# Weak Interactions between Small Systems. Models for Studying the Nature of Intermolecular Forces and Challenging Problems for ