weak symmetry forcing.

2. Strong Symmetry Forcing—One-State Theories

The theories based on the strong symmetry forcing can be divided into two classes: one-state and multistate theories. In one-state theories[39,58,59,62,165-169] only one state from all states resulting from the resonance tunneling is considered and only one symmetry projector, usually the antisymmetrizer, appears in the perturbation equations. In multistate theories[56,61,144,161,170-174] all states resulting from the resonance tunneling between equivalent minima, including those violating the Pauli principle, are simultaneously considered. The perturbation equations in these theories contain then permutation operators needed to generate all resonance structures from the one corresponding to the initial assignment of electrons to interacting monomers.

Early numerical experimentation and analytical solutions for the H_2^+ system[64,90,172,175-177] have shown that the one-state theories involving the strong symmetry forcing[39,58,59,62,165-169] suffer from a very serious drawback. These theories are asymptotically incompatible with the polarization theory and, therefore, are not able to recover in finite order such important and well understood interaction energy components as the induction and dispersion energies. These components of the interaction energy can be obtained[64] only in an infinite-order treatment as a sum of nonphysical, long-range exchange term. For this reason the one-state theories employing the strong symmetry forcing are not expected to be useful and have not been applied in practice, but for model systems. An exception is the so called "intermediate symmetry forcing" (ISF) theory of ref 64 when applied through second order. At this level the ISF theory is equivalent to the SRS theory and, therefore, recovers the induction and dispersion energies in the second-order treatment. In the third and higher order, however, the ISF energies asymptotically differ from the corresponding polarization energies.

3. Strong Symmetry Forcing—Multistate Theories

The multistate theories—the best known being the Hirschfelder–Silbey (HS) theory[56]—are free from the defect discussed above since the exchange contributions to the interaction energy, defined in each order n as $E_{exch}^{(n)} = E^{(n)} - E_{pol}^{(n)}$, vanish exponentially. Although the multistate theories tested thus far for small systems[50,174,178] converge very well, they presently do not offer a viable alternative to the SRS theory because of their complexity in applications to many-electron systems. When the interacting monomers have N_A and N_B electrons, respectively, the number of quantum states resulting from the resonance tunneling is $(N_A + N_B)!/(N_A!N_B!)$. All these states would have to be taken into account to guarantee the asymptotic compatibility with the polarization theory. This difficulty does not appear if the interaction energy is calculated within an approximate method like the Hartree–Fock theory[174] or a pair theory in a perturbative or nonperturbative formulation. Since the basic ideas of the multistate approach are quite interesting and potentially useful, we give here a brief presentation of this approach in the simple case of the tunneling between two minima (H_2^+ or H_2 systems).

The main idea of the multistate approach is as follows. Since the simple product function $\Phi_0 = \Phi_A\Phi_B$ is a bad approximation to the exact function Ψ and since we want to keep Φ_0 as a "good" zeroth-order wave function, we have to find a replacement for Ψ. Instead for Ψ we will be looking for a linear combination F of two exact asymptotically degenerate states (in the case of H_2^+ and H_2 the lowest *gerade* Ψ_g and *ungerade* Ψ_u states)

$$F = c_1\Psi_g + c_2\Psi_u \tag{35}$$

such that F is "close" to Φ_0. When F, usually referred to as a "primitive" function,[81] is known, the exact functions Ψ_g and Ψ_u can easily be recovered by projecting the u and g symmetry components from F. It is easy to show that the "primitive" function F satisfies equation

$$HF = QF - K\mathscr{R}F \tag{36}$$

where Q and K are the Coulomb and exchange energies defined in section II.C and $\mathscr{R}$ stands for the reflection operator in the case of H_2^+ and the permutation operator P_{12} in the case of H_2. Equation 36 holds for any choice of the coefficients c_1 and c_2. The extra condition, needed to uniquely specify F, must follow from the demand that F is close to Φ_0. Since the function Φ_0 is localized at a single minimum, this condition can also be viewed as a localization condition for F.[168] Several such localization conditions have been proposed thus far. The condition employed in the Hirschfelder–Silbey theory

$$\langle \mathscr{R}\Phi_0|H_0-E_0|F\rangle = 0 \tag{37}$$

is the simplest because it is linear and involves only the unperturbed operator. Other conditions proposed in the literature follow from some extremum principle. Polymeropoulos and Adams[168,173] determined the coefficients c_1 and c_2 by requiring that F minimizes the expectation value of H_0. Chipman[167] demanded that F is least distorted from Φ_0 in the sense of the L^2 norm, or equivalently, that a fully normalized F has the highest overlap with Φ_0. Klein[144] in his very general formulation of the multistate perturbation theory assumed that F can be obtained from Φ_0 by the action of the Bloch operator of the quasidegenerate perturbation theory.[179] This condition can also be formulated[174] as a requirement of a closeness of F and Φ_0. When a localization condition is specified, the perturbation expansion can be derived in a straightforward manner by parametrizing H as $H_0 + \zeta V$ and by developing F, Q, and K as series in powers of ζ. The localization conditions of refs 167 and 144 were tested in large-order calculations[174] for the He_2 system at the Hartree–Fock level of approximation. The convergence of the resulting perturbation expansions was very fast, also at small interatomic distances, but no improvement was observed in comparison with the convergence rate of the Hirschfelder–Silbey expansion in this case. Still, it is possible that the localization conditions based on extremum principles will be necessary in applications to more difficult cases.

C. Low-Order Exchange Effects

In this section we shall analyze the physical content of the exchange contributions to the interac-

tion energy predicted through the second order of the SRS theory. These results apply also to the MSMA[57] and ISF[64] theories, which are fully equivalent to the SRS theory through second order. All discussed contributions appear also in the first and second order of the Hirschfelder–Silbey and other multistate theories. The latter theories predict also some additional exchange contributions in the second order, which have been shown to be practically negligible in calculations for H_2^+,[175] H_2,[178] and He_2.[65,140]

1. First-Order (Heitler–London) Exchange

The first-order energy in almost all symmetry-adapted perturbation theories is given by

$$E^{(1)} = \frac{\langle \Phi_0 | V \mathscr{A} \Phi_0 \rangle}{\langle \Phi_0 | \mathscr{A} \Phi_0 \rangle} \qquad (38)$$

This energy is identical with the so-called Heitler–London energy defined as

$$E_{HL} = \frac{\langle \mathscr{A}\Phi_0 | H - E_A - E_B | \mathscr{A}\Phi_0 \rangle}{\langle \mathscr{A}\Phi_0 | \mathscr{A}\Phi_0 \rangle} \qquad (39)$$

To separate the exchange and polarization part of $E^{(1)}$ one has to use the following decomposition of the total antisymmetrizer[180]

$$\mathscr{A} = \frac{N_A! N_B!}{(N_A + N_B)!} \mathscr{A}_A \mathscr{A}_B (1 + \mathscr{P}) \qquad (40)$$

where $\mathscr{A}_A$ and $\mathscr{A}_B$ are the antisymmetrizers for systems A and B, respectively and $\mathscr{P}$ is the sum of permutations (with appropriate sign factors) interchanging at least one pair of electrons betweeen interacting monomers. Using eq 40 one finds that

$$E^{(1)} = E_{pol}^{(1)} + E_{exch}^{(1)} \qquad (41)$$

where

$$E_{exch}^{(1)} = \frac{\langle \Phi_0 | (V - \bar{V}) \mathscr{P} \Phi_0 \rangle}{1 + \langle \Phi_0 | \mathscr{P} \Phi_0 \rangle} \qquad (42)$$

and $\bar{V} = \langle \Phi_0 | V \Phi_0 \rangle$. This expression vanishes exponentially at large $\mathscr{R}$ since the functions Φ_A and Φ_B decay exponentially with the distance from the centers of the respective molecules.[181] $E_{exch}^{(1)}$ represents the main exchange contribution to the interaction energy. At the van der Waals minima it usually accounts for over 90% of the total exchange effect. The interpretation of $E_{exch}^{(1)}$ is very simple. In view of eq 39 $E_{exch}^{(1)}$ represents the effect of taking the expectation value of the full Hamiltonian with the simplest possible function ($\mathscr{A}\Phi_0$) representing in zeroth order the resonance tunneling of electrons between all available equivalent minima.

An accurate evaluation of $E_{exch}^{(1)}$ is difficult because multiple electron exchanges present in $\mathscr{P}$ prevent us from expressing this quantity through monomer properties. A density matrix formalism in principle capable of handling the evaluation of eq 42 has been presented in ref 182. For the intermonomer distances corresponding to typical van der Waals minima eq 42 can be dramatically simplified by neglecting

higher than single electron exchanges.[183,182] Since the resulting approximate value of $E_{exch}^{(1)}$ is quadratic in intermolecular overlap integrals $S_{\lambda\mu} = \langle \psi_\lambda | \psi_\mu \rangle$ [or strictly speaking in the intermolecular overlap densities $\varrho_{\lambda\mu}(\mathbf{r}) = \psi_\lambda(\mathbf{r})\psi_\mu(\mathbf{r})$], it is denoted by $E_{exch}^{(1)}(S^2)$

$$E_{exch}^{(1)}(S^2) = -\langle \Phi_0 | (V - \bar{V}) \mathscr{P}_1 \Phi_0 \rangle \qquad (43)$$

where $\mathscr{P}_1$ denotes the sum of all $N_A N_B$ transpositions of electrons between monomers. Equation 43 represents a very good approximation since its error is of the fourth order in the intermonomer overlap densities. $E_{exch}^{(1)}(S^2)$ can be expressed through one- and two-particle density matrices of *unperturbed* monomers[73]

$$E_{exch}^{(1)}(S^2) = \int (v_{ij} - \bar{v}) \varrho_{int}(ij) \, d\tau_i \, d\tau_j \qquad (44)$$

where

$$\varrho_{int}(ij) = -\varrho_A(i|j)\varrho_B(j|i) - \int \Gamma_A(ik|ij)\varrho_B(j|k) \, d\tau_k + $$
$$- \int \varrho_A(i|l)\Gamma_B(jl|ji) \, d\tau_l - \int \Gamma_A(ik|il)\Gamma_B(jl|jk) \, d\tau_k \, d\tau_l \qquad (45)$$

$$\bar{v} = N_A^{-1} N_B^{-1} \int \varrho_A(i|i) v_{ij} \varrho_B(j|j) \, d\tau_i \, d\tau_j \qquad (46)$$

v_{ij} is a modified interelectronic interaction potential defined such that $\sum_{ij} v_{ij} = V$

$$v_{ij} = r_{ij}^{-1} - N_B^{-1} \sum_{\beta \in B} Z_\beta \, r_{\beta i}^{-1} - N_A^{-1} \sum_{\alpha \in A} Z_\alpha r_{\alpha j}^{-1} + $$
$$N_A^{-1} N_B^{-1} \sum_{\alpha \in A} \sum_{\beta \in B} Z_\alpha Z_\beta R_{\alpha\beta}^{-1} \qquad (47)$$

and ϱ_X and Γ_X, $X = A$ or $X = B$, are the conventional one- and two-particle density matrices for the monomer X, normalized to N_X and $N_X(N_X - 1)$, respectively. In formulas 44–46 $d\tau_i$ denotes integration over the spin and space coordinates of the ith electron. Since methods of the evaluation of the density matrices ϱ_X and Γ_X for many-electron molecules are well developed, eqs 44–46 enable practical calculations of the first-order exchange energy using accurate electronic wave functions.[73,91,93]

2. Exchange–Induction Interaction

The second-order exchange energy in the SRS theory, defined as $E_{exch}^{(2)} = E_{SRS}^{(2)} - E_{pol}^{(2)}$, separates naturally into two contributions: *exchange–induction* and *exchange–dispersion* energies

$$E_{exch}^{(2)} = E_{exch-ind}^{(2)} + E_{exch-disp}^{(2)} \qquad (48)$$

At the distances corresponding to the van der Waals wells, it is sufficient to consider only the single-exchange part of the exchange–induction energy. Higher order terms (in S^2) have been computed for the helium dimer and found to be negligible in the region of the van der Waals minimum.[184] In this approximation $E_{exch-ind}^{(2)}$ is given by the following expression[185]

$$E_{exch-ind}^{(2)}(S^2) = -\langle \Phi_0 | (V - \bar{V})(\mathscr{P}_1 - \bar{\mathscr{P}}_1) \Phi_{ind}^{(1)} \rangle \qquad (49)$$

where $\bar{\mathscr{P}}_1 = \langle \Phi_0 | \mathscr{P}_1 \Phi_0 \rangle$ and $\Phi_{ind}^{(1)} = \Phi_{ind}^{(1)}(A)\Phi_B + $

Table 3. Convergence of Symmetrized Rayleigh–Schrödinger (SRS) and the Hirschfelder–Silbey (HS) Perturbation Theories at the Distance R_e Corresponding to the Bottom of the van der Waals Minimum for H_2^+ ($2p\sigma_u$ state, $R_e = 12.5$ bohr), for H_2 ($b^3\Sigma_u^+$ state, $R_e = 8.0$ bohr), and for He_2 ($X^1\Sigma_g^+$ state, $R_e = 5.6$ bohr)[a]

	H_2^+		H_2		He_2	
n	SRS[b]	HS[c]	SRS[d]	HS[e]	SRS[f]	HS[f]
1	−1.506 22	−1.506 22	−1.687 84	−1.687 84	−2.225 78	−2.225 78
2	−0.006 33	−0.006 29	0.020 77	0.020 78	−0.018 84	−0.018 82
3	0.002 77	0.002 87	−0.015 71	−0.015 69	−0.030 26	−0.030 23
4	0.001 75	0.001 88	−0.001 25	−0.001 21	−0.018 70	−0.018 66
5	0.000 69	0.000 83	−0.002 38	−0.002 34	−0.014 42	−0.014 38
6	0.000 21	0.000 37	−0.001 05	−0.001 00	−0.010 95	−0.010 90
7	0.000 00	0.000 16	−0.000 80	−0.000 75	−0.008 40	−0.008 35
8	−0.000 09	0.000 07	−0.000 50	−0.000 44	−0.006 46	−0.006 41
9	−0.000 13	0.000 03	−0.000 35	−0.000 29	−0.004 99	−0.004 94
10	−0.000 15	0.000 02	−0.000 24	−0.000 18	−0.003 86	−0.003 81
15	−0.000 16	0.000 00	−0.000 08	−0.000 02	−0.001 13	−0.001 09
20	−0.000 17	0.000 00	−0.000 06	−0.000 00	−0.000 38	−0.000 33
25	−0.000 17	0.000 00	−0.000 06	0.000 00	−0.000 16	−0.000 12

[a] The numbers quoted are relative errors defined as $(\sum_{k=1}^{n} E^{(k)} - E_{int})/E_{int}$. [b] Reference 64. [c] Reference 50. [d] Reference 142. [e] Reference 178. [f] Reference 140.

$\Phi_A \Phi_{ind}^{(1)}(B)$. $\Phi_{ind}^{(1)}(A)$ and $\Phi_{ind}^{(1)}(B)$ are the induction functions (discussed in section II.B.2) accounting for the deformation of monomers' wave functions induced by the averaged electrostatic field of their interacting partners. The exchange–induction energy appears since the induction contribution to the wave function must be antisymmetrized, i.e., must be transferred by the permutation operators to all equivalent minima in the potential energy surface governing the electronic motion. In the repulsive part of the intermolecular potential the exchange–induction energy quenches a substantial part of the induction contribution and cannot be neglected in any quantitatively accurate calculation.[91]

3. Exchange–Dispersion Interaction

The exchange–dispersion energy $E_{exch-disp}^{(2)}$ is the energetic effect (linear in V) of the antisymmetrization of the dispersion function $\Phi_{disp}^{(1)}$ introduced in section II.B.3. In the single exchange approximation, which is expected to be sufficient for all practical purposes, $E_{exch-disp}^{(2)}$ is given by the formula[185]

$$E_{exch-disp}^{(2)}(S^2) = -\langle \Phi_0 | (V-\bar{V})(\mathscr{P}_1 - \bar{\mathscr{P}}_1) \Phi_{disp}^{(1)} \rangle \quad (50)$$

The effect of multiple exchanges has been computed for the He dimer and found to be negligible in the region of the van der Waals minimum.[184] The evaluation of $E_{exch-disp}^{(2)}(S^2)$ for many-electron systems is a difficult task, because this quantity cannot be expressed through monomer properties. Moreover, even a rough estimation of the exchange–dispersion energy requires inclusion of ionic (charge-transfer) components into the wave function.[186] Fortunately the exchange–dispersion contribution is relatively small, quenching usually only a few percent of the dispersion energy.

D. Convergence Properties of Symmetry-Adapted Theories

Calculations similar to those described in section II.C for the polarization expansion have been performed for several SAPT expansions applied to $H_2^{+,50,51,64}$ $H_2,^{142,178}$ and $He_2.^{140}$ Although all those
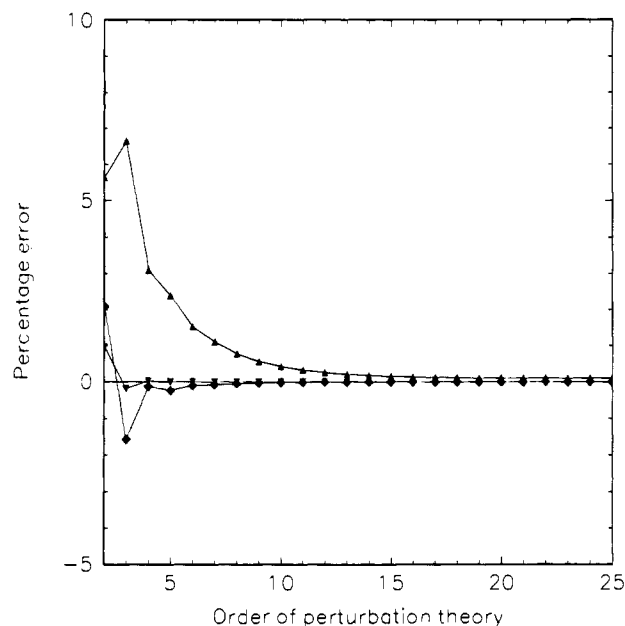

Figure 2. Percentage error of the nth-order SRS theory for H_2 at $R = 6$ (triangles up), 8 (diamonds), and 10 bohr (triangles down) for the antisymmetry projection. The error is given with respect to the variational energy for the triplet state computed using the same basis set.

calculations have been done using finite basis sets, for the two former systems the quality of the basis sets was so good that the observed convergence patterns are expected to be closely matching the exact ones. In all cases the convergence is evaluated with respect to the variational energy computed with the same basis set. In the case of He_2 the variational energy is the full CI energy for this system.

In Table 3 the convergence of the SRS and HS expansions is shown for H_2^+, H_2, and He_2 at the corresponding van der Waals minima. We consider here only the ungerade state of H_2^+, the triplet state of H_2, and the physical state of He_2. The interatomic potentials for these states correspond to typical intermolecular potentials for interactions of closed-shell systems. More distances and other states have been considered in the original papers cited above. The results for H_2 are also illustrated in Figures 2 and 3 for a large number of internuclear separations. It is seen that, in contrast to the polarization expan-
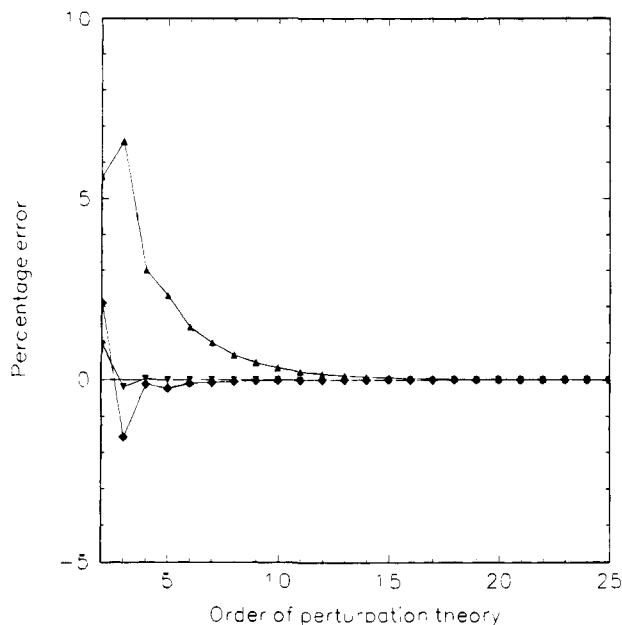
Figure 3. Percentage error of the nth-order HS theory for H_2. See Figure 2 for details.

Figure 4. The SRS interaction energy through second order (solid line) and the variational interaction energy (broken line) for H_2 computed in the same basis set as functions of R.

sion, both SAPT series converge rapidly. It is quite remarkable that the SRS and HS energies are very close to each other, even at quite high order (especially for He_2). Thus, the SRS method can be considered as an excellent approximation to the HS method. At very high order the convergence of the HS method should be much better than that of SRS. This fact is seen from the displayed data for H_2^+ and H_2 but not for He_2. However, since the convergence radius of the HS expansion is close to 1.3 both for H_2[178] and He_2,[140] while the convergence radius of the SRS theory is very close to unity (it must be the same as for the polarization approximation), at sufficiently high order the differences between the HS and SRS results must show up also for He_2.

It should also be mentioned that for the considered states the SRS expansion converges to an energy slightly different from the true physical value. The difference between the limit of the SRS series and the true value of the interaction energy is referred to as the *residual exchange energy*.[52,64] The residual exchange energy is negligibly small and the fact that it is not accounted for in the SRS theory is of no practical consequence.

The HS method cannot be applied at present to many-electron systems due to its multistate character. In practical calculations for many-electron systems the SRS theory is applied only through the second order in V (although $E_{disp}^{(30)}$ has been coded and calculated for a few systems[11]). Therefore it is important to establish how large the error is in second order and how much the SRS expansion differs from the HS expansion. As the results in Table 3 demonstrate, the difference between the two theories is completely negligible at the van der Waals minimum. For H_2 even at a rather small internuclear separation of 6 bohr the two energies agree to four significant digits. Clearly, at least for those systems it would not matter which theory is applied.

The comparison of the interaction energy for H_2 through second order with the exact interaction energy for the triplet state is presented in Figure 4.
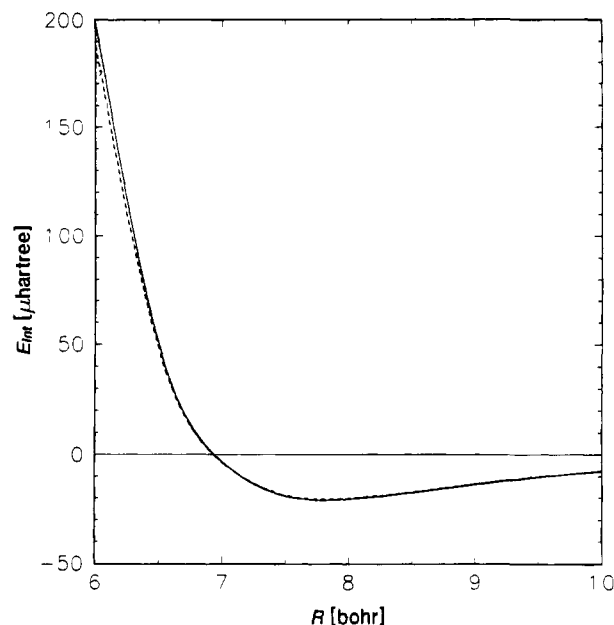
Clearly, the SRS approach recovers the accurate interaction energy very closely. For the shortest distance of 6 bohr the error is 5.6% and drops to 2% at the van der Waals minimum distance of 8 bohr. The results included in Table 3 also show that addition of the third-order correction leads to a minor improvement.

The convergence of the polarization expansion can be accelerated using either the analytic continuation or large-order perturbation techniques, as discussed in section II. Similar techniques can be applied to SAPT expansions and have been shown to work very well.[51,163]

IV. Multipole Expansion of Interaction Energy

A. General Asymptotic Expansion of Interaction Energy

According to London's theory[38] the interaction energy can be represented as an asymptotic ("multipole") expansion in powers of R^{-1}

$$E_{int}(R,\zeta_A,\zeta_B,\hat{R}) \sim \sum_{n=1}^{\infty} \frac{C_n(\zeta_A,\zeta_B,\hat{R})}{R^n} \quad (51)$$

The coefficients $C_n(\zeta_A,\zeta_B,\hat{R})$, referred usually to as the van der Waals constants, depend on the Euler angles ζ_A and ζ_B specifying the orientation of the monomers in an arbitrary space-fixed frame and on the polar angles $\hat{R} = (\theta,\phi)$ determining the orientation of the intermolecular axis (vector R is usually assumed to join the monomers' centers of mass) with respect to the same space-fixed frame. The coefficients $C_n(\zeta_A,\zeta_B,\hat{R})$ are uniquely defined by the function $E_{int}(R,\zeta_A,\zeta_B,\hat{R})$ and in principle can be deduced from the equations

$$C_1(\zeta_A,\zeta_B,\hat{R}) = \lim_{R \to \infty} R E_{int}(R,\zeta_A,\zeta_B,\hat{R}) \quad (52)$$

and

$$C_n(\zeta_A, \zeta_B, \hat{R}) =$$

$$\lim_{R \to \infty} R^n \left(E_{\text{int}}(R, \zeta_A, \zeta_B, \hat{R}) - \sum_{k=1}^{n-1} \frac{C_k(\zeta_A, \zeta_B, \hat{R})}{R^k} \right) \quad (53)$$

Equation 51 is nontrivial since it tells us that the large R asymptotic expansion of the function $E_{\text{int}}(R, \zeta_A, \zeta_B, \hat{R})$ does not contain fractional powers of R or logarithmic singularities of the form of $R^{-n} \log R$. London's derivation of eq 51 can be regarded only as a heuristic one since he applied the ordinary Rayleigh–Schrödinger perturbation theory to a highly singular perturbation, which was mathematically unjustified at that time. Mathematically rigorous proofs of eq 51 have been given only recently by Ahlrichs[44] and by Morgan and Simon.[45]

Since the interaction energy as a function of R has an essential singularity at infinity[44] (due to the exponential terms resulting from the charge overlap and exchange effects), the knowledge of the van der Waals constants would not be sufficient to reconstruct the function $E_{\text{int}}(R, \zeta_A, \zeta_B, \hat{R})$ at finite R even if the series 51 were convergent. Actually, it appears that the series 51 diverges for any finite value of R and is probably not summable using standard summation techniques.[187] For H_2^+, a system for which a mathematically rigorous analysis could be carried out, the constants C_n behave for large n as $-2^{-n} e^{-2} \times (n+1)!$,[45,188,189] which shows that in this case the expansion 51 is indeed strongly divergent for each value of R. Moreover, since all values of C_n are of the same sign, the asymptotic expansion for the H_2^+ ion is not summable (for positive, physical values of R) using conventional summation techniques (e.g., Padé or Borel methods,[187] see refs 46 and 47 for a detailed discussion of the summability of the expansion 51 for this system). These results have not been extended to systems larger than the H_2^+ ion but there is no reason to expect that series 51 will behave better for interactions of many-electron systems.

In view of its asymptotic character, expansion 51 can approximate the exact interaction energy arbitrarily closely at large R, in the sense that[190]

$$\left| E_{\text{int}}(R, \zeta_A, \zeta_B, \hat{R}) - \sum_{n=1}^{N} \frac{C_n(\zeta_A, \zeta_B, \hat{R})}{R^n} \right| = O(R^{-N-1})$$

$$(54)$$

Therefore, the knowledge of the van der Waals constants is very useful in estimating the interaction energy at large distances and is necessary to guarantee the correct large R asymptotic behavior of the potential energy surface $E_{\text{int}}(R, \zeta_A, \zeta_B, \hat{R})$. Although the constants $C_n(\zeta_A, \zeta_B, \hat{R})$ could in principle be computed using eqs 52 and 53, the multipole expansion can be useful only if direct methods of calculating them without the prior knowledge of the interaction energy are available. This section will be devoted to a discussion of such methods.

B. Multipole Expansion of Intermolecular Interaction Operator

The asymptotic expansion of the interaction energy follows from the *multipole* expansion of the intermolecular interaction operator V. The latter expansion can be formulated using either the irreducible spherical tensor formalism[191–200] or the Cartesian tensors.[201–206] In an arbitrary space-fixed coordinate system, this expansion can be written as

$$V = \sum_{n=1}^{\infty} \frac{V_n}{R^n} \quad (55)$$

where the operator V_n is given by

$$V_n = \sum_{l=0}^{n-1} V_{l, n-l-1} \quad (56)$$

The operator V_{l_A, l_B} is physically interpreted as representing the interaction of the instantaneous 2^{l_A} moment with respect to center A with the instantaneous 2^{l_B} moment with respect to center B and can be expressed in terms of tensor operators of multipole moments.

We will first follow here the approach based on the spherical tensor formalism developed by Wormer and collaborators[195,197] which fully utilizes the SO(3) invariance of the intermolecular interaction operator. The irreducible spherical components of the multipole moment operators of the molecule X will be denoted by $M_{l_X}^{m_X}$

$$M_{l_X}^{m_X} = \sum_{p \in X} Z_p r_p^{l_X} C_{l_X}^{m_X}(\hat{r}_p) \quad (57)$$

where the summation index p runs over all particles, both nuclei and electrons, of molecule X, Z_p are the charges of those particles, and $C_l^m(\hat{r})$ is a spherical harmonic in the Racah normalization.[207] All the coordinates are defined in an arbitrary space-fixed coordinate system with its origin at the center of mass of the molecule X. The operator V_{l_A, l_B} can be written as

$$V_{l_A, l_B} =$$

$$X_{l_A, l_B} R^{-l_A - l_B - 1} \sum_{m=-l_A-l_B}^{l_A+l_B} (-1)^m C_{l_A+l_B}^{-m}(\hat{R}) [M_{l_A} \otimes M_{l_B}]_{l_A+l_B}^m$$

$$(58)$$

where the numerical constant X_{l_A, l_B} is given by

$$X_{l_A, l_B} = (-1)^{l_B} \binom{2l_A + 2l_B}{2l_A}^{1/2} \quad (59)$$

and the irreducible tensor product of two multipole moment tensors $M_{l_A} = \{M_{l_A}^{m_A}, m_A = -l_A, ..., +l_A\}$ and $M_{l_B} = \{M_{l_B}^{m_B}, m_B = -l_B, ..., +l_B\}$ is defined by

$$[M_{l_A} \otimes M_{l_B}]_l^m =$$

$$\sum_{m_A=-l_A}^{l_A} \sum_{m_B=-l_B}^{l_B} M_{l_A}^{m_A} M_{l_B}^{m_B} \langle l_A, m_A; l_B, m_B | l, m \rangle \quad (60)$$

where $\langle l_1, m_1; l_2, m_2 | L, M \rangle$ is the Clebsch–Gordan coefficient.[207] In practice it is convenient to replace the complex spherical harmonics C_l^m in eq 58 by real tesseral harmonics.[208] Explicit expressions for the tesseral harmonics as functions of x, y, and z can be found in ref 209 for $l \le 6$.

The spherical form of the multipole expansion is most appropriate for expressing the explicit orientational dependence of the interaction energy. In some applications the use of the conceptually simpler Cartesian form may be more convenient. To express the operator V_{l_A,l_B} in terms of Cartesian tensors, the reducible [with respect to SO(3)] tensorial components of multipole moments are defined as

$$M_{l_X}^{\{\gamma\}} = \sum_{p \in X} Z_p r_{p,\gamma_1} r_{p,\gamma_2} ... r_{p,\gamma_{lX}} \quad (61)$$

where r_{p,γ_i} is the γ_ith Cartesian coordinate of particle p, i.e., $\gamma_i = 1$, 2, or 3, so that $r_{p,\gamma_i} = x_p$, y_p, and z_p, respectively, $\{\gamma\}$ denotes the set of indices $\{\gamma_1, \gamma_2, ..., \gamma_{lX}\}$ and the coordinates are measured in a space-fixed system with its origin at the center of mass of molecule X. In this notation the operator V_{l_A,l_B} can be written as

$$V_{l_A,l_B} = \sum_{\{\alpha\}} \sum_{\{\beta\}} M_{l_A}^{\{\alpha\}} T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]} M_{l_B}^{\{\beta\}} \quad (62)$$

where the tensor $T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]}$ describing the orientational dependence of the interaction between the instantaneous 2^{l_A} moment on molecule A and the instantaneous 2^{l_B} moment on molecule B is given by

$$T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]} =$$
$$R^{l_A+l_B+1} \frac{(-1)^{l_A}}{l_A! l_B!} (\nabla_{\alpha_1} \nabla_{\alpha_2} ... \nabla_{\alpha_{l_A}} \nabla_{\beta_1} \nabla_{\beta_2} ... \nabla_{\beta_{l_B}}) \left(\frac{1}{R}\right) \quad (63)$$

and the sums run over all distinct sets $\{\alpha_1, \alpha_2, ..., \alpha_{l_A}\}$ and $\{\beta_1, \beta_2, ..., \beta_{l_B}\}$. Explicit expressions for the tensors $T_{\{\alpha\},\{\beta\}}^{[l_A+l_B]}$ have been derived by Mulder et al.[206] for $l_A + l_B \leq 6$. Specific formulas applying to linear and tetrahedral molecules have been reported in ref 210 for $l_A + l_B \leq 7$.

The expressions for the transformations between the spherical and Cartesian form are quite complex. In view of the Laplace equation, the partial traces $\nabla_\gamma \nabla_{\gamma'} (1/R)$ vanish. Therefore, the operators $M_{l_X}^{\{\gamma\}}$ can be expressed in terms of $M_{l_X}^{mx}$. The formal relationship between Cartesian tensors and their irreducible spherical components has been thoroughly investigated by Coope et al.[211–213] and by Stone.[214,215] Stone derived[214] a general scheme of reducing a Cartesian tensor of rank n into several spherical components and investigated in detail properties of Cartesian–spherical transformation coefficients.[215] (Some applications of these results can be found in refs 200, 216, and 217).

Unlike the individual operators V_{l_A,l_B} the operators V_n of eq 56 are *invariant* under identical translations and rotations of the local molecular axes.[218,219] Moreover, the multipole expansion truncated at the R^{-N} term

$$V^N = \sum_{n=1}^{N} \frac{V_n}{R^n} \quad (64)$$

is also invariant under arbitrary translation and/or rotation of one of the local molecular coordinate systems[220] in the sense that this operation introduces errors into eq 64 smaller than the truncation error itself, i.e., errors of the order of $O(R^{-N-1})$.

The multipole expansion of the intermolecular interaction operator is divergent in most part of the configuration space, the region of convergence being restricted to the Cartesian product of all spheres $r_i \leq R/2$, $r_\alpha \leq R/2$, $r_j \leq R/2$, and $r_\beta \leq R/2$, for i, $\alpha \in A$, and j, $\beta \in B$,[219] where the indices i and j refer to electrons while α and β to nuclei. This particular region corresponds to that part of the configuration space in which the electrons initially assigned to molecules A and B are "localized" on their original monomers. If the operators V_n are interpreted as multiplicative operators in the Hilbert space, the series 55 is divergent for each R.

C. van der Waals Constants

Despite the divergence discussed above, the truncated multipole expansion, eq 64, can be used to define van der Waals constants. By applying the Rayleigh–Schrödinger perturbation theory to the Schrödinger equation with the Hamiltonian H^N

$$H^N = H_0 + V^N \quad (65)$$

and using $1/R$ as the expansion parameter Ahlrichs[44] has shown that the van der Waals constants entering the asymptotic expansion[51] can be computed from the following recursive formulas (see also ref 8 for a proof):

$$C_n = \sum_{k=1}^{n} \langle \Phi^{[0]} | V_k \Phi^{[n-k]} \rangle \quad (66)$$

and

$$\Phi^{[n]} = -\sum_{k=1}^{n} \hat{R}_0 (C_k - V_k) \Phi^{[n-k]} \quad (67)$$

where the superscript $[n]$ at $\Phi^{[n]}$ denotes the order in $1/R$. For simplicity we have omitted the dependence of the van der Waals constants on the angles $(\zeta_A, \zeta_B, \hat{R})$ in eqs 66 and 67. Note that similar to the Hamiltonian in the theory of the Stark effect[221] the Hamiltonian H^N has a purely continuous spectrum. Consequently, the operator V^N cannot be considered as a small perturbation and the RS perturbation theory based on the partitioning 65 of the Hamiltonian H^N is divergent for each R.

Although a direct application of eqs 66 and 67 is straightforward, in practice van der Waals constants are obtained by first performing the asymptotic expansion of the polarization energies $E_{\text{pol}}^{(k)}$

$$E_{\text{pol}}^{(k)} \sim \sum_{n=1}^{\infty} \frac{C_n^{(k)}}{R^n} \quad (68)$$

and then representing each constant C_n as a *finite* perturbation series in V

$$C_n = \sum_{k=1}^{M} C_n^{(k)} \quad (69)$$

Here M denotes the smallest integer satisfying $M >$

$n/\kappa - 1$, where $\kappa = 3$ if both interacting molecules are neutral and $\kappa = 2$ if one molecule has a net charge. Such a procedure is legitimate since, in view of eq 30, the polarization expansion of the interaction energy gives a correct asymptotic representation of the interaction energy. It can also be shown[8] that the constants $C_n^{(k)}$ can be computed from the *standard* equations of the polarization perturbation theory, provided that the operator V is replaced by its truncated multipole expansion 64 with $N \geq n$. In particular, the van der Waals constants $C_n^{(1)}$ and $C_n^{(2)}$ are given by

$$C_n^{(1)} = \langle \Phi_0 | V_n \Phi_0 \rangle \tag{70}$$

$$C_n^{(2)} = \sum_{k=\kappa}^{n-\kappa} \langle \Phi_0 | V_k \hat{R}_0 V_{n-k} \Phi_0 \rangle \tag{71}$$

Equations 70 and 71 have been applied with success to compute van der Waals constants for quite large systems.[222-225]

D. Convergence Properties of Multipole Expansion of Interaction Energy

The asymptotic expansions of the polarization corrections $E_{pol}^{(k)}$, eq 68, are probably divergent for all values of R, although this fact has been proven rigorously only for $k = 2$ and only for the H_2^+ and H_2 systems. The convergence of the multipole expansion for the electrostatic energy $E_{pol}^{(1)}$ has been the subject of many computational studies (see, e.g., refs 132 and 226). The numerical results for the water dimer[132] and for the N_2 dimer[226] suggested that the multipole expansion of $E_{pol}^{(1)}$ converges even in the region of the van der Waals minimum, although the sum of the series appears to be quite different from the exact value of $E_{pol}^{(1)}$. This is not surprising, however, since in view of the results of Ng et al.[227-229] the charge-overlap (penetration) effects, entirely neglected in the multipole approximation, play an important role in this region (see section V). Recently, Vigné-Maeder and Claverie[230] have shown that the multipole expansion of the electrostatic energy *is* convergent (alas to a spurious value) if the unperturbed charge distributions of the interacting molecules are approximated by Gaussian functions. For large molecules the multipole expansion provides better results if multipole moments localized at various points of a molecule are used instead of global multipole moments. This idea forms the basis of the so-called *distributed multipole analysis* of electrostatic interactions between molecules[99,100,102,103] (see ref 101 for a recent review) which has been a popular field of research in recent years.

Little is known about the convergence properties of the multipole expansions of the second-order induction and dispersion energies. Dalgarno and Lewis[231] have shown that the multipole expansion of the second-order induction energy for the H_2^+ system is given by

$$E_{ind}^{(2)} \sim - \sum_{n=1}^{\infty} \frac{(2n + 2)!(n + 2)}{n(n + 1)2^{2n+2}R^{2n+2}} \tag{72}$$

Later Young[232] proved that the multipole expansion of the second-order dispersion energy for the H_2 molecule can be written as

$$E_{disp}^{(2)} \sim - \sum_{l_A=1}^{\infty} \sum_{l_B=1}^{\infty} \frac{C_{l_A,l_B}^{(2)}}{R^{2l_A+2l_B+2}} \tag{73}$$

where

$$C_{l_A,l_B}^{(2)} > \frac{(2l_A + 2l_B)!(l_A + 1)(l_B + 1)}{2^{2l_A+2l_B+1}} \tag{74}$$

Both series are rapidly divergent for any R. Moreover, they are neither Padé nor Borel summable.[187] Since the observed divergence occurs for the interaction of spherical atomic systems it is not clear how it could be circumvented using the so-called *distributed polarizabilities analysis*[116,233-235] of the induction and dispersion energies. These results strongly suggest that for many-electron systems the multipole expansions of the induction and dispersion energies are divergent and that this divergence cannot be eliminated using the distributed polarizabilities analysis.

E. Angular Dependence of Interaction Energy

The van der Waals constants $C_n^{(k)}$ depend on the angles $(\zeta_A, \zeta_B, \hat{R})$. If these constants were computed from eqs 70 and 71, such calculations would have to be performed for each orientation of interacting molecules. Instead, one may introduce the multipole expansions for the interaction energy components in a such a way that the whole angular dependence is separated. In fact, for all intermolecular separations the kth-order polarization correction $E_{pol}^{(k)}$ can be written in terms of a complete orthogonal set of angular functions labeled by $\{\Lambda\} = \{L_A, K_A, L_B, K_B, L\}$

$$E_{pol}^{(k)} = \sum_{\{\Lambda\}} {}^{\{\Lambda\}}\tilde{\mathcal{C}}_{pol}^{(k)}(R)A_{\{\Lambda\}}(\zeta_A, \zeta_B, \hat{R}) \tag{75}$$

$$A_{\{\Lambda\}}(\zeta_A, \zeta_B, \hat{R}) = \sum_{M_A=-L_A}^{L_A} \sum_{M_B=-L_B}^{L_B} \sum_{M=-L}^{L} \times$$
$$\begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} D_{M_A,K_A}^{L_A}(\zeta_A)^* D_{M_B,K_B}^{L_B}(\zeta_B)^* C_L^M(\hat{R}) \tag{76}$$

where $D_{M,K}^L(\zeta)$ denotes an element of the Wigner rotation matrix,[207] and the expression in large parentheses is a $3j$ symbol.[207] The components of R are determined with respect to an arbitrary space-fixed coordinate system. The Euler angles specify the rotation of a body-fixed coordinate system located at the center of mass of monomer X with respect to a system located at the same point with axes parallel to the chosen space fixed system, $X = A$ or B. See refs 123, 124, 198, 199, and 236 for various rederivations of eqs 75 and 76.

If the interaction operator V is replaced by its multipole expansion, the radial expansion coefficients ${}^{\{\Lambda\}}\tilde{\mathcal{C}}_{pol}^{(k)}(R)$ in eq 75 are approximated by ${}^{\{\Lambda\}}\mathcal{C}_{pol}^{(k)}(R)$ and, consequently, can be written[195,197] exclusively in terms of irreducible spherical tensors of multipole

moments and polarizabilities (see ref 6 for a review). In particular, the radial part of the electrostatic energy in the multipole approximation is given by[195,197-199]

$$\{^{\Lambda}\}\mathscr{E}_{\text{pol}}^{(1)}(R) =$$

$$(-1)^{L_A}\delta_{L_A+L_B,L}\left[\frac{(2L_A+2L_B+1)!}{(2L_A)!(2L_B)!}\right]^{1/2}\frac{Q_{L_A}^{K_A}Q_{L_B}^{K_B}}{R^{L_A+L_B+1}} \quad (77)$$

where $Q_{L_X}^{K_X} \equiv \langle\Phi_0^X|\tilde{M}_{L_X}^{K_X}\Phi_0^X\rangle$ denotes the spherical component of the 2^{L_X} moment of the molecule X, and $\tilde{M}_{L_X}^{K_X}$ denotes the multipole moment operator in the body-fixed coordinate system. Equation 77 clearly shows that the first-order polarization energy in the multipole approximation is represented by the classical electric interaction between the permanent multipole moments of the unperturbed monomers. It follows from eqs 75–77 that the electrostatic energy is strongly anisotropic—it may change sign upon a rotation of the monomers.

Denoting by $\{\lambda\}$ the set of indices $\{\lambda\} = \{l_A,l'_A,l_B,l'_B\}$ and by n the sum $n = l_A + l'_A + l_B + l'_B + 2$, the radial component of the second-order induction energy in the multipole approximation can be written as[195,197-199]

$$\{^{\Lambda}\}\mathscr{E}_{\text{ind}}^{(2)}(R) = -\frac{1}{2}\sum_{l_A=1}^{\infty}\sum_{l'_A=1}^{\infty}\sum_{l_B=0}^{\infty}\sum_{l'_B=0}^{\infty}\frac{C_{\{\lambda\},\text{ind-}A}^{\{\Lambda\}}}{R^n} -$$

$$\frac{1}{2}\sum_{l_A=0}^{\infty}\sum_{l'_A=0}^{\infty}\sum_{l_B=1}^{\infty}\sum_{l'_B=1}^{\infty}\frac{C_{\{\lambda\},\text{ind-}B}^{\{\Lambda\}}}{R^n} \quad (78)$$

where the long-range induction coefficient describing the polarization of the monomer A, $C_{\{\lambda\},\text{ind-}A}^{\{\Lambda\}}$, is given by

$$C_{\{\lambda\},\text{ind-}A}^{\{\Lambda\}} = \xi_{l_A l'_A l_B l'_B}^{L_A L_B L}\alpha_{(l_A l'_A)L_A}^{K_A}(0)[\mathbf{Q}_{l_B} \otimes \mathbf{Q}_{l'_B}]_{L_B}^{K_B} \quad (79)$$

The symbol $\alpha_{(l_X,l'_X)L_X}^{K_X}(0)$ denotes the irreducible component of the multipole polarizability

$$\alpha_{(l'_X l'_X)L_X}^{K_X}(\omega) = \sum_{n\neq 0}\frac{2(E_n^X - E_0^X)}{(E_n^X - E_0^X)^2 - \omega^2}[\langle\Phi_0^X|\tilde{\mathbf{M}}_{l_X}\Phi_n^X\rangle \otimes$$

$$\langle\Phi_n^X|\tilde{\mathbf{M}}_{l'_X}\Phi_0^X\rangle]_{L_X}^{K_X} \quad (80)$$

the irreducible tensor product of two sets of tensors, $[\mathbf{m}_l \otimes \mathbf{m}_{l'}]_L^K$, is defined by eq 60, and the numerical constant $\xi_{l_A l'_A l_B l'_B}^{L_A L_B L}$ is given by

$$\xi_{l_A l'_A l_B l'_B}^{L_A L_B L} =$$

$$(-1)^{l_A+l'_A}\left[\frac{(2l_A+2l_B+1)!(2l'_A+2l'_B+1)!}{(2l_A)!(2l_B)!(2l'_A)!(2l'_B)!}\right]^{1/2} \times$$

$$[(2L_A+1)(2L_B+1)(2L+1)]^{1/2} \times$$

$$\langle l_A+l_B,0;l'_A+l'_B,0|L,0\rangle\begin{Bmatrix} l_A & l'_B & L_A \\ l_B & l'_B & L_B \\ l_A + l_B & l'_A + l'_B & L \end{Bmatrix} \quad (81)$$

where the quantity between curly braces denotes a $9j$ symbol.[207] The energies and wave functions appearing in eq 80 belong to the spectrum of the total Hamiltonian of monomer X. In view of eq 79 the first term on the right hand side of eq 78 corresponds to the energy of the polarization of the monomer A by the permanent multipole moments of the monomer B. Thus, the induction energy in the multipole approximation is represented by the classical interaction between permanent multipole moments of one monomer and induced multipole moments of the other.

Finally, the expression for the radial part of the dispersion energy in the multipole approximation reads[195,197-199]

$$\{^{\Lambda}\}\mathscr{E}_{\text{disp}}^{(2)}(R) = -\sum_{l_A=1}^{\infty}\sum_{l'_A=1}^{\infty}\sum_{l_B=1}^{\infty}\sum_{l'_B=1}^{\infty}\frac{C_{\{\lambda\},\text{disp}}^{\{\Lambda\}}}{R^n} \quad (82)$$

The long-range dispersion coefficient $C_{\{\lambda\},\text{disp}}^{\{\Lambda\}}$ is given by

$$C_{\{\lambda\},\text{disp}}^{\{\Lambda\}} = \frac{1}{2\pi}\xi_{l_A l'_A l_B l'_B}^{L_A L_B L}\int_0^{\infty}\alpha_{(l_A l'_A)L_A}^{K_A}(i\omega)\alpha_{(l_B l'_B)L_B}^{K_B}(i\omega)\,d\omega \quad (83)$$

where $\alpha_{(l_X l'_X)L_X}^{K_X}(i\omega)$ ($X = A$ or B), defined by eq 80, is the dynamic multipole polarizability at imaginary frequency $i\omega$.

Equations 75–83 are valid in an arbitrary space-fixed coordinate system. However, since the angular functions $A_{\{\Lambda\}}(\zeta_A,\zeta_B,\hat{R})$ are invariant with respect to any frame rotation (for the proof, see the Appendix of ref 6), a specific choice of the coordinate system may considerably simplify eq 76. In particular, in the body-fixed coordinate system with the z axis along the vector R the polar angles $\hat{R} = (\theta, \phi)$ are zero. Using the fact that $C_L^M(\hat{R} = (0,0)) \equiv \delta_{M,0}$,[207] eq 76 simplifies to

$$\tilde{A}_{\{\Lambda\}}(\zeta_A,\zeta_B) =$$

$$\sum_{M_A=-L_A}^{L_A}\begin{pmatrix} L_A & L_B & L \\ M_A & -M_A & 0 \end{pmatrix}D_{M_A,K_A}^{L_A}(\zeta_A)^*D_{-M_A,K_B}^{L_B}(\zeta_B)^* \quad (84)$$

Further simplifications may be obtained if one considers the molecular symmetry groups of the monomers. For all point groups, except for the tetrahedral and cubic groups, all symmetry operators can be constructed from the inversion I, n-fold rotation about the principal (z) axis $R_z(2\pi/n)$, and 2-fold rotation about the x axis $R_x(\pi)$. Therefore, to determine the components of the multipole moment and polarizability tensors that span the totally symmetric representation of the symmetry group (i.e., that are invariant under operations of the symmetry group), it is enough to determine the action of these three operators on the multipole moment and polarizability tensors.[198] It follows from ref 198 that the multipole moment and polarizability tensors transform under these operations according to

$$I: \quad Q_L^M \to (-1)^L Q_L^M, \quad \alpha_{(ll')L}^M \to (-1)^{l+l'} \alpha_{(ll')L}^M \quad (85)$$

$$R_z(2\pi/n): \quad Q_L^M \to e^{-2\pi i M/n} Q_L^M, \quad \alpha_{(ll')L}^M \to e^{-2\pi i M/n} \alpha_{(ll')L}^M \quad (86)$$

$$R_x(\pi): \quad Q_L^M \to (-1)^L Q_L^{-M}, \quad \alpha_{(ll')L}^M \to (-1)^L \alpha_{(ll')L}^{-M} \quad (87)$$

Using the transformation rules given above one can easily derive the (nonzero) components of spherical tensors that are invariant under the molecular symmetry group. This result, in turn, can be used to obtain the multiple expansions of the electrostatic, induction, and dispersion energies for the interactions of specific systems (see, *e.g.*, refs 237 and 238 for expressions applying to atom–diatom and diatom–diatom interactions). In general, the symmetry-adaptation of a tensor to the molecular symmetry group can be obtained by a reduction with respect to the full rotation–reflection group O(3), followed by a subduction of the O(3) irreducible representations to the point symmetry group of the molecule.[239] This symmetry-adaptation scheme has been applied with success to derive all components of the (hyper)-polarizability tensors that are invariant under $D_{\infty h}$.[240]

Although the spherical form of the multipole expansion, eq 75, is definitely superior if the orientational dependence of the electrostatic, induction, or dispersion energies is of interest, the Cartesian form[43,202,241,242] may be useful in some cases (*e.g.*, in the studies of the collision-induced multipole moments[243–245]). Mutual transformations between the spherical and Cartesian forms of the multipole moment and (hyper)polarizability tensors have been derived by Gray and Lo.[246] The symmetry adaptation of the Cartesian tensors of quadrupole, octopole, and hexadecapole moments to all 51 point groups can be found in ref 247, while the symmetry adaptation of the Cartesian tensors of multipole (hyper)polarizabilities to simple point groups has been considered in refs 43 and 246.

As discussed above, the multipole expansions of the electrostatic, induction, and dispersion energies, truncated after the R^{-N} term are invariant under identical translations and rotations of the local molecular axes. Sometimes it is useful to shift only one of the expansion centers. This can be done using translation formulas for the spherical tensors of multipole moments and dynamic polarizabilities. These formulas can be applied for example to obtain the long-range coefficients for the isotope substitutes (*i.e.*, when the center of mass of the complex is shifted by isotopic substitution). Using the addition (translation) theorem for solid spherical harmonics[207] (see ref 248 for a simple proof), Bulski *et al.*[249] derived explicit formulas for the translation of the multipole moment and polarizability tensors. Denoting by $\tilde{Q}_l^m$ and $\tilde{\alpha}_{(ll')L}^M(\omega)$ the tensors of multipole moments and polarizabilities with respect to an origin translated by a vector $t = (t, \hat{t})$, the translation formulas read:

$$Q_L^M = \sum_{l=0}^{L} \sum_{m=-1}^{l} \left[\binom{L+M}{l+m}\binom{L-M}{l-m} \right]^{1/2} \tilde{Q}_l^m t^{L-l} C_{L-l}^{M-m}(\hat{t}) \quad (88)$$

$$\alpha_{(ll')L}^M(\omega) = \sum_{\lambda,\lambda'} \sum_{\Lambda,\Lambda'} t^{l+l'-\lambda-\lambda'} \langle l-\lambda,0; l'-\lambda',0 | \Lambda,0 \rangle \times$$

$$[(2l+1)(2l'+1)(2\lambda+1)(2\lambda'+1)]^{1/2} \left[\binom{2l}{2\lambda}\binom{2l'}{2\lambda'} \right]^{1/2} \times$$

$$\begin{Bmatrix} l-\lambda & \lambda & l \\ l'-\lambda' & \lambda' & l' \\ \Lambda & \Lambda' & L \end{Bmatrix} \sum_{\Omega=-\Lambda}^{\Lambda} \sum_{\Omega'=-\Lambda'}^{\Lambda'} C_{\Lambda}^{\Omega}(\hat{t}) \tilde{\alpha}_{(\lambda\lambda')\Lambda'}^{\Omega'}(\omega) \quad (89)$$

Equations 88 and 89 can be used to obtain the translated long-range coefficients appearing in the expressions for ${}^{\{\Lambda\}}\mathcal{E}_{pol}^{(1)}(R)$, ${}^{\{\Lambda\}}\mathcal{E}_{ind}^{(2)}(R)$, and ${}^{\{\Lambda\}}\mathcal{E}_{disp}^{(2)}(R)$, *cf.*, eqs 77, 78, and 82. Note that the backward transformation can be obtained by multiplying the expressions under the summation symbols in eqs 88 and 89 by $(-1)^{L-l}$ and $(-1)^{\Lambda}$, respectively.

Few attempts have been done in the past to apply the multipole approximation to nonadditive interactions.[121,122] Only recently, Piecuch[250] generalized the spherical tensor formalism introduced by Wormer *et al.*[195,197] for the two-body case, to systems of M molecules and to arbitrary orders of perturbation theory. Specific expressions that can be applied to systems of M molecules were derived for the anisotropic induction energies,[125] anisotropic dispersion energies,[136] and isotropic interaction energies[251] through the third order of the perturbation theory. Later, the fourth-order induction terms were also discussed.[252,253] For a review of these results, we refer the reader to ref 254. These very general formulas were recently applied to study nonadditive contributions to the induction energy in the Ar_2-HF and Ar_2-HCl systems.[255,256]

F. Computations of van der Waals Constants

It should be noted that despite the divergent nature of the multipole expansions for the induction and dispersion energies, eqs 78 and 82 were often used to compute attractive contributions to the interaction potentials (see refs 226 and 257 for examples of typical applications and ref 258 for a review). Since the long-range electrostatic and induction coefficients are expressed exclusively via multipole moments and polarizabilities of the isolated monomers, they can be routinely computed at various levels of approximation. See, *e.g.*, ref 258 for a collection of review papers discussing the current status of the theory and its applications to various atomic and molecular properties. The calculations of the long-range dispersion coefficients are somewhat more sophisticated, as they require the knowledge of dynamic multipole polarizabilities at imaginary frequency. Nowadays this problem is solved, however, and accurate long-range dispersion coefficients can be computed. The review of all methods that can be applied to obtain such coefficients is beyond the scope of the present paper. Here we only want to mention that at present these coefficients can be calculated using the time-dependent coupled-Hartree–Fock (TD-CHF) or the random phase approximation (RPA),[260–263] the (limited) configuration interaction (CI) approach,[264,265] the multiconfigurational time-dependent Hartree–Fock (MCTDHF) method,[266,267] the second-order polarization propagator approach (SOPPA),[268] and the many-body perturbation theory (MBPT).[48,269–272] In particular, the MBPT approach has been successfully applied to various van der Waals complexes providing

state-of-the-art values of the long-range dispersion coefficients.[48,273-275] These coefficients, in turn, can be used to define the exact asymptotics of the dispersion energy, or may serve as an *ab initio* input to empirical potentials fitted to reproduce the high-resolution spectroscopic data (see, *e.g.*, refs 48 and 276). Let us mention, finally, that very accurate values of the isotropic $C_6^{\{0\}}$ dispersion coefficients can be obtained from pseudospectral expansions in terms of (experimental) dipole oscillator strengths.[277] These data, available now for many systems (see refs 277-297), are considered to constitute benchmark values for *ab initio* calculations.

V. Charge-Overlap Effects and Bipolar Expansion of Polarization Energies

The energy corrections of the polarization theory computed with the exact, nonexpanded intermolecular interaction operator can be referred to as *nonexpanded* polarization energies. Such computation gives the polarization energies pointwise, *i.e.*, as a single number for each dimer's geometry and therefore has to be performed for all geometries of interest. In contrast, as discussed in section IV, the multipole expansion of polarization energies is obtained by calculating the van der Waals constants only once. The polarization energies in this approximation can then be computed for all geometries from simple expressions involving these constants and Wigner's angular functions. The difference between the non-expanded value of a given energy correction and the value computed from a truncated multipole expansion is due to the so-called overlap (or penetration) effects. Notice that this definition of the overlap effects does not allow one to determine a unique numerical value for these effects since it depends on the place where the multipole expansion is truncated. Since the multipole expansion is divergent at all orders (except possibly in the first order), the overlap effects clearly cannot be defined with respect to this expansion summed to infinity. A more precise definition of the overlap effects will be given below.

While the multipole expansion constants have been computed since the 1930s, calculations of the complete polarization energies including overlap effects for many-electron systems date back only to the 1970s. In fact even for the interaction of two hydrogen atoms accurate nonexpanded second-order dispersion energies were computed for the first time in the late 1960s.[298-300] (The work of Murrell and Shaw[298] presented at the same time the first calculation of the dispersion energy for a many-electron system, He₂.) For generaly many-electron systems, calculations of the nonexpanded first-order electrostatic energy date back to the early 1970s and have often been performed as a part of Morokuma's partition of the SCF interaction energy.[301] The first calculations of nonexpanded dispersion energies for such systems were those of Murrell and Shaw[298] and Kochanski[302] for the case of two-electron monomer's, and by Jeziorski and van Hemert[132] for general molecules. All of the work cited above has been performed with a complete neglect of intramonomer correlation effects. These effects were included for the first time in refs 303-305 where the first-order contributions $E_{pol}^{(1)}$ and $E_{exch}^{(1)}$ were calculated for He₂

with short CI expansions, then in ref 227 where $E_{pol}^{(1)}$ was computed for two interacting hydrogen molecules using accurate correlated densities, and in ref 65 where the lowest-order intramolecular correlation effects on the induction and dispersion energies (as well as on the first-order exchange energy) were computed for two helium atoms using explicitly correlated functions. The present many-body implementation of SAPT (see section VI) computes the first-order polarization energy up to the fourth order in the intramolecular fluctuation potential W, the induction energy up to infinite order in W at the coupled-Hartree-Fock (CHF) level, and the dispersion energy up to second-order in W plus an infinite summation of random-phase approximation (RPA) type terms—all of this with a complete account of the overlap effects.

There exists a method of calculating the polarization energies at a level of approximation intermediate between the multipole expansion and the nonexpanded method. This method is based on the so-called *bipolar* expansion of the intermolecular interaction operator.[306] The resulting expansion of a polarization correction ($E_{pol}^{(1)}$, $E_{ind}^{(2)}$, $E_{disp}^{(2)}$) is referred to as the bipolar expansion (or representation) of this correction. Although a calculation of bipolarly expanded polarization energies is usually more difficult than a nonexpanded calculation and the former energies always contain a truncation error, this approach has been actively explored in order to provide semiempirical methods of improving over the multipole expansion results. In the bipolar expansion a polarization correction is represented as a sum of terms decaying at large intermonomer separations as single powers of R^{-1} or exponentially, making the comparison with the multipole expansion straightforward. This comparison also provides a precise definition of the overlap effects for each term in the multipole expansion. The polarization corrections in the form of the bipolar expansion are sometimes referred to as *nonexpanded* corrections meaning that the multipole expansion has not been utilized. This terminology is somewhat misleading since this representation *always* involves a truncated expansion of the intermolecular interaction operator.

There are several reasons for development of methods allowing an extension of the multipole expansion results to finite intermonomer separations, including the van der Waals minimum region. The constants of the multipole expansion are much easier to compute than the nonexpanded polarization energies and, as pointed out above, need to be computed only once (as opposed to computations for each intermonomer geometry). Moreover, accurate constants can be obtained semiempirically, as discussed in section IV. A direct use of the multipole expansion in the van der Waals minimum regions is out of question. Some time ago one might have hoped that despite the formal divergence of this expansion, its truncated form might still provide a reasonable approximation of the polarization corrections. As we know now from comparisons with nonexpanded energies, such results are highly unreliable. A comparison of the bipolar and multipole expansion enables calculation of the damping functions defined as the ratios of the bipolar components to their multipole

counterparts. Knowledge of such *ab initio* damping functions may lead to construction of useful semiempirical formulas, as shown by Tang and Toennies.[307] With the use of such damping functions one may hope to obtain a reasonable representation of the polarization interaction energies at finite R, and, in fact, semiempirically damped multipole expansions are presently a very popular method of describing intermolecular potentials.

The bipolar expansion of polarization energies is related to the general angular expansion of the interaction energy already discussed in section IV. For two interacting rigid molecules the total interaction energy as well as any of its components are functions depending on the vector $\boldsymbol{R}$ connecting the centers of mass of the monomers and on the Euler angles $\zeta_A = (\alpha_A, \beta_A, \gamma_A)$ and $\zeta_B = (\alpha_B, \beta_B, \gamma_B)$ determining the mutual orientation of the two molecules. The components of $\boldsymbol{R}$ are determined with respect to an arbitrary space-fixed coordinate system. The Euler angles specify the rotation of a body-fixed coordinate system located at the center of mass of monomer X with respect to a system located at the same point with axes parallel to the chosen space-fixed system, $X = A$ or B. The interaction energy (as well as any scalar function of those variables) can be expressed as an infinite expansion in a complete orthonormal set of functions depending on the angular subset of variables, *cf.* eqs 75 and 76 in section IV. This kind of expansion has been introduced for the first time by Steele.[308] In this section it is convenient to use a simplified form of the angular functions, sufficient when only the interaction potential is discussed, and connected straightforwardly to the general form needed for applications of this potential in dynamical calculations. Since the interaction energy cannot depend on the orientation of the dimer with respect to the space-fixed coordinate system, one may choose a coordinate system such that $\boldsymbol{R}$ is along its z axis, which eliminates two angular components of $\boldsymbol{R}$. In this way the interaction energy or any other scalar function of the same variables can be written analogously to eq 75 as

$$E(R, \zeta_A, \zeta_B) = \sum_{l_A, l_B, j, k_A, k_B} \tilde{A}_{l_A l_B j}^{k_A k_B}(\zeta_A, \zeta_B) E_{l_A l_B j}^{k_A k_B}(R) \quad (90)$$

where $\tilde{A}_{l_A l_B j}^{k_A k_B}(\zeta_A, \zeta_B)$ is the angular function $\tilde{A}_{\{\Lambda\}}(\zeta_A, \zeta_B)$ of eq 84 with $\{\Lambda\} = \{l_A, k_A, l_B, k_B, j\}$. The summations over l_A, l_B, and j run from zero to infinity, while $k_X = -l_X, ..., l_X$. Equation 90 can be called the *angular expansion* of a polarization correction. Except for the first-order energy the angular expansion is not equivalent to the bipolar expansion since the coefficients $E_{l_A l_B j}^{k_A k_B}(R)$ are not monomials in $1/R$ at large R. On the other hand, the bipolar expansion can always be rearranged into the form of eq 90.

For the interaction of two hydrogen atoms at the second order, the bipolar expansion results automatically if the dispersion energy is computed using only products of orbitals of given symmetries (similarly for the induction part).[299,309] The same is true for the dispersion energy with complete neglect of intraatomic correlation effects in the case of interactions of atoms with s orbitals only like He_2.[186,298,310] For general atoms, the bipolar expansion of the second-

order energy also results automatically if the function in eq 13 are eigenfunctions of the squares and of the z components of the total angular momentum operators for atoms A and B. Knowles and Meath[311] used this fact to calculate the bipolarly expanded atomic second-order interaction energies in the time-dependent Hartree−Fock approach. Recently Wheatley and Meath extended this method by using CI functions for ground and excited states of monomers in interactions involving H, He, Li, and their ions.[312,313]

A. Bipolar Expansion of Buehler and Hirschfelder

For interactions of general atoms or molecules in the first and second order of the polarization theory the bipolar expansion of a given energy correction can be achieved by representing the interaction potential by its *exact* bipolar expansion proposed by Buehler and Hirschfelder.[306] Consider the two space-fixed coordinate systems introduced above with origins at the centers of masses of monomers A and B, their x and y axes parallel, aligned along their z axes, with the origins separated by a distance R. The inverse of the distance between two particles in space can then be expressed in the form of the following expansion (using notation of Meath *et al.*[227])

$$\frac{1}{r_{12}} = \sum_{l_A, l_B = 0}^{\infty} \sum_{m=-l_<}^{l_<} J_{l_A l_B}^{|m|}(r_1, r_2, R) Y_{l_A}^m(\tilde{\theta}_1, \tilde{\phi}_1) Y_{l_B}^{-m}(\tilde{\theta}_2, \tilde{\phi}_2) \quad (91)$$

where r_i, $\tilde{\theta}_i$, $\tilde{\phi}_i$ are the polar coordinates of ith particle and $l_<$ denotes the smaller of l_A and l_B. The coordinates of particle 1 are measured in system A while those of particle 2 are measured in system B. The expression for the function $J_{l_A l_B}^{|m|}(r_1, r_2, R)$ has a different form in each of the four regions:

$$
\begin{array}{ll}
R > r_1 + r_2 & r_2 > R + r_1 \\
r_1 > R + r_2 & |r_1 - r_2| \leq R \leq r_1 + r_2
\end{array}
\quad (92)
$$

The functions $J_{l_A l_B}^{|m|}(r_1, r_2, R)$ used by Meath *et al.*[227] are proportional to the functions $B_{l_A l_B}^{|m|}(r_1, r_2, R)$ used by Buehler and Hirschfelder. In the first three regions the expressions for $J_{l_A l_B}^{|m|}(r_1, r_2, R)$ are simple combinatorial formulas containing l_A, l_B, and m times a product of powers of r_1, r_2, and R. In the last region the expression contains a (finite) sum of powers of r_1, r_2, and R. The expansion given above is exact (except at $r_{12} = 0$). If the terms resulting from the regions II−IV are neglected, one obtains the standard multipole expansion of the interaction potential.

When the bipolar expansion of $1/r_{12}$ (and analogous expansions for other terms in the operator V) is substituted into each matrix element $\langle \Phi_0 | V | \Phi_n \rangle$, one obtains a bipolar expansion of a given polarization correction. For interactions of atoms that is all that is to be done. For interactions involving molecules, however, the coefficients of such an expansion would have to be calculated separately for each molecular orientation and the form of eq 90 would not be recovered. This problem is solved by a transformation from the space-fixed coordinate systems used in eq 91 to the body-fixed coordinate systems defining the Euler angles.[314]

B. Bipolar Expansion via Fourier Integral

The bipolar expansion of the interaction potential can also be obtained by using an alternative approach, proposed for the first time by Kay et al.,[315] which leads directly to expressions of the form of eq 90. The basic idea of this alternative approach is to represent the interaction potential as its Fourier transform

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2} \int \frac{d^3k}{k^2} e^{ik\cdot R} e^{-ik\tilde{r}_1} e^{ik\tilde{r}_2} \qquad (93)$$

where R is a vector from the center of mass of molecule A to the center of mass of molecule B and as before the vectors $\tilde{r}_1$ and $\tilde{r}_2$ are expressed in the coordinate systems centered on the molecules A and B, respectively, with their axes parallel to an arbitrary space-fixed coordinate system. At this point it is more convenient to use a general space-fixed coordinate system as in section IV. The plane waves are next expanded in terms of Bessel functions and spherical harmonics

$$e^{ik\cdot\tilde{r}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l \frac{2^l l!}{(2l)!} C_l^{-m}(\hat{k}) q_l^m(k,\tilde{r}) \qquad (94)$$

where $\hat{k} = k/k$ is the unit vector with components θ_k, ϕ_k and

$$C_l^m(\hat{k}) = \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_l^m(\theta_k,\phi_k) \qquad (95)$$

is a Racah spherical harmonic.[207] The other quantities in eq 94 are the so-called wave number (k) dependent multipole operators

$$q_l^m(k,r) = \frac{(2l+1)!}{2^l l!} C_l^m(\hat{r}) j_l(kr) \qquad (96)$$

where $j_l(kr)$ is a spherical Bessel function. Substitution of eq 94 into eq 93, integration over angles of k, and the transformation to monomer-fixed coordinate systems leads to the following expression

$$\frac{1}{r_{12}} = \sum_{l_A l_B j k_A k_B} i^{l_A - l_B - j} (2j+1) 2^{l_A + l_B + 1} \frac{l_A! l_B!}{\pi(2l_A)!(2l_B)!} \times$$

$$\begin{pmatrix} l_A & l_B & j \\ 0 & 0 & 0 \end{pmatrix} A_{l_A l_B j}^{k_A k_B}(\zeta_A,\zeta_B,\hat{R}) \times$$

$$\int_0^\infty dk\, j_j(kR) q_{l_A}^{m_A}(k,r_1) q_{l_B}^{m_B}(k,r_2) \qquad (97)$$

where the angular function $A_{l_A l_B j}^{k_A k_B}(\zeta_A,\zeta_B,\hat{R})$ is defined by eq 76 with $\{\Lambda\} = \{l_A,k_A,l_B,k_B,j\}$. This equation can be simplified by choosing a special space-fixed coordinate system such that R is along its z axis. Substitution of the expansion derived above into the matrix elements $\langle\Phi_0|V|\Phi_n\rangle$ and the use of this special space-fixed coordinate system gives an expansion of this matrix element exactly in the form of eq 90. For details of this approach in the context of the polarization energies and for a discussion of its equivalence to the Buehler–Hirschfelder expansion see refs 316 and 317.

C. Applications to First-Order Polarization Energies

The bipolarly expanded first-order electrostatic energy has been calculated by Meath and co-workers in a series of papers[227-229,318] for interactions of diatomics. The earlier work[227-229] utilized the potential in the form of eq 91, while more recently Koide et al.[318] switched to the expansion of eq 97 since it provides a scheme which is superior from the numerical point of view. In most cases these calculations completely neglect the intramonomer correlation effects, however, for some two-electron monomers correlated densities were used. Although expansions 91 or 97 can be substituted for V in the general expression 10 for the first-order polarization energy, it is more convenient to start with the alternative form 11. By substituting expression 91 for $1/r_{12}$, $E_{pol}^{(1)}$ can be written as a sum of contributions

$$E_{pol}^{(1)} = \sum_{l_A,l_B=0}^{\infty} E_{l_A l_B}^{(1)} = \sum_{l_A,l_B=0}^{\infty} \sum_{m=-l_<}^{l_<} E_{l_A l_B m}^{(1)} \qquad (98)$$

Performing the transformation to monomer-fixed coordinate systems one obtains the following expression for the components of $E_{pol}^{(1)}$

$$E_{l_A l_B m}^{(1)} =$$

$$\sum_{k_A=-l_A}^{l_A} \sum_{k_B=-l_B}^{l_B} \chi_{l_A l_B k_A k_B}^{|m|}(R) D_{m,k_A}^{l_A}(\zeta_A)^* D_{-m,k_B}^{l_B}(\zeta_B)^* \qquad (99)$$

where

$$\chi_{l_A l_B k_A k_B}^{|m|}(R) = \left[\frac{2l_A+1}{4\pi}\right]^{1/2} \left[\frac{2l_B+1}{4\pi}\right]^{1/2} \times$$

$$\int_0^\infty \int_0^\infty J_{l_A l_B}^{|m|}(r_1,r_2,R) \varrho_{l_A}^{k_A}(r_1) \varrho_{l_B}^{k_B}(r_2) r_1^2 r_2^2\, dr_1\, dr_2 \qquad (100)$$

The so-called partial-wave components of the electron density $\varrho_A(1) \equiv \varrho_A(r_1,\theta_1,\phi_1)$ are defined by

$$\varrho_{l_A}^{k_A}(r_1) = \left[\frac{4\pi}{2l_A+1}\right]^{1/2} \int_0^{2\pi} \int_0^\pi \varrho_A(r_1,\theta_1,\phi_1) \times$$

$$Y_{l_A}^{k_A}(\theta_1,\phi_1) \sin\theta_1\, d\theta_1\, d\phi_1 \qquad (101)$$

and similarly for system B. The partial wave components of the electron density need to be computed only once for each monomer. All the orientational dependence is then obtained via the simple products of Wigner's functions. (Meath et al. have not transformed their expression into the form of eq 90.) The double radial integral of eq 100 has to be evaluated separately for each R.

Using the method outlined above Meath and co-workers[227-229] calculated the first-order polarization energies for interactions of several atoms and diatomic molecules. In the case of H_2 interactions they have also used correlated electron densities. They found that the importance of the overlap effects strongly depends on the interacting species. For several of the investigated molecules the charge

overlap effects were found to be large showing that the multipole expansion of the electrostatic energy is not a particularly reliable representation of this correction in the van der Waals minimum region.

D. Applications to Second-Order Polarization Energies

Either of the two bipolar expansions of the intermolecular interaction operator can formally be used in any order of polarization perturbation theory by expanding all the matrix elements $\langle \Phi_m | V | \Phi_n \rangle$ appearing in the spectral representation of a given correction. Although the exact spectral sums cannot be evaluated in practice, various pseudospectral expansions based on Hylleraas-type variational principles can be used. Alternatively, the expansion can be applied to one- and two-electron integrals appearing in many-body formulas for polarization energies. Similarly as in the first order, radial coefficients in the expansion of the matrix elements decay either exponentially or as monomials in R^{-1}. This approach makes a direct comparison of the coefficients at each power of R and the definition of damping functions possible. The final expression will, of course, contain products of several angular functions $\tilde{A}_{l_A l_B j}^{k_A k_B}(\zeta_A, \zeta_B)$. For example, the second-order (induction or dispersion) contribution can be written as

$$E(R, \zeta_A, \zeta_B) = \sum_{l_A, l_B j, k_A, k_B} \sum_{l'_A, l'_B j', k'_A, k'_B} \tilde{A}_{l_A l_B j}^{k_A k_B}(\zeta_A, \zeta_B) \times$$
$$\tilde{A}_{l'_A l'_B j'}^{k'_A k'_B}(\zeta_A, \zeta_B) E_{l_A l_B j l'_A l'_B j'}^{k_A k_B k'_A k'_B}(R) \quad (102)$$

At large R expansion 102 becomes equivalent to the multipole expansion since for $R \to \infty$ the radial coefficients $E_{l_A l_B j l'_A l'_B j'}^{k_A k_B k'_A k'_B}(R) \to C_{l_A l_B j l'_A l'_B j'}^{k_A k_B k'_A k'_B}/R^{l_A + l_B + l'_A + l'_B + 2}$ for $j = l_A + l_B$, $j' = l'_A + l'_B$, and none of l_A, l_B, l'_A, l'_B equal to zero. The other combinations of indices give exponentially decaying terms which do not have counterparts in the multipole expansion. Notice that this multipole expansion is equivalent but not identical to that defined by eqs 78 and 82 and a recoupling of spherical tensors is required to transform from one form to another.[195,197]

Equation 102 enables the determination of damping functions for each term in the multipole expansion of $E_{\text{ind}}^{(2)}$ and $E_{\text{disp}}^{(2)}$. The damping function for a general term $C_{l_A l_B j l'_A l'_B}^{k_A k_B k'_A k'_B}/R^{l_A + l_B + l'_A + l'_B + 2}$ can now be precisely defined as the ratio

$$\chi_{l_A l_B j l'_A l'_B}^{k_A k_B k'_A k'_B}(R) =$$
$$-E_{l_A l_B j l'_A l'_B j'}^{k_A k_B k'_A k'_B}(R) R^{l_A + l_B + l'_A + l'_B + 2} [C_{l_A l_B j l'_A l'_B}^{k_A k_B k'_A k'_B}]^{-1} \quad (103)$$

where $j = l_A + l_B$, $j' = l'_A + l'_B$, and none of l_A, l_B, l'_A, l'_B equal to zero. By grouping terms with the same explicit dependence on the inverse power of R one may find the damping function corresponding to a fixed power of R. Note that such damping functions depend now on angles.

Knowles and Meath[319] have calculated the dispersion and induction energies for He–HF by expanding each matrix element appearing in (pseudo)spectral expressions for these corrections in the RPA approximation (following the method of Jaszunski and McWeeny[320]). In fact these authors have not used

the bipolar expansion of the interaction operator explicitly. Instead, they utilized the orthogonality properties of Wigner's functions and integrated the particular components out from the matrix elements. Since each component is asymptotically a monomial in R^{-1}, or decays exponentially, the bipolar expansion of the second-order polarization energy can be obtained in this way. The considered matrix elements are known only pointwise, so that the angular integration has to be done numerically. For general systems the needed integration is five dimensional and therefore not possible in practice. However, for interaction of atoms with linear molecules only one-dimensional integrals are needed, and the method can be applied. The terms in expansion 102 which decay as inverse powers of R were compared with those given by the multipole expansion, the ratio providing the damping function. Knowles and Meath[319] computed such damping functions for most terms with up to R^{-10} dependence, showing that damping is very significant in the region of van der Waals minimum. Moreover, the exponential terms were shown to contribute quite substantially for such distances.

The bipolar expansion of eq 97 was first applied to intermolecular interactions by Koide[321] and by Linder et al.[322] In addition to the first-order work discussed above,[318] it has been used to compute dispersion interactions of two hydrogen atoms[321,309] and of general atoms.[323] It was extended to interactions of atoms with diatomics by Rosenkrantz and Krauss[324] and later to arbitrary systems by Knowles and Meath.[314] The latter work represents the most advanced application of the bipolar expansion. The authors used the Fourier integral form of the bipolar expansion of the intermolecular interaction operator to compute the dispersion energies at the RPA level. In the case of the second-order dispersion energy the expression for $E_{l_A l_B j l'_A l'_B j'}^{k_A k_B k'_A k'_B}(R)$ contains a two dimensional integral over k and k' (k' comes from the complex conjugate matrix element in the expression for the second-order energy) with an integrand containing matrix elements of generalized multipole operators. In this form the expression still couples systems A and B. The Casimir–Polder formula could be utilized here (as has been done for the H_2 case[321]), but it would introduce one more difficult integral. Instead, Knowles and Meath[314] expanded the Bessel functions in a power series. Although the resulting expansion of the dispersion energy components was slowly convergent or divergent, it was possible to sum it using Padé approximants. The accuracy of the final results was, however, rather limited. Using this approach Knowles and Meath computed the damping functions for all dimers resulting from the interaction of He, Ne, and HF.

E. Summary

One may conclude from the above work that the overlap effects are significant in the region of the van der Waals minimum and for smaller separations. This fact is not surprising since the very existence of the van der Waals minimum and of the repulsive wall is connected with overlap of monomer's charge distributions. The information about the damping functions for electrostatic, induction, and dispersion

energies obtained from such calculations is being utilized in construction of the damping functions for semiempirical potentials. This work also shows that the spherical, exponentially decaying components of the polarization corrections are significant at the van der Waals minimum and smaller distances. So far, these components have not been included directly in empirical potentials although they are effectively taken into account by the Born—Mayer exchange terms.

Calculation of polarization energies using the bipolar expansion represents apparently a very attractive approach if a complete potential energy surface is to be obtained. Such a calculation formally involves less effort than a nonexpanded one since only the radial coefficients have to be recomputed for each R, while the angular dependence is given by simple products of Wigner's functions. This effort is larger than that of the multipole expansion approach but still is many times smaller than the effort of a full nonexpanded calculation. Unfortunately, already in the second order the number of coefficients to be computed for each R is very large and the numerical methods for such calculations are not well developed yet.

VI. Intramonomer Electronic Correlation Problem and Many-Body Formulation of Symmetry-Adapted Perturbation Theory

A. Double Perturbation Theory Approach to Intramonomer Correlation

The theory presented in the preceding sections cannot be applied directly to interactions of many-electron atoms or molecules since the exact unperturbed monomer wave functions are not known for these systems. For two-electron monomers highly accurate, practically exact wave functions are available,[325-328] but they are difficult to use in perturbation theory because of the explicit dependence on the interelectronic distance. Thus far, such wave functions have been applied only to calculate highly accurate values of the van der Waals constants for He_2[329,330] and for $(H_2)_2$[331] and of the first-order polarization and exchange energies for He_2.[327]

For very small monomers one can perform direct calculations within the full configuration interaction (FCI) model. Such calculations (through high orders of perturbation theory) have been recently performed for four-electron dimers,[84-86,140] but the aim of this work was an analysis of mathematical models of intermolecular interactions rather than actual calculations of accurate interaction energies.

In evaluating the first-order energies one does not have to assume that the zeroth-order problem has been solved exactly. In this case approximate monomer wave functions can be used to evaluate the first-order energy expressions. In fact, CI wave functions were used with success to compute the first-order contributions ($E_{pol}^{(1)}$ and $E_{exch}^{(1)}$) to the interaction energy for two-electron monomers[227,332-337] and for larger systems.[338]

For many-electron atoms and molecules the only widely available wave functions are the Hartree—Fock determinants. Using these determinants as

zeroth-order wave functions in the polarization theory or in SAPT amounts to a complete neglect of the effects of the correlation of electronic motion within monomers. These effects can be taken into account by an application of the powerful techniques of the many-body perturbation theory and/or coupled-cluster theory.[339,340] Since the Hartree—Fock determinants are eigenfunctions of the monomer's Fock operators F_A and F_B, we have to consider a new perturbation operator $W = W_A + W_B$, where W_A and W_B are the intramonomer correlation operators corresponding to the Møller—Plesset[66] partitioning of the monomer Hamiltonians, $W_A = H_A - F_A$ and $W_B = H_B - F_B$. The interaction energy can now be calculated using a suitable double perturbation theory in which $F = F_A + F_B$ serves as the unperturbed operator while the intermolecular interaction operator V and the intramonomer correlation operator W act as perturbations. Such a double perturbation theory proposed in ref 65 is based on the following parametrization of the Schrödinger equation for the dimer AB

$$(F + \zeta V + \lambda W)\Phi_{AB}(\zeta,\lambda) = E_{AB}(\zeta,\lambda)\Phi_{AB}(\zeta,\lambda) \quad (104)$$

The parameters ζ and λ have the physical values equal to unity and are introduced to define the perturbation theory orders. The parametrized wave function of the dimer satisfies

$$\Phi_{AB}(0,0) \equiv \Phi_0^{HF} \quad (105)$$

where Φ_0^{HF} denotes the product the Hartree—Fock determinants for the isolated monomers A and B, respectively, and

$$\Phi_{AB}(0,\lambda) = \Phi_A(\lambda)\Phi_B(\lambda) \quad (106)$$

where $\Phi_A(\lambda)$ and $\Phi_B(\lambda)$ are the ground-state eigenfunctions of the parametrized monomer Hamiltonians $H_A = F_A + \lambda W_A$ and $H_B = F_B + \lambda W_B$. Expanding $E_{AB}(\zeta,\lambda)$ and $\Phi_{AB}(\zeta,\lambda)$ in powers of ζ and λ and combining terms of the same order in ζ one obtains[65] the following perturbation expansions for the nth-order polarization wave function and energy:

$$\Phi_{pol}^{(n)} = \sum_{i=0}^{\infty} \Phi_{pol}^{(ni)} \quad (107)$$

$$E_{pol}^{(n)} = \sum_{i=0}^{\infty} E_{pol}^{(ni)} \quad (108)$$

where $\Phi_{pol}^{(ni)}$ and $E_{pol}^{(ni)}$ are the double perturbation theory corrections of the nth order in V and of the ith order in W.

The corresponding double perturbation expansion of the SRS energies $E_{SRS}^{(n)}$ is obtained in a similar way by parametrizing the expression for the SRS interaction energy of eq 32 with the intramonomer correlation parameter λ

$$E_{SRS}(\zeta,\lambda) = \frac{\langle\Phi_{AB}(0,\lambda)|\zeta V \mathscr{A}\Phi_{AB}(\zeta,\lambda)\rangle}{\langle\Phi_{AB}(0,\lambda)|\mathscr{A}\Phi_{AB}(\zeta,\lambda)\rangle} \quad (109)$$

Expanding $E_{SRS}(\zeta,\lambda)$ as a double power series in ζ and in λ, and grouping terms of the same order in ζ one

obtains[12] the following expansion for $E_{SRS}^{(n)}$

$$E_{SRS}^{(n)} = \sum_{i=0}^{\infty} E_{SRS}^{(ni)} \qquad (110)$$

where the corrections $E_{SRS}^{(ni)}$ are formally defined as the coefficients at $\zeta^n \lambda^i$ in the Taylor expansion of the function $E_{SRS}(\zeta,\lambda)$.

The SRS corrections $E_{SRS}^{(ni)}$ naturally decompose as

$$E_{SRS}^{(ni)} = E_{pol}^{(ni)} + E_{exch}^{(ni)} \qquad (111)$$

where the polarization corrections are defined by eq 108. For a fixed n the exchange contributions $E_{exch}^{(ni)}$ sum up to the total nth-order SRS exchange energy $E_{exch}^{(n)}$

$$E_{exch}^{(n)} = \sum_{i=0}^{\infty} E_{exch}^{(ni)} \qquad (112)$$

The corrections $E_{pol}^{(n0)}$ and $E_{exch}^{(n0)}$ can be viewed as describing the interaction of "Hartree–Fock" molecules, while the remaining terms in the expansions 108 and 112, i.e., $E_{pol}^{(n)} - E_{pol}^{(n0)}$ and $E_{exch}^{(n)} - E_{exch}^{(n0)}$, represent the intramonomer correlation effects.

The conventional perturbation theory expressions for the perturbed wave functions $\Phi_{pol}^{(ni)}$ and the perturbation energies $E_{pol}^{(ni)}$, eqs 107 and 108, are given in terms of Φ_0^{HF}, V, W, and the reduced resolvent $\hat{R}_0^{HF}$ of F.[65,341] Final expressions in terms of molecular integrals and orbital energies can then be obtained using the Slater–Condon rules or many-body techniques. The derivation of the explicit orbital formulas for the exchange energies $E_{exch}^{(ni)}$ is much more difficult because of the necessity of handling overlap integrals for nonorthogonal sets of orbitals. When the intramonomer correlation is neglected, the nonorthogonality problem becomes easier and it was solved some time ago both in the case of the first-order exchange energy $E_{exch}^{(10)}$ [182,342] and the exchange–induction $E_{exch-ind}^{(20)}$ and exchange–dispersion $E_{exch-disp}^{(20)}$ energies.[185] The conventional orbital expressions for the corrections $E_{pol}^{(ni)}$ and $E_{exch}^{(ni)}$ contain disconnected terms[341] (or diagrams) which behave incorrectly when the size of the system increases. Although the final formulas can be written exclusively in terms of connected contributions, the cancellation of disconnected terms requires considerable algebraic manipulations. Therefore, in practice such an approach has only been used to derive the simplest approximations to the first- and second-order polarization and exchange energies, namely: $E_{pol}^{(10)}$,[132] $E_{exch}^{(10)}$,[182] $E_{ind}^{(20)}$,[132] $E_{ind}^{(21)}$,[343] $E_{disp}^{(20)}$,[132] $E_{disp}^{(21)}$,[8,344] and $E_{exch}^{(20)}$.[185]

To derive higher-order terms in the intramonomer correlation, it is advantageous to rewrite the perturbational equations in an explicitly connected form, which guarantees the extensivity[339,340] of the energy. Such a form can be obtained by a generalization of the ideas of the coupled-cluster (CC) theory[339,340,345–352] to intermolecular interactions. This approach leads

to an explicitly connected formulation of the RS and SRS perturbation equations.[11,12,67,69] Rybak et al.[11] postulated a coupled-cluster ansatz for the wave function Φ_{AB} based on the product of Hartree–Fock determinants of the isolated monomers and derived explicitly connected expressions for the polarization components of the interaction energy. Generalization of the results of ref 11 to the case of the symmetrized polarization expansion is difficult, and an explicitly connected form of eq 109 has not yet been obtained. Only recently has an explicitly connected expansion of the first-order exchange energy in the single-exchange approximation[55,180,353] been derived.[12] Using the second-quantized representation of the single-exchange operator $\mathscr{P}_1$ and the explicitly connected expansion of the expectation value in the coupled-cluster theory,[354] the present authors have shown[12] that the first-order exchange energy can be expressed directly through the monomer cluster operators in a form showing explicitly its connected and size-extensive character. The coupled-cluster formulation of the many-body SAPT theory has been applied to derive orbital expressions for the corrections $E_{pol}^{(1l)}$,[11] $E_{exch}^{(1l)}$,[12] and $E_{disp}^{(2l)}$ [11] for $l \leq 2$, as well as some coupled-cluster approximations to $E_{exch}^{(1)}$ [12] and to $E_{disp}^{(2)}$.[71]

The alternative formulas of eqs 11, 44, 19, and 23 expressing the electrostatic, first-order exchange, induction, and dispersion energies, respectively, through the density matrices and polarization propagators can also be used to derive many-body perturbation expansions of these components. In some situations this approach may offer advantages compared to the coupled-cluster approach discussed above, and it has recently been used to define many-body perturbation expansions of the electrostatic,[70,72] exchange,[73] and induction[74] energies.

One advantage of using the formulas expressed in terms of density matrices and polarization propagators is that techniques developed for those quantities can be utilized in the theory of intermolecular interactions. Another reason for considering this approach is that there exist alternative many-body perturbation expansions of the density matrices,[110–112] and polarization propagators,[355] referred to as relaxed expansions or as expansions including response. The alternative expansions are obtained by differentiation of the Møller–Plesset correlation energies corresponding to an external field dependent partitioning of the Hamiltonian.[110,111] The perturbation corrections corresponding to the relaxed expansions will be denoted by adding the subscript "resp", e.g., $E_{ind,resp}^{(20)}$. The relaxed expansion for the electrostatic energy was introduced in ref 70 and applied to compute $E_{pol,resp}^{(12)}$. Recently, this approach has been generalized to higher orders in the intramonomer correlation[72] and applied to study the convergence properties of both expansions. Possible applications of the two expansions for the electron densities and polarization propagators in calculations of the induction energy have been discussed in ref 74. Calculations of the dispersion energy using the leading-order terms from both many-body perturbation expansions of the polarization propagators have been described in refs 320 and 356.

B. Many-Body Perturbation Expansions for the Interaction Energy Components

1. Electrostatic Energy

The importance of the intramonomer correlation contributions to the electrostatic energy can be assessed by comparing the Hartree−Fock and correlated multipole moments of monomers. Such a comparison[110] suggests that at least for the interaction of polar molecules at large intermolecular distances the intramonomer correlation effects on the electrostatic energy are important. In addition, calculations for the He, Be, and H_2 dimers at the full CI level[327,332−335] suggested that even for nonpolar dimers the correlation part of the electrostatic energy is nonnegligible.

The leading correlation correction $E_{pol}^{(12)}$ has been first derived and computed in ref 11, while the correction $E_{pol,resp}^{(12)}$ has been developed in ref 70 and further considered in ref 357. Here we will discuss methods which use eq 11 as the starting point for various many-body perturbation expansions of the electrostatic energy.[70,72] To introduce a perturbation series of the electrostatic energy it is useful to rewrite eq 11 as

$$E_{pol}^{(1)} = \int \varrho_A(r_i) v_{ij} \varrho_B(r_j) \, d^3 r_i \, d^3 r_j \qquad (113)$$

where $\varrho_X(r_i)$ is the electron density of the monomer X, and v_{ij} is the generalized interaction potential defined by eq 47. Equation 113 can be easily expanded as a perturbation series in terms of the correlation operators W_A and W_B. The electron density can be represented as the Møller−Plesset perturbation expansion of the form

$$\varrho_X(r) = \sum_{k=0}^{\infty} \lambda_X^k \varrho_X^{(k)}(r) \qquad (114)$$

where λ_X is a formal expansion parameter set equal to 1 later. The consecutive terms in eq 114 are defined by expanding the expectation value of the electron density operator $\hat{D}(r)$[354]

$$\hat{D}(r) = \sum_{i=1}^{N_X} \delta(r - r_i) \qquad (115)$$

Substitution of the expansion 114 for the monomer A and B into eq 113 defines the intramonomer correlation corrections to $E_{pol}^{(10)}$

$$E_{pol}^{(1n)} = \sum_{l=0}^{n} \int \varrho_A^{(n-l)}(r_i) v_{ij} \varrho_B^{(l)}(r_j) \, d^3 r_i \, d^3 r_j \quad (116)$$

Another expansion of the electron densities can be obtained by considering a new "perturbed" monomer Hamiltonian $\tilde{H}_X = H_X + \xi \hat{D}(r)$ parametrized in the following way

$$\tilde{H}_X = \tilde{F}_X(\xi;r) + \lambda \tilde{W}_X(\xi;r) \qquad (117)$$

where $\tilde{F}_X(\xi;r)$ is the Fock operator corresponding to the Hamiltonian $\tilde{H}_X$ (which includes the operator $\xi \hat{D}(r)$) and $\tilde{W}_X(\xi;r)$ is defined as the difference $\tilde{H}_X(\xi;r) - \tilde{F}_X(\xi;r)$. The operators $\tilde{F}_X$ and $\tilde{W}_X$ differ from the standard operators F_X and W_X since the occupied

Hartree−Fock orbitals used to construct $\tilde{F}_X(\xi;r)$ now depend on the parameters ξ and r. The nth-order correlation correction to the electron density can now be defined as the derivative of the nth-order MBPT energy $\mathscr{E}_X^{(n)}(\xi;r)$ computed using the Hamiltonian partitioning of eq 117

$$\tilde{\varrho}_X^{(n)}(r) = \left. \frac{\partial \mathscr{E}_X^{(n)}(\xi;r)}{\partial \xi} \right|_{\xi=0} \qquad (118)$$

These density corrections will be referred to as *relaxed* ones or as those including *orbital relaxation (response)* effects.[110,111] The use of the relaxed density corrections in eq 113 will lead to a different expansion of $E_{pol}^{(1)}$ with corrections denoted by $E_{pol,resp}^{(1n)}$. The relaxed corrections are of infinite order in $\tilde{W}$, so that the corresponding (truncated) perturbative expansions may be viewed as nonperturbative, infinite-order summation schemes. Only in the zeroth-order do the two approaches lead to the same result, which is a simple consequence of the fact that the Hartree−Fock wave function fulfills the Hellmann−Feynman theorem.

Substitution of the multipole expansion of v_{ij} (which can be obtained in an analogous way as the expansion of V discussed in section IV) into eq 113 shows that for interactions of polar molecules at large intermonomer distances R the two corrections behave like

$$E_{pol}^{(1n)} \sim \sum_{k=0}^{n} \mu_A^{(n-k)} \mu_B^{(k)} R^{-3} \qquad (119)$$

$$E_{pol,resp}^{(1n)} \sim \sum_{k=0}^{n} \tilde{\mu}_A^{(n-k)} \tilde{\mu}_B^{(k)} R^{-3} \qquad (120)$$

where $\mu_X^{(n)}$ and $\tilde{\mu}_X^{(n)}$ denote the nth-order correlation correction to the dipole moment in the nonrelaxed and relaxed approach, respectively.

Rybak et al.[11] computed the leading-order correlation correction $E_{pol}^{(12)}$ for the water and HF dimers, and showed that $E_{pol}^{(12)}$ represents as much as 10% of the total interaction energy for these systems in the region of the van der Waals minimum. The two perturbative expansions of the electrostatic energy discussed above have been applied in ref 70 through the second order in the respective intramonomer correlation operators for the interaction of two hydrogen molecules. It has been found that the convergence is only moderately fast: the second-order results reproduced only 50% to 70% of the correlated part of the electrostatic energy computed with monomers' FCI functions obtained in the same orbital basis set. Recently, the study of ref 70 has been extended in ref 72 to higher orders in the intramonomer correlation. General expressions for the intramonomer correlation corrections $E_{pol}^{(1k)}$ and $E_{pol,resp}^{(1k)}$, $k \leq 4$, have been derived and the convergence properties of the nonrelaxed and relaxed perturbation expansions of the electrostatic energy have been investigated for model four-electron dimers containing He and H_2.

The numerical results of these calculations[72] are presented in Table 4. To demonstrate the convergence properties of the two perturbation expansions

Table 4. Convergence of the Many-Body Perturbation Expansions for the Electrostatic Energy of the He and H_2 Dimers[a]

	He$_2$[b]		(H$_2$)$_2$[c]	
n	nonrelaxed	relaxed	nonrelaxed	relaxed
0	$-0.4955(-5)$	$-0.4955(-5)$	$0.7568(-4)$	$0.7568(-4)$
2	$-0.2689(-6)$	$-0.3949(-6)$	$-0.1130(-4)$	$-0.1434(-4)$
3	$-0.1755(-6)$	$-0.1114(-6)$	$-0.6568(-5)$	$-0.5122(-5)$
4	$-0.8842(-7)$	$-0.4804(-7)$	$-0.2805(-5)$	$-0.1721(-5)$
$\epsilon_{pol}^{(1)}(4)$	$-0.5328(-6)$	$-0.5543(-6)$	$-0.2068(-4)$	$-0.2118(-4)$
$\epsilon_{pol}^{(1)}(\text{FCI})$	$-0.5882(-6)$	$-0.5882(-6)$	$-0.2218(-4)$	$-0.2218(-4)$

[a] The energies are given in hartree. The expression $(-N)$ denotes the factor of 10^{-N}. For details of calculations, see ref 72. [b] $R = 5.6$ bohr. [c] Linear HH–HH geometry. The distance between the centers of mass of H_2 is 6.5 bohr while the H–H distance is 1.4 bohr.

Table 5. Convergence of the Many-Body Perturbation Expansions for the Electrostatic Energy of the H_2O and HF Dimers[a]

	(H_2O)$_2$[b]		(HF)$_2$[c]	
n	nonrelaxed	relaxed	nonrelaxed	relaxed
0	-7.124	-7.124	-6.327	-6.327
2	0.233	-0.014	0.460	0.219
3	-0.172	0.140	-0.305	0.053
4		0.045		0.068
$\epsilon_{pol}^{(1)}(k)$[d]	0.061	0.171	0.155	0.340

[a] Energies are given in kcal/mol. For the details of calculations, see ref 358. [b] Geometry is the same as specified in Table 3 of ref 11 except that $R = 5.67$ and the angle between the O–O axis and the HOH bisector of the proton acceptor is 120°. The basis set T^- (2d, 2p)* from ref 11 was used. [c] The nonlinear geometry specified in Table 4 of ref 11. The basis set T^{-S} (2df, 2pd)′ from ref 11 was used. [d] k equals 3 and 4 for the nonrelaxed and relaxed approaches, respectively.

for these systems the consecutive corrections $E_{pol}^{(1k)}$ and $E_{pol,resp}^{(1k)}$, the sum of the series truncated after the fourth-order $\epsilon_{pol}^{(1)}(4)$, and the total *electrostatic–correlation* energy, defined as

$$\epsilon_{pol}^{(1)}(\text{FCI}) = E_{pol}^{(1)} - E_{pol}^{(10)} \qquad (121)$$

calculated at the full CI level using the same basis sets are given. These results show that the convergence properties of both many-body perturbation expansions of the electrostatic energy are satisfactory. For the He and H_2 dimers the sum of corrections through the fourth order reproduces well over 90% of the total electrostatic–correlation energy. The leading, second-order term represents approximately 50% or more of the total intramonomer correlation effect. Taking into account the third-order correction adds an additional 20–30%. Note also, that the inclusion of the orbital relaxation effects results in a faster convergence. Through the fourth order the results of both methods are very close to each other confirming that both methods have converged from a practical point of view. The total intramonomer correlation contribution to the electrostatic energy amounts to 11% and 23% for the He and H_2 dimers, respectively.

In Table 5 convergence of the many-body perturbation expansion of the electrostatic energy is presented for the H_2O and HF dimers.[358] Somewhat surprisingly the total intramonomer correlation effect is relatively small, amounting to 2% and 5% of $E_{pol}^{(10)}$,

respectively. Mostly likely there is some cancellation between the long-range and overlap effects for the geometries chosen. In fact the leading term $E_{pol}^{(12)}$ is larger for other geometries investigated in ref 11. Nevertheless, contributions of the order of a few tenths of kilocalories per mole are significant at the level of accuracy presently achieved for those systems. The convergence pattern is somewhat erratic (and very different for the relaxed and nonrelaxed approaches) but this fact can be attributed to the smallness of the correction.

2. First-Order Exchange Energy

The most important short-range contribution to the interaction energy between closed-shell molecules is the exchange part of the first-order energy, $E_{exch}^{(1)}$. If the interacting monomers are described by the Hartree–Fock wave functions, the corresponding exchange energy $E_{exch}^{(10)}$ can be routinely calculated even for large systems. The studies performed for small systems using FCI wave functions[327,332–335] have shown that the intramonomer electron correlation effects are significant. For the He dimer rather large orbital basis sets could be used and even explicitly correlated Gaussian-type geminals (GTG) have been applied,[327] so that the values of $E_{exch}^{(1)}$ for this system are known to accuracy of a few digits. Until very recently, perturbative studies of the intramonomer correlation part of the first-order exchange energy have also been restricted to the interaction of two He atoms. The leading correlation correction, $E_{exch}^{(11)}$, has been considered in ref 65. Jankowski *et al.*[68] computed the corrections $E_{exch}^{(11)}$ and $E_{exch}^{(12)}$ and found that the sum $E_{exch}^{(11)} + E_{exch}^{(12)}$ reproduces only ~60% of the total intramonomer correlation contribution to $E_{exch}^{(1)}$.[327]

Two general schemes for calculations of the intramonomer correlation corrections to $E_{exch}^{(10)}$ have been recently proposed: a CC-based method utilizing the second-quantized representation of the single-exchange operator $\mathscr{P}_1$[12] and a straightforward application of the Møller–Plesset expansions of density matrices in eqs 44 and 45[73]

$$\varrho_X(1|1') = \sum_{k=0}^{\infty} \lambda_X^k \varrho_X^{(k)}(1|1') \qquad (122)$$

$$\Gamma_X(12|1'2') = \sum_{k=0}^{\infty} \lambda_X^k \Gamma_X^{(k)}(12|1'2') \qquad (123)$$

Both approaches give identical numerical results when dimer-centered basis sets are used, but the final expressions for the corrections $E_{exch}^{(1l)}$ differ distinctly. In particular, the latter scheme gives formulas for the correlation corrections $E_{exch}^{(1l)}$ with a smaller number of summations and it is fully valid also in monomer-centered basis sets. Although in some cases the use of the dimer-centered basis set is essential for an accurate description of the exchange effect,[359] in other cases computationally less demanding monomer-centered basis sets may be preferred.[360]

Recently, extensive numerical studies of the convergence properties of the many-body perturbation expansion of the $E_{exch}^{(1)}$ correction for model four-electron systems[12] and many-electron systems[73] have

Table 6. Convergence of the Many-Body Perturbation Expansions for the First-Order Exchange Energy of the He₂, (H₂)₂, He−HF, and Ar−H₂ Systems[a]

	He₂[b]	(H₂)₂[c]	He−HF[d]	Ar−H₂[e]
$E_{exch}^{(10)}$	0.3559(−4)	0.2493(−3)	0.8295(−4)	0.4799(−3)
$E_{exch}^{(11)}$	0.5318(−6)	0.1786(−4)	0.2742(−5)	0.2360(−4)
$E_{exch}^{(12)}$	0.1448(−5)	−0.7369(−5)	0.2114(−4)	0.1543(−4)
$\epsilon_{exch}^{(1)}(2)$	0.1980(−5)	0.1049(−4)	0.2389(−4)	0.3903(−4)
$\Delta_{exch}^{(1)}(CCSD)$	0.1866(−5)	−0.2257(−5)	0.2942(−5)	0.5705(−5)
$\epsilon_{exch}^{(1)}(CCSD)$	0.3845(−5)	0.8234(−5)	0.2683(−4)	0.4474(−4)
$\epsilon_{exch}^{(1)}(FCI)$	0.3914(−5)	0.8354(−5)		

[a] The expression (−N) denotes the factor of 10^{-N}. For the details of calculations, see refs 12 and 73. [b] $R = 5.6$ bohr. [c] Linear HH−HH geometry. The distance between the centers of mass of H₂ is 6.5 bohr while the H−H distance is 1.4 bohr. [d] Linear He−HF geometry. The distance between the He atom and the center of mass of HF is 6.5 bohr while the H−F distance is 1.7328 bohr. [e] Linear Ar−H₂ geometry. The distance between the Ar atom and the center of mass of H₂ is 6.7 bohr while the H−H distance is 1.4 bohr.

been reported. Since the results of Jankowski et al.[68] suggested that the convergence of the many-body expansion of the first-order exchange energy is only moderately fast, nonperturbative infinite-order summation techniques based on the coupled-cluster singles and doubles theory (CCSD)[361] have been proposed. The simplest way of performing such infinite-order summations, introduced in ref 12, is to approximate $E_{exch}^{(1)}$ by

$$E_{exch}^{(1)}(CCSD) =$$
$$E_{exch}^{(10)} + E_{exch}^{(11)} + E_{exch}^{(12)} + \Delta_{exch}^{(1)}(CCSD) \quad (124)$$

where the term $\Delta_{exch}^{(1)}(CCSD)$ collects all higher-order terms in W obtained by replacing the first and second-order cluster operators entering the expression for $E_{exch}^{(12)}$ by the converged CCSD operators. This method of performing an infinite-order summation of selected perturbation theory contributions is similar in spirit to the CCSD(T) method of Urban et al.[362] widely used in correlation energy calculations.

In Table 6 numerical results of perturbative calculations through the second order in W as well as the results of coupled-cluster calculations (using eq 124) for He₂, (H₂)₂, He−HF, and Ar−H₂ are presented. To demonstrate the convergence properties of the perturbation series for various dimers, consecutive corrections $E_{exch}^{(1l)}$, the sum of the correlated part of the series truncated after the lth order $\epsilon_{exch}^{(1)}(l)$, the higher-order contribution $\Delta_{exch}^{(1)}(CCSD)$, the total correlation part of the CCSD exchange energy

$$\epsilon_{exch}^{(1)}(CCSD) = E_{exch}^{(1)}(CCSD) - E_{exch}^{(10)} \quad (125)$$

and the full CI (FCI) exchange−correlation energy

$$\epsilon_{exch}^{(1)}(FCI) = E_{exch}^{(1)} - E_{exch}^{(10)} \quad (126)$$

computed for four-electron dimers at full CI level using the same basis sets have been tabulated. The results show that the convergence of the many-body perturbation expansion of the first-order exchange energy is only moderately fast. For the He dimer the

sum of the first two terms reproduces only 50% of the FCI result, while for the H₂ dimer the sum of perturbation series overestimates the FCI result by 25%. The inclusion of the higher-order terms by means of the CCSD approximation improves the situation considerably, and $\epsilon_{exch}^{(1)}(CCSD)$ recovers the full CI exchange−correlation energy to within a few percent.

For many-electron systems it is not possible to compute the total first-order exchange energy $E_{exch}^{(1)}$. However, in view of the results for four-electron systems, $\Delta_{exch}^{(1)}(CCSD)$ should to a good approximation represent the sum of the corrections $E_{exch}^{(1l)}$ with $l \geq 3$. If this assumption is correct, an inspection of Table 6 shows that the convergence of $E_{exch}^{(1)}$ as a power series in W is actually faster than it was the case for four-electron systems. The values of higher order terms included in $\Delta_{exch}^{(1)}(CCSD)$ are only about 10% of $\epsilon_{exch}^{(1)}(CCSD)$. Nevertheless, in accurate calculations the use of the CCSD approach will be necessary. The iterations of the CCSD equations[361] for the monomers add somewhat to the total time of calculation, but when the CCSD cluster amplitudes are available, the calculation of the $\epsilon_{exch}^{(1)}(CCSD)$ correction is computationally equivalent to the calculation of $E_{exch}^{(12)}$. For He₂ and He−HF $E_{exch}^{(11)}$ is smaller than $E_{exch}^{(12)}$ while for other systems the two corrections are of the same order of magnitude. This behavior does not indicate a divergence of the many-body perturbation series but is related to the fact that $E_{pol}^{(11)}$ vanishes due to the Brillouin theorem.

3. Induction Energy

Until recently studies of the intramonomer correlation effect on the energy of induction interactions were restricted to large distances, where the use of the multipole expansion of the intermolecular interaction operator is legitimate. In this region the importance of the correlation contributions to the induction energy could be assessed by comparing the Hartree−Fock and correlated multipole moments and polarizabilities of monomers. Such a comparison[363−365] indicates that the effect of the intramonomer correlation on the induction energy may be important. Recently, a general form of the many-body perturbation expansion for the induction energy based on eq 19 has been introduced.[74] Similarly as in the case of the electrostatic energy two types of such expansions were introduced: the *nonrelaxed* one based on the standard Møller−Plesset expansion of the electron densities and polarization propagators,[354,366] and the *relaxed* one based on the relaxed expansions of the electron densities and polarization propagators.[110−112,355] The corrections computed using the former scheme will be simply denoted by $E_{ind}^{(2l)}$, while the latter ones will be denoted by $E_{ind,resp}^{(2l)}$. The long-range behavior of the corrections $E_{ind}^{(2l)}$ and $E_{ind,resp}^{(2l)}$ can be obtained in an analogous way to that discussed before for the electrostatic energies.

Each correction $E_{ind}^{(2l)}$ can be decomposed as

$$E_{ind}^{(2l)} = {}^{a}E_{ind}^{(2l)} + {}^{t}E_{ind}^{(2l)} \quad (127)$$

where ${}^{a}E_{ind}^{(2l)}$ and ${}^{t}E_{ind}^{(2l)}$ denote the so-called "appar-

Table 7. Convergence of the Many-Body Perturbation Expansions for the Induction Energy of the He–K$^+$, He–F$^-$, (H$_2$O)$_2$, and He–HCl Systems^a

	He–K$^{+\ b}$	He–F$^{-\ c}$	(H$_2$O)$_2{}^d$	He–HCl^e
$E_{\text{ind,resp}}^{(20)}$	−0.9375	−0.5625	−3.4629	−0.0363
$E_{\text{ind,resp}}^{(22)}$	−0.0419	−0.0560	−0.9531	−0.0008

^{a} Energies are in mhartree. For details of calculations, see refs 74 and 93. ^{b} R = 5.4 bohr. ^{c} R = 6.0 bohr. ^{d} The equilibrium geometry from ref 370. The distance between the O atoms is 5.66918 bohr. ^{e} Linear He–HCl geometry. The distance between the He atom and the center of mass of HCl is 7.5 bohr while the H–Cl distance is 2.40940 bohr.

ent"and "true" correlation contributions to the induction energy.[119] The apparent correlation contribution is defined rigorously as that part of the induction energy which can be computed using the RPA propagator. It can be represented diagrammatically by a set of linear diagrams without rings,[367] while the diagrammatic representation of the true correlation contribution involves at least one ring. Tuan et al.[343] have proved that $E_{\text{ind}}^{(21)} = {}^a E_{\text{ind}}^{(21)}$, which shows that the leading-order contribution to the induction–correlation energy can hardly be considered as a correlation effect. By definition the zeroth-order term in the relaxed many-body perturbation expansion of the induction energy sums up to infinity all apparent contributions of eq 127

$$E_{\text{ind,resp}}^{(20)} = \sum_{l=0}^{\infty} {}^a E_{\text{ind}}^{(2l)} \tag{128}$$

Thus, a large part of the intramonomer correlation contribution to $E_{\text{ind}}^{(2)}$ with respect to W is already included in the first term of the relaxed expansion, $E_{\text{ind,resp}}^{(20)}$. Note also that $E_{\text{ind,resp}}^{(20)}$ is fully included in the Hartree–Fock interaction energy.[119,174,368,369] Clearly, the induction–correlation energy

$$\epsilon_{\text{ind,resp}}^{(2)} = E_{\text{ind}}^{(2)} - E_{\text{ind,resp}}^{(20)} \tag{129}$$

is a more appropriate representation of the intramonomer correlation effects in the induction component than $\epsilon_{\text{ind}}^{(2)} = E_{\text{ind}}^{(2)} - E_{\text{ind}}^{(20)}$. The leading-order term in the relaxed many-body expansion of $E_{\text{ind}}^{(2)}$ is the $E_{\text{ind,resp}}^{(22)}$ correction since the first-order correction $E_{\text{ind,resp}}^{(21)}$ vanishes on account of the Brillouin theorem.

In Table 7 results of perturbative calculation of the induction energy through the second-order in $\tilde{W}$ are presented for several representative van der Waals complexes: a rare gas atom and an ion, He–K$^+$ and He–F$^-$, two polar molecules, (H$_2$O)$_2$, and a rare gas atom and a polar molecule, He–HCl. In these systems the induction contribution plays a varying role, from the dominant one in the complexes of rare gas atoms and ions, to a significant one in the complexes of rare gases and polar molecules. The ratios of the $E_{\text{ind,resp}}^{(22)}$ contribution to the $E_{\text{ind,resp}}^{(20)}$ term depend strongly on the system studied and can be related to the correlation effect on the polarizability. The induction–correlation term is completely negligible in the interaction of rare gas atoms with nonpolar molecules, so small that for such systems $E_{\text{ind,resp}}^{(22)}$ does not need to be computed unless a very

high accuracy is needed. For interactions of rare gas atoms with polar molecules the induction–correlation can be significant as examplified by the results for the Ar–HF molecule discussed in more detail in section VII.E.3. For the He–F$^-$ system, the induction–correlation contribution is very important: it represents about 10% of $E_{\text{ind,resp}}^{(20)}$ in the minimum region. This is partly due to the fact that in the interactions involving negative ions a partial electronic transfer from the anion toward an atom or molecule may occur. The discussed effect is even larger in interactions of polar molecules. For the water dimer in the region of the van der Waals minimum $E_{\text{ind,resp}}^{(22)}$ represents as much as 30% of the uncorrelated result. Thus, in this case even higher-order (in correlation) terms may be quite important.

4. Dispersion Energy

The dispersion energy always constitutes a significant part of the interaction energy. For interactions involving a nonpolar molecule the dispersion interaction is the dominant attractive component of the interaction energy. Therefore the effects of intramonomer correlation in the dispersion energy deserve special attention. Early calculations for the He dimer[65] have shown that already the first term in the many-body expansion of the dispersion energy, $E_{\text{disp}}^{(21)}$, reproduces a large part of the intramonomer correlation contribution to $E_{\text{disp}}^{(2)}$. The expansion of the dispersion energy in terms of the intramonomer correlation operator W can be obtained by using the explicitly connected formulation of polarization theory discussed in section VI.A. Rybak et al.[11] derived orbital expressions for the corrections $E_{\text{disp}}^{(2l)}$ for $l \leq 2$ and computed these corrections for the water and hydrogen fluoride dimers. For these systems the correction $E_{\text{disp}}^{(22)}$ turned out to be important, in some cases even larger than $E_{\text{disp}}^{(21)}$.[11,69]

The multipole representation of the corrections $E_{\text{disp}}^{(2n)}$ can be obtained by utilizing the standard Møller–Plesset expansions of the dynamic polarizabilities. The relevant long-range dispersion coefficients are given by the Casimir–Polder integral (eq 83) with exact polarizabilities replaced by their kth- and lth-order correlation corrections in the Møller–Plesset series with $k + l = n$. Recently, Wormer et al.[48,270–272] developed a diagrammatic many-body perturbation theory of the correlation effects on dynamic polarizabilities and a general scheme for calculations of correlated long-range dispersion coefficients. The long-range dispersion coefficients corresponding the sum $E_{\text{disp}}^{(20)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)}$ can now be routinely computed using the Polcor package developed by Wormer and Hettema.[48,272] [Note, however, that the so-called exclusion principle violating diagrams must not be included, i.e., the scheme A of ref 48 must be used.]

The dispersion energy can alternatively be computed using the expression of eq 23 involving the polarization propagators. A many-body perturbation expansion of the polarization propagator provides the consecutive corrections $E_{\text{disp}}^{(2l)}$. Jaszunski and McWeeny[320] argued that eq 23 represents an advantage relative to conventional techniques[11,132] since the polarization propagators for the isolated monomers

Table 8. Convergence of the Many-Body Perturbation Expansions of the Dispersion Energy for the He$_2$, (H$_2$)$_2$, and (HF)$_2$ Systems[a]

	He$_2$[b]	(H$_2$)$_2$[c]	(HF)$_2$[d]
$E_{disp}^{(20)}$	−0.0490	−0.9098	−1.8525
$E_{disp}^{(21)}$	−0.0091	−0.0913	0.0406
$E_{disp}^{(22)}$ (RA)	−0.0017	−0.0486	−0.1078
$E_{disp}^{(22)}$	−0.0042	−0.3816	−0.4003
$E_{disp}^{(2)}$ (2)	−0.0623	−1.3827	−2.2122
$\sum_{i=3}^{\infty} E_{disp}^{(2i)}$ (RA)	−0.0004	0.0087	−0.0078

[a] Energies are in mhartree. For details of calculations, see ref 71. [b] R = 5.6 bohr. [c] Linear HH−HH geometry. The distance between the centers of mass of H$_2$ is 6.5 bohr while the H−H distance is 1.4 bohr. [d] Nonlinear geometry from ref 11.

can be computed once and the calculations of the dispersion energy at various geometries would require only a recalculation of two-electron integrals and repeated applications of eq 23. This advantage is only apparent, however, since accurate calculations of dispersion energies require the use of dimer-centered basis sets, which means that the polarization propagator would have to be recomputed at each geometry.

Recently much attention has been paid[159,160,311,320,356] to that part of the dispersion energy which behaves at large R as C_6^{RPA}/R^6, where C_6^{RPA} is the long-range dispersion coefficient corresponding to the use of the random-phase approximation (RPA) polarizabilities in eq 83.[260,261,264] Since this part of $E_{disp}^{(2)}$ is the sum of ring diagrams,[71] it has also been referred to as the dispersion energy in the *ring approximation* (RA), and denoted accordingly by $E_{disp}^{(2)}$(RA). The dispersion energy in the ring approximation can be obtained in an order-by-order summation of contributions of ring diagrams to $E_{disp}^{(2l)}$ [71] (these contributions will be denoted as $E_{disp}^{(2l)}$(RA)), by the use of the RPA polarization propagators in eq 23,[320,356] or by the use of coupled-cluster equations derived in ref 71. Jaszunski and McWeeny[320] suggested that $E_{disp}^{(2)}$(RA) may be a significantly better approximation to the exact dispersion energy than the zeroth-order term $E_{disp}^{(20)}$. Further studies by Cybulski[356] have shown, however, that for many van der Waals complexes the dispersion energy in the ring approximation is not a considerable improvement over $E_{disp}^{(20)}$.

The convergence of the many-body series for the dispersion energy has been studied already some time ago but only for the He$_2$ system[67] or at large intermonomer distances[262] where the use of the multipole expansion of V is legitimate. Results obtained from a more recent work[71] are shown in Table 8 where dispersion energies through second order in W are presented for the He, H$_2$, and HF dimers. Also included in this table are the sum of the series truncated at the second order, $E_{disp}^{(2)}$(2), and the sum of terms $E_{disp}^{(2l)}$(RA) with $l \geq 3$. These results show that the convergence of the many-body expansion is relatively fast. The sum of third and higher-order terms $E_{disp}^{(2l)}$(RA) is indeed very small compared to the sum of the series through the second order. On the other hand, the contribution of diagrams of more complex topologies, *i.e.*, the difference

$E_{disp}^{(22)} − E_{disp}^{(22)}$(RA), turns out to be very important, and it remains to be seen whether the higher order contributions from these diagrams are also significant. These results show that the inclusion of ring diagrams through the second order in W reproduces 99% of the exact value of $E_{disp}^{(2)}$(RA). Such a second-order calculation is much simpler since it does not require solving RPA equations or iterating coupled-cluster equations.

VII. Applications

The first applications of SAPT to systems larger than H$_2$ appeared in the 1970s. Initially interactions of "Hartree−Fock" molecules were considered, *i.e.*, all intramolecular correlation effects were neglected. These effects were included in calculations for small atoms at the end of 1970s and for general systems at the end of 1980s. The many-body SAPT codes performing such calculations are available through the METECC-94 project.[371] These codes include terms up to the second-order in the intermolecular interaction operator. The order with respect to the intramolecular correlation operator depends on particular type of interaction and some effects include even terms of the fourth order (for electrostatic interaction) or infinite CCSD-type summations. The list of the corrections programed so far is given in Table 9. Below we will present a discussion of recent applications of many-body SAPT. We will compare the potential energy surfaces to empirical ones as well as to supermolecular calculations when available. Since recently the SAPT potentials have been used to compute directly measured quantities. This most unambiguous test of the quality of intermolecular potentials is now available for SAPT and will be discussed below. In this section we will also briefly mention some approaches of approximate nature which are based on ideas of SAPT.

A. Accuracy of Potentials Computed by Many-Body SAPT

An important aspect of a theoretical result is the possibility of providing a reliable estimation of its accuracy. Before we start a discussion of applications of SAPT, let us briefly elaborate on how it is possible to get such estimations for this theory. The error of truncation of the double SAPT expansion has already been discussed in sections III and VI. The conclusion—drawn from calculations on few-electron systems and from asymptotic analysis—is that we may expect errors of the order of a few percent from this source. Moreover, for some of the energy terms infinite-order (in W) summations in the spirit of CCSD method have been developed.[12,71,73] In the majority of calculations a more important source of error will be that resulting from incompleteness of orbital basis sets. Since each term in the SAPT expansion can be computed separately using a basis set designed specifically for this term, this source of error can be conveniently investigated on a term by term basis. This feature turns out to be important since the basis set convergence patterns do depend to a large extent on the type of interaction considered. It follows that the use of a single orbital basis set for all corrections may not lead to an optimal conver-

Table 9. List of the Many-Body SAPT Corrections Developed to Date[a]

symbol	name	physical interpretation
$E_{pol}^{(10)}$	electrostatic energy	accounts for damped electrostatic interactions of Hartree−Fock permanent electric multipole moments of the monomers
$E_{pol}^{(1l)}$ l=2,3,4	intramonomer correlation corrections to electrostatic energy	account for damped electrostatic interaction of correlated multipole moments of the monomers; contain correlation effects of the lth-order in W
$E_{exch}^{(10)}$	exchange repulsion	results from exchange of electrons (quantum mechanical tunneling) between unperturbed monomers described at the Hartree−Fock level
$E_{exch}^{(1l)}$ l=1,2	intramonomer correlation corrections to exchange repulsion	account for the effects of the intramonomer correlation (of the lth order in W) on the exchange repulsion
$E_{ind}^{(20)}$	induction energy	originates from the damped interactions between the permanent and induced multipole moments obtained at the Hartree−Fock approximation
$E_{ind}^{(22)}$	intramonomer correlation correction to induction energy	accounts for the damped interactions between correlated permanent and induced multipole moments
$E_{exch-ind}^{(20)}$	exchange−induction energy	additional exchange repulsion due to the coupling of electron exchange and the induction interaction in zeroth order with respect to W
$E_{disp}^{(20)}$	dispersion energy	originates from damped interactions of *instantaneous* electric multipole moments of the monomers described at the Hartree−Fock approximation
$E_{disp}^{(2l)}$ l=1,2	intramonomer correlation correction to dispersion energy	intramonomer correlation correction (of the lth order in W) to the dispersion energy; originates from the coupling of the intramonomer correlation effects and the intermolecular dispersion interaction
$E_{exch-disp}^{(20)}$	exchange−dispersion energy	additional exchange repulsion due to the coupling of electron exchange and the dispersion interaction in zeroth order with respect to W

[a] The superscripts n and l in $E^{(nl)}$ denote the orders of perturbation in V and W, respectively. Most of the electrostatic and induction corrections have been programed in both the regular and response versions. Some corrections are available in CCSD versions, see text.

gence with the number of orbitals. Also it so happens that the terms least rapidly converging are at the same time computationally least demanding, which allows one to compute them with very large basis sets leading to reliable final results. In contrast, it is very difficult to estimate accuracy of supermolecular calculations. Since the supermolecular approach provides only the total interaction energy which is usually a rather small sum of large components, small relative changes of those components may change the interaction energy quite significantly. The basis set superposition errors can often "make up" for deficiencies of the method and of the basis set and lead to fortuitous agreement with experiment. Subsequent improvements of the basis set or the method may as well increase as decrease the agreement with experiment.

Applications of SAPT at the highest coded level of theory have been performed for several representative systems. These systems include dimers bound mainly by dispersion forces like those of rare gas atoms or the Ar−H_2 molecule, systems dominated by the induction interaction like He−K^+, and systems where electrostatic effects play a leading role like the water dimer. Most SAPT calculations have been performed for systems for which large amounts of experimental data are available (in particular data sensitive to intermolecular potentials, such as ion mobilities, diffusion coefficients, near- and far-infrared transition energies, and lifetimes for excited rovibrational states) and for which accurate empirical potentials exist. Of particular interest for testing the many-body SAPT are experimental results sensitive to anisotropies of the potential energy surfaces and to many regions of the potentials (short range *vs* the van der Waals minimum region).

B. Approximate Implementations of SAPT

There exists several methods of calculating intermolecular interactions which can be viewed as approximations to SAPT. The most popular is the so-called Hartree−Fock plus dispersion (HFD) model.[372] This approach first calculates the Hartree−Fock interaction energy which, as discussed elsewhere in this review, can be viewed as a quantity summing several lowest SAPT corrections.[174,369] Since SCF calculations are much faster than correlated ones, large basis sets can be used making the basis set superposition effects relatively unimportant. This energy is then supplemented by the dispersion energy which is usually calculated from the asymptotic expansion with some damping function. Since damping is introduced in a more or less arbitrary manner, such method should be viewed as a heuristic model of intermolecular interactions. The dispersion energy can also be easily included in a nonempirical way by computing the $E_{disp}^{(20)}$ correction. The exchange quenching of the dispersion energy can be included by computing $E_{exch-disp}^{(20)}$.[185]

The accuracy of the HFD model can be now assessed using the results of recent extensive SAPT calculations. The model neglects all the effects of the intramonomer correlation on the first-order interaction energy. As discussed in section VI, these effects typically give contributions of the order of 10 to 20 percent of the interaction energy. In the second-order semiempirical treatment the main source of error is due to *ad hoc* assumptions in construction of the damping functions. This error is very difficult to estimate. The asymptotic coefficients, on the other hand, can often be quite accurate and include high-level intramonomer correlation effects. For small systems the leading coefficients can be obtained

semiempirically.[277-297] Recently it has become possible to compute these coefficients by many-body methods developed by Wormer et al.[48,269-272]

A somewhat different method has been recently applied to interactions of several systems by the Nijmegen group.[226,249,373-375] In this method the first-order polarization and exchange energies are computed at the Hartree–Fock level, i.e., including only the correction $E^{(10)}$. The induction and dispersion effects are taken into account by using damped asymptotic expansions. An important advantage of this method is its computational efficiency. A calculation of $E^{(10)}$ is much faster than a calculation of E_{int}^{HF}. In addition $E^{(10)}$ was calculated in monomer-centered basis sets which leads to further computational savings (but may introduce significant errors resulting from too fast decay of the tails of wave functions). Calculations of the dispersion and induction energies from asymptotic expansions are also computationally relatively undemanding since each such calculation involves only one monomer at a time and has to be done just once. The consecutive computation of the values of the dispersion or induction energies at particular geometries requires only a calculation of Wigner's D functions defined in section IV. In the work of the Nijmegen group the long-range coefficients have been calculated using the many-body method of Wormer et al.[48,269-272] The damping parameter in the generalized Tang-Toennies[307] damping functions was set equal to the value of the exponent from the Born–Mayer fit to $E^{(10)}$. The replacement of E_{int}^{HF} by $E^{(10)}$ plus the damped asymptotic induction is a very reasonable idea. Although the results are somewhat less accurate than in the HFD model, this loss of accuracy is insignificant compared to the important effects neglected by both models, while computational saving are significant. Because of the small computational demands of this method, the authors have been able to compute complete potential energy surfaces including some variations of molecular coordinates for N_2–N_2,[373] CO–CO,[374] Ar–H_2O,[249] and Ar–NH_3[375] (e.g., for Ar–NH_3 calculations have been performed for four different HNH "umbrella" angles of ammonia). The analytical potentials obtained for N_2–N_2 and CO–CO have been successfully applied to compute transport properties and in studies of dynamics of molecular crystals (see refs 376 and 377, respectively, for a review of those two applications). Several of the potentials computed by this group have been applied in dynamical calculations of the rovibrational levels of the investigated systems.[378-383] (See also ref 384 for a summary of these results.)

C. Dimers of Rare Gas Atoms

Rare gas dimers are the simplest van der Waals molecules and several ab initio SAPT potentials at various levels of approximation have been computed for these systems. Except for the He dimer, all other dimers have been observed in UV and/or Raman spectra. A detailed discussion of the spectroscopy of these molecules can be found in ref 19. For a long time there were speculations that the He–He potential does support a single bound state but no experimental evidence for the existence of He_2 molecule was available. Very recently, however, the helium dimer has been indirectly detected[385-387] in experiments involving electron impact ionization of a supersonic beam of helium gas at very low temperatures. The analysis of the experimental data revealed that the He_2^+ ions detected in a mass spectrometer can arise only from the ionization of the neutral He_2 molecule.

The helium dimer has been traditionally the most often theoretically studied system due to its simplicity and availability of very accurate empirical potentials for comparison. The first large-scale SAPT calculation was that of ref 65, later improved upon in refs 68, 67, and 327. Recently all presently coded many-body SAPT corrections have been computed for this system.[388] These results, together with the previously computed limits of some corrections in (explicitly correlated) Gaussian geminal basis sets,[68,327] provide the potential energy curve with the minimum depth of 10.86 K[388] which compares very well with the best empirical value of 10.97 K.[389] The SAPT results are also in very good agreement with the supermolecular results of Vos et al.[390] obtained by using the multireference CI method, and with those from quantum Monte Carlo calculations.[391]

Several calculations of ab initio SAPT intermolecular interaction energies between the "Hartree–Fock" rare gas atoms have been published by Chalasinski et al. In refs 392 and 393 the potential energy curve for Ne_2 interaction has been computed using large spdfgh orbital basis sets. Since the exchange-correlation effects seem to be large for Ne_2, the potential of Chalasinski et al. had the minimum about 12% too deep and shifted to smaller R by about 0.5 bohr compared to the accurate semiempirical potential of Aziz et al.[394] The other reason for the discrepancy could be the use of a nonstandard expression for $E_{disp}^{(20)}$, with the Møller–Plesset denominators replaced by the so-called Epstein–Nesbet ones.

D. Interactions of Rare Gas Atoms with Ions

The mobilities of ions moving through a dilute neutral gas under the influence of an externally applied electric field are closely related to the interaction potential in the region of the potential well.[395-397] In principle the atom–ion potentials can be obtained by a direct inversion of the ion transport data which does not require arbitrary assumptions about the analytic form of the interaction potential. Using the rigorous kinetic theory of ion mobilities in gases[398] one can determine directly the numerical values of the interaction energies for a wide range of internuclear distances. In this way the interaction potentials for all alkali ion–rare gas atom[399,400] and halide ion–rare gas atom[401] complexes have been obtained. The correctness of these potentials depends critically on the accuracy of the (experimental) transport data, but at present reliable mobility data are available for several ion–atom combinations.[402]

Recently an ab initio SAPT potential for the He–K^+ system has been computed.[93] It agrees very well with the mobility-derived potential of Viehland[400] obtained by inversion of gaseous ion mobility data (typical errors are 2% in the repulsive region, 0.5% at the van der Waals minimum, and 1% in the attractive region). In particular, the minimum depth has been found to be equal to 170.9 cm^{-1} while the

empirical potential[400] predicts 169.9 cm^{-1}. The SAPT potential has been applied in simulations of K$^+$ mobilities and diffusion coefficients in the He gas providing results supporting one set of experimental observables over another. (See ref 93 for details.) This is the first time that a theoretical potential achieved such a level of predictability.

Similar application of the many-body SAPT approach has been recently reported for the He$-$Na$^+$ system.[403] The calculations of the transport coefficients for the Na$^+$ ions in the He gas have shown that the SAPT potential for this system predicted the mobility and diffusion data with an accuracy comparable to that of a semiempirical potential[404] obtained by fitting the mobility-derived potential of ref 400 to a functional form.

Other atom$-$ion interaction potential computed recently by many-body SAPT is the He$-$F$^-$ potential.[405] In this case the mobility-derived potential[401] is known only in the highly repulsive region. Two semiempirical potentials for this system have been reported in the literature.[404,406] Koutselos et al.[404] constructed a model potential by approximating its long-range part by the sum of induction and dispersion energies calculated using the HFD model,[372] and representing the remaining short-range part, derived from the empirical potential,[401] with a suitably scaled "universal" function describing the exchange interaction of the halide ion$-$rare gas atom system. The semiempirical potential of Ahlrichs et al.[406] can be viewed as an extension of the Tang$-$Toennies model,[307] originally developed for interactions of rare gas atoms. The SAPT potential agrees well with the supermolecular results of Diercksen and Sadlej[407,408] computed at the MBPT4 level (MBPTn will always denote the *supermolecular* MBPT calculation through the nth order based on the Møller$-$Plesset partitioning of the dimer Hamiltonian) and corrected for the basis set superposition error using the Boys$-$Bernardi counterpoise correction.[32] The depths of all *ab initio* potentials for this system[405,407,408] are much smaller than those predicted by the semiempirical potentials. The reasons for the discrepancy between the SAPT potential and the semiempirical potential of Ahlrichs et al.[406] have been later traced down[405,409] as due to an incorrect theoretical input, while the lack of agreement with the model of Koutselos et al.[404] is probably due to an incorrect extrapolation from the repulsive region to the region of the van der Waals minimum.[405] The supermolecular MBPT series which usually seems to converge relatively fast behaves for He$-$F$^-$ in a rather erratic way.[407,408] This convergence pattern has been rationalized by the SAPT results.[405] Recently Chalasinski and Szczesniak[31] have shown that the CCSD(T) contribution beyond the fourth order of MBPT increases the depth in the minimum by as much as 24%. It remains to be seen if this increase can be related to the contribution from CCSD-type summations of the induction and dispersion energies.

E. Interactions of Rare Gas Atoms with Molecules

Since the nuclear dynamics calculations for atom$-$small molecule systems can be presently performed in a virtually exact way,[24] the empirical potentials fitted to spectroscopic and scattering measurements are free from uncertainties related to dynamical part of the inversion procedure. The empirical intermolecular potentials for Ar$-$H$_2$, He$-$HF, and Ar$-$HF, discussed in this subsection, are based on a large amount of high-resolution spectroscopic data and are believed to be very accurate. These potentials present a very challenging test for theory. For argon$-$ammonia and argon$-$water systems the number of parameters in empirical potentials is not much smaller than the number of measured transitions, so that the resulting potentials may be somewhat less accurate. Since only an approximate version of SAPT has been applied to these systems thus far, the accuracy of the obtained theoretical potentials is also lower than the accuracy of the potentials computed for atom$-$diatom systems.

1. Ar$-$H$_2$

The most elaborate application of many-body SAPT was that to the Ar$-$H$_2$ interaction[91] where the complete potential energy surface (including the variation of the H$-$H distance) was computed using spdfg-quality basis sets. The Ar$-$H$_2$ van der Waals molecule is one of the most thoroughly investigated atom$-$diatom complexes, and the empirical potential energy surface for this system is probably the most accurately determined of any atom$-$diatom potentials. Using the high-resolution near-infrared spectra,[410] hyperfine spectra,[411] and molecular beam differential cross sections,[412] Le Roy and Hutson[413] determined a multiproperty fitted potential for Ar$-$H$_2$. Their final potential reproduced the results of all the measurements to within the experimental error bars, including some data not utilized in the fit. The comparison of the SAPT and empirical potentials is presented in Figure 5. As one may see the agreement is excellent. In fact, the agreement is uniform in the whole configuration space, including angular variation and the variation of the H$-$H distance. The positions of minima agree to 0.03 bohr and the depths are 164.7 and 161.9 cal/mol for the SAPT and empirical potentials, respectively. For the first time such an agreement has been reached between theory and experiment for a system that large.

More recently Schwenke et al.[414] computed the complete (including a variation of the H$-$H distance) potential energy surface for Ar$-$H$_2$ using a large spdf basis set and the averaged coupled-pair functional method. These authors have used a variant of the Boys$-$Bernardi counterpoise method (with an additional correction aimed at partially remedying the size nonextensivity of their method). At the region near the van der Waals minimum their fitted potential energy surface is significantly above the Le Roy and Hutson results$-$the minimum depth is only 67% of the empirical depth. Thus, the authors had to resort to an empirical scaling of their potential. They have attributed the problem to the inadequacy of the orbital basis set. However, their basis was relatively large and most likely deficiencies of the method (such as incomplete account of multiple electron excitations, size nonextensivity, and the basis set superposition effects) are responsible for a large part of this disagreement.
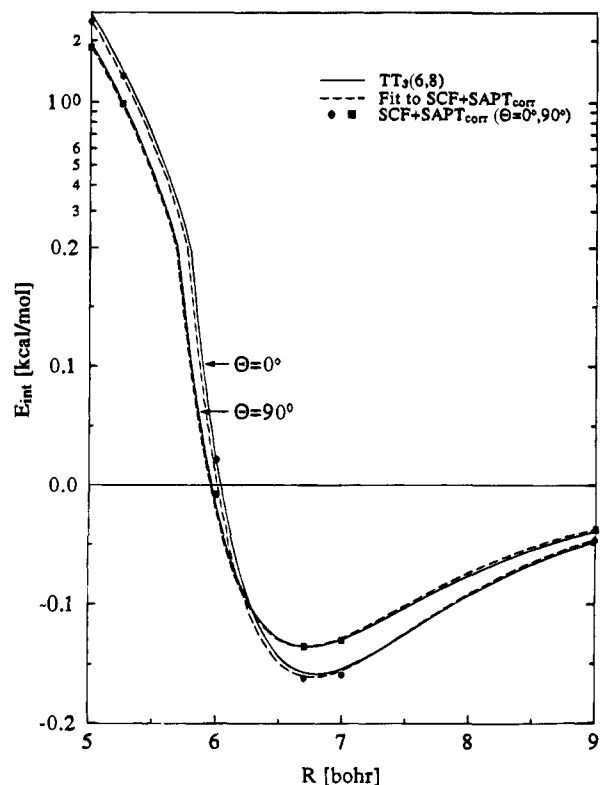
Figure 5. Comparison of computed interaction energies for $Ar-H_2$ (broken line) with the empirical $TT_3(6,8)$ potential of Le Roy and Hutson (solid line).[413] The energies are shown as functions of R for $\theta = 0°$ and 90° and for $r_{H-H} = 1.4$ bohr.

The SAPT potential[91] has recently been applied in dynamical calculations of the rovibrational energy levels of $Ar-H_2$ and $Ar-D_2$.[415] It reproduced very accurately transition frequencies for all the measured bands in the near- and far-infrared:[410,416] typical errors are of the order of 0.1 cm^{-1} (see also ref 384 for a discussion of dynamical calculations). This very good agreement between the results of *ab initio* calculations[415] and high-resolution measurements[410,416] show that SAPT calculations correctly account not only the dominant isotropic part of the true interaction potential, but also its dependence on the diatom stretching distance and small anisotropic terms.

2. He–HF

The He–HF complex is very weakly bound and it was investigated mainly using scattering techniques.[417,418] Only recently Lovejoy and Nesbitt[419] reported the first spectroscopic study of the high-resolution near-infrared vibration–rotation spectra corresponding to the simultaneous excitation of the vibration and rotation of HF within the He–HF complex. The broadening of the spectra due to rapid rotational predissociation of the system was also measured.

Many *ab initio* studies of the He–HF interaction have been reported in the literature[420,421] and the depths of the van der Waals minima predicted by these potentials range from 8 to 40 cm^{-1}. The most advanced of the *ab initio* potentials, developed by Rodwell *et al.*,[421] follows closely the HFD model[372] and neglects important intramonomer correlation effects. Lovejoy and Nesbitt[419] reported calculations of bound and quasibound rovibrational levels and of the line
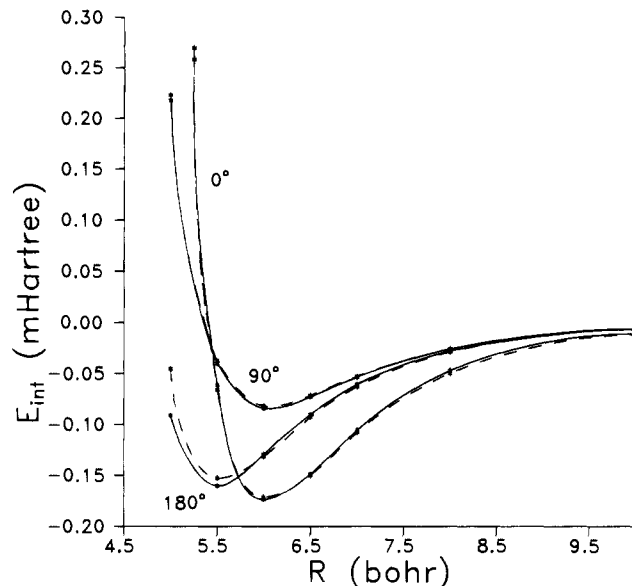

Figure 6. Comparison of computed interaction energies for He–HF (solid line) with the empirical potential of Lovejoy and Nesbitt[419] (dashed line). The energies are shown as functions of R for $\theta = 0°$, 90°, and 180°, and for $r_{H-F} = 1.7328$ bohr.

widths using the *ab initio* potential of Rodwell *et al.*[421] Their results have shown that this potential reproduces the near-infrared spectrum of the complex rather poorly. However, by a simple scaling of the long-range dispersion coefficients in this potential Lovejoy and Nesbitt[419] were able to obtain an anisotropic potential energy surface which satisfactorily reproduced all spectroscopic data available for He–HF.

Recently, SAPT calculations were performed on the He–HF system.[92] In this work the potential has been computed for three H–F separations. Since only a basis set of spdf quality has been employed, the dispersion energy has been asymptotically scaled in the final potential. The idea of this asymptotic scaling of the dispersion energy was that the penetration part of the dispersion energy (*i.e.*, the short-range charge-overlap contributions to $E_{disp}^{(2)}$) are less sensitive to the quality of the basis set than the multipole part (*i.e.*, the long-range dispersion coefficients), provided that dimer-centered basis set is used in calculations. The scaling was then achieved by replacing the long-range dispersion coefficients $C_{n,disp}^l$ used in the functional fit to the computed dispersion energy (calculated in the same basis set as that used in the finite R calculations and at the same level of theory, *cf.* section VI) by the coefficients computed in a much larger basis. The scaled potential energy surface of ref 92 agrees very well with the HFD2-M1 empirical potential of Lovejoy and Nesbitt,[419] as shown in Figure 6. The depths of the two potentials are 39.68 and 39.20 cm^{-1}, respectively.

The SAPT potential has been subsequently used[422] in dynamical calculations of rovibrational energy levels of He–HF ($v = 0$) and He–HF ($v = 1$). For a detailed account of these calculations we refer the reader to the original paper[422] (see also ref 384 for a review of these results). The agreement between the results of high-resolution measurements[419] and *ab initio* calculations[422] was excellent: the SAPT potential energy surface[73] predicted all infrared transitions
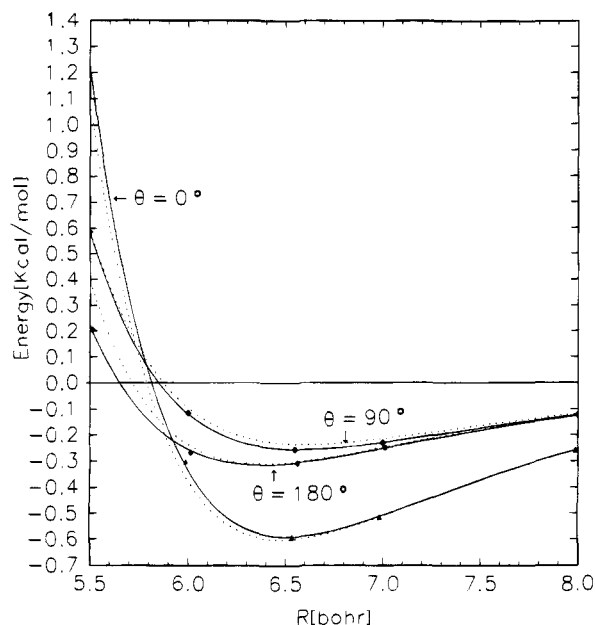
Figure 7. Comparison of computed interaction energies for Ar–HF (solid line) with the empirical potential of Hutson[423] (dashed line). The energies are shown as functions of R for $\theta = 0°$, 90°, and 180°, and for $r_{H-F} = 1.7328$ bohr.

with accuracy comparable to that of the empirical potential.[419] Absolute errors were always smaller than 0.1 cm^{-1}, and some transition energies were predicted even more accurately by the SAPT potential. The *ab initio* potential failed, however, to reproduce correctly the line widths. Minor scaling of the short-range contribution to the small $l = 1$ angular component of the potential was necessary to obtain agreement with the experimental data.[419] This scaling introduces, in fact, a very small change in the interaction potential: the depth of the van der Waals minimum was affected by only 2%.

3. Ar–HF

The Ar–HF molecule is also one of the most thoroughly investigated rare gas–hydrogen halide systems. Recently, Hutson[423] developed a complete potential energy surface for this system (including explicitly the dependence on the vibrational quantum number v of the HF monomer) by fitting extensive high-resolution microwave, near-infrared, and far-infrared spectra.[424] The resulting potential energy surface[423] has been recently thoroughly tested[425-428] and proven to be very accurate. The empirical potential predicted accurately new bands in the spectra[425,426] and reproduced correctly inelastic scattering cross sections[427] and pressure broadening and shifting coefficients.[428]

A SAPT calculation of the interaction potential for Ar–HF[94] (for a fixed H–F distance) has recently been completed. Also in this case the many-body SAPT potential is very close to the empirical potential of Hutson,[423] the differences being pronounced only in the short-range repulsive region (see Figure 7). The SAPT potential predicts a global minimum of $\epsilon_m = -207.3$ cm^{-1} at $R_m = 6.51$ bohr and a secondary minimum of $\epsilon_m = -110.1$ cm^{-1} at $R_m = 6.38$ bohr, in very good agreement with $\epsilon_m = -211.1$ cm^{-1} and $R_m = 6.50$ bohr for the primary minimum and $\epsilon_m = -108.8$ cm^{-1} and $R_m = 6.38$ bohr for the secondary

minimum as predicted by the empirical potential (at the equilibrium separation of HF). Taking into account the intramonomer correlation effects on the induction and exchange–induction energies was essential for achieving this agreement. The SAPT potential is now being tested in dynamical computations of transition energies in the far-infrared region.

Very recently, Chang et al.[426] reported an *ab initio* potential for this system computed using the supermolecular MBPT4 method corrected for the basis set superposition error using the Boys–Bernardi counterpoise correction.[32] Despite the use of spdf basis sets including bond functions, the depths of the predicted primary and secondary minima $\epsilon_m = -193.15$ cm^{-1} and about -90 cm^{-1}, respectively, differ somewhat from those obtained from the SAPT calculations[94] or from the empirical potential.

4. Ar–H$_2$O

The Ar–H$_2$O van der Waals molecule is considered to be a prototype of systems which exhibit hydrophobic interactions. Therefore, it attracted much attention of both experimentalists and theoreticians. High-resolution spectra in the microwave, near-infrared, and far-infrared regions have been measured for this system[429] and these data have been used to construct empirical potential energy surfaces. Hutson[430] reported a series of effective angular potentials. Cohen and Saykally determined a three-dimensional intermolecular potential[431] by fitting 9 parameters to 11 spectroscopic measurements. Very recently, these authors improved their potential and a new detailed potential energy surface has been obtained[432] by a direct nonlinear least square fit of 12 parameters to 37 spectroscopic measurements. Some parameters in the latter potential were fixed at their *ab initio* values from ref 249.

Chalasinski and collaborators[433] performed supermolecular MBPT2 calculations of two cuts through the potential energy surface using an spd basis set. In addition, for two points these authors reported supermolecular MBPT4 results in spdf basis sets. The anisotropy of the interaction energy at the Hartree–Fock and correlated MBPT2 levels of theory was interpreted using low-level SAPT corrections: $E_{pol}^{(10)}$, $E_{exch}^{(10)}$, and $E_{ind,resp}^{(20)}$ at the Hartree–Fock level, $E_{pol,resp}^{(12)}$ and $E_{disp}^{(20)}$ at the correlated MBPT2 level, and $E_{disp}^{(21)}$ at MBPT3 level. Since several important SAPT corrections have been neglected, the agreement between the SAPT and MBPT results is only qualitative. The minimum depth obtained by Chalasinski et al. at the MBPT4 level of theory in spdf basis is 108 cm^{-1} which can be compared to the value of 158 cm^{-1} computed by Bulski et al.[249] Empirical estimation of this quantity is 142.98 cm^{-1}.[432] All potentials have the minima at the planar geometries. The most striking difference between the empirical potential[432] and the potential of Bulski et al.[249] is that the former potential obtains the equilibrium geometry close to the nonlinear hydrogen-bond configuration at $\theta = 106°$ (where $\theta = 0°$ corresponds to Ar on the O side), while the latter finds the minimum at $\theta = 50°$. The potential of Chalasinski et al. predicts an essentially flat minimum valley between $\theta = 70°$ and 120° (with varying R). The potential energy surface of Bulski et al.[249] has been tested in dynamical calculations of

the rovibrational energy levels.[434] See ref 384 for a discussion of these results.

5. Ar–NH₃

Similarly as for the Ar–H₂O complex, high-resolution spectra in the microwave and far-infrared region have been measured[435] for the Ar–NH₃ system. Recently, Schmuttenmaer *et al.*[276] determined a three-dimensional potential energy surface from a least square fit of 13 parameters to 61 spectroscopic measurements. Important ingredients in this potential were *ab initio* long-range induction and dispersion coefficients from ref 48.

Chalasinski *et al.*[436] reported two cuts through the potential energy surface of Ar–NH₃ computed using the supermolecular MBPT2 method and an spd basis set. Similarly as in the case of the Ar–H₂O interaction, the anisotropy of the interaction energy was interpreted in terms of low-level SAPT corrections. In addition, the interaction energy at the minimum was computed at the MBPT2 level of theory using an spdf basis set. Bulski *et al.*[375] in the work discussed above compared their results to those of ref 436. In general the agreement was reasonably good. The minimum depth found by Bulski *et al.* is larger by about 20% than that obtained by Chalasinski *et al.* which can be attributed mainly to a better basis set saturation of the dispersion energy and to the effects of intramonomer correlation included for this component in the former work. On the other hand, the result of Bulski *et al.* contains a hard to estimate inaccuracy resulting from the model damping functions. The depth of the potential of Bulski *et al.* is 134.2 cm⁻¹ which compares reasonably well with the empirical result of 147.0 cm⁻¹ from ref 276. Notice that if the $E_{\text{pol}}^{(12)}$ correction, computed by Chalasinski *et al.* to be equal to -7.2 cm⁻¹, were added to the minimum found by Bulski *et al.*, the agreement with experiment would improve quite significantly. van Bladel *et al.*[381-383] used the potential energy surface of Bulski *et al.*[375] to generate the infrared spectrum of the Ar–NH₃ complex. For a discussion of these results we refer the reader to the original papers[381-383] (see also ref 384 for a review).

F. Hydrogen-Bonded Dimers

The water dimer is a benchmark system for hydrogen-bonded interactions and an early version of SAPT has been applied to this system already in 1976.[132] More recently the Hartree–Fock plus $E_{\text{disp}}^{(20)}$ level of theory has been used in calculations with large orbital basis sets.[35] Hess *et al.*[437] computed the $E^{(10)}$ and $E^{(20)}$ corrections for the water dimer using spd basis sets. Notice that Hess *et al.* have not used the standard dimer-centered basis set in their work but a basis constructed in such a way that the occupied orbitals are expressed in monomer-centered basis functions only while the virtual orbitals extend over all centers. This choice leads to minor differences when compared to dimer-centered results. A higher level of SAPT was included in ref 11 where two cuts through the potential energy surface have been computed using spdf basis sets. The computed SAPT interaction energy at the minimum is -5.6 kcal/mol which agrees well with the experimental

estimate of -5.4 ± 0.7 kcal/mol[438] (based mainly on bulk properties). However, Rybak *et al.* were aware that some of the SAPT corrections not available at that time may change their theoretical result appreciably. These corrections were estimated by taking into account also the supermolecular results, and the final recommended minimum depth, arrived at in ref 11, was 4.7 ± 0.2 kcal/mol. All the presently coded SAPT corrections have recently been computed[358] for the water dimer providing in fact the same minimum depth as estimated by Rybak *et al.*[11] The results of SAPT are in agreement with recent very careful, large basis set supermolecular calculations of van Duijneveldt-van de Rijdt and van Duijneveldt[439] who estimated the water dimer binding energy at 4.7 ± 0.1 kcal/mol.

Reference 11 also presented a calculation of the interaction energy for the hydrogen fluoride dimer which gave the minimum depth of 4.85 kcal/mol. When the additional SAPT corrections estimated as in the case of the water dimer were added, the recommended value of the minimum depth was 4.2 ± 0.2 kcal/mol.[11] Recent calculations of these corrections gives the depth of 4.56 kcal/mol,[358] in excellent agreement with the empirical depth of 4.46 kcal/mol[440,441] obtained from spectroscopical data and quite likely accurate to all digits given. For a recent review of supermolecular results for this system see ref 442.

G. Interactions of Large Molecules

The many-body SAPT has also been applied to much large systems than discussed so far. At the $E_{\text{int}}^{\text{HF}}$ plus $E_{\text{disp}}^{(20)}$ level it was used to compute the potential energy surface for the nitromethane dimer.[443] Recently single-point calculations have been performed for the uracil–water complex[444] using a higher level of theory. The computed value of the interaction energy is in reasonable agreement with the empirical result of Sukhodub.[445]

VIII. Summary

We have reviewed here the present state of the perturbational theory of the intermolecular interactions phenomenon. The whole potential energy surface, from the short-range repulsive region to the long-range asymptotic regions, can be described by the currently developed level of symmetry-adapted perturbation theory. The presently available implementation of this theory at the second-order level with respect to the intermolecular interaction operator is capable of reproducing interaction energies with only few percent errors. This conclusion has been reached on the basis of extensive tests of the convergence properties of various formulation of SAPT on model systems: H₂⁺, H₂, and He₂. This work has first shown that the simplest polarization theory which uses wave functions of incorrect permutational symmetry cannot provide an adequate description of the potential energy surface, except for very large intermolecular separations. It has been further demonstrated that at least one of the variants of SAPT, the Hirschfelder–Silbey method, provides a well convergent expansion of the interaction energy. While the HS method is too complicated to be at present

practically applied to larger many-electron systems, a much simpler symmetrized Rayleigh–Schrödinger method is in low order practically equivalent to the HS method. In particular the differences between the two methods are negligible at the second order, *i.e.*, at the level of theory which can be practically computed for larger systems. Thus, the SRS theory takes a proper account of the electron exchange effects and it is the SRS method which has been programed and applied to many-electron systems.

The polarization expansion can be legitimately used at large intermolecular separations. It is usually applied then in conjunction with the multipole expansion of the interaction operator. This expansion simplifies the calculations significantly, allowing a construction of the long-range potentials utilizing only monomer-specific information. Actual values of the interaction energy are then obtained by a multiplication of the radial part by simple angular functions. The long-range constants can now be computed using many-body techniques closely related to those employed in many-body SAPT. Use of the data obtained from long-range multipole expansion results in significant savings of computer time since SAPT calculations need not be performed for larger R. The information from the asymptotic expansion is also utilized in the construction of the analytical potentials used to fit the computed points.

An important question in construction of analytical potentials is the form of the damping functions describing the charge-overlap effects, *i.e.*, accounting for the difference between the exact value of the polarization energy of a given order and the multipole approximation to it. A lot of effort has been invested in *ab initio* calculations of the damping functions. These calculations have shown that semiempirical accounts of damping are difficult since it is dependent on properties of interacting systems in a complicated way. Fortunately, recent experience has shown that in fitting the points computed *ab initio* by SAPT the standard form of the damping function (inferred from accurate results for H_2) is flexible enough.

The many-body perturbation expansion of the first- and second-order interaction energies is made with respect to the Møller–Plesset fluctuation potentials for monomers. This expansion is presently truncated at various orders, depending on a particular component. This truncation has been determined by analyzing the convergence patterns for several test systems. It is believed that the error introduced by this truncation is of similar magnitude as the error resulting from the truncation of the expansion in powers of the intermolecular interaction operator. It has been shown that inclusion of electron correlation is critical for almost all intermolecular interactions. In particular the hard-to-compute effects of intramonomer correlation on the dispersion and exchange energies are far from being negligible.

Actual calculations for systems of interest require dealing with the question of preparing orbital basis sets which would furnish reliable results at lowest computational cost. It has been found that the interaction energies converge with the number of basis functions even slower than the total correlation energies. Large basis sets containing up to g orbitals are needed to reach accuracies better than 10%.

Moreover, the orbital exponents optimal for calculations of interaction energy are somewhat different from those optimal for describing correlation effects within monomers which requires some extra effort on optimization of such orbitals. Proper computational strategies have been developed to make calculations of complete potential surfaces possible despite these significant computational demands.

At the first- and second-order (in V) level of theory the energy components computed by SAPT can be classified as describing the electrostatic, induction, dispersion, or exchange interactions. The relative contributions from these components change depending on the intermonomer separation. The relative contributions depend also on the type of the interacting systems and can be approximately related to monomer's properties, providing some guidance in understanding the shapes and depths of the potentials for various systems. SAPT calculations show that the form of potential energy surfaces for most regions and most systems results from a subtle balance of the four components. While computationally this fact means the necessity to calculate the components to a higher accuracy than it would otherwise be needed, it is this feature of intermolecular interactions which makes them so specific and selective that they can determine complicated structures and activity of biological systems.

In view of above observations the following remark can be made about supermolecular calculations. In the supermolecular approach all the components of the interaction energy included at a given level of theory have to be computed simultaneously. Therefore, there exists no method of investigating the basis set convergence of a given physical component of interaction energy, nor is there a possibility of computing the slowly convergent components in a larger basis set. Further, it is sometimes expected that if there existed a method of removing the basis set superposition error completely, the supermolecular method would give the exact interaction energy. This expectation clearly cannot be correct since even if the basis set superposition errors were removed, various interaction energy components would still be far from saturation even in relatively large size basis sets. Neither can it be true that once the basis set superposition error is removed, the supermolecular approach would give a potential energy surface parallel to the exact surface. Since the interaction energy results from a subtle balance of components of diverse radial and angular dependence, and each of those components is computed to a different degree of basis set saturation, uniform cancellation of these errors over the whole potential energy surface is highly improbable.

The many-body SAPT has been applied to quite a broad and diversified group of interacting systems. In all cases, except perhaps for very small systems, recent SAPT results (which include all components developed so far) are superior to any theoretical data available. These results match the accuracy of the best existing empirical potentials. Recently SAPT potentials have been used to compute the directly measured quantities such as the rovibrational spectra or ion mobilities. These results have already been used to guide experiments and more of such interac-

tion is expected in the near future. The SAPT method has already been applied to quite complex systems (like uracil–water) and more of such applications should appear soon, leading to a new reliable set of potentials for use in molecular dynamics simulations of biological systems.

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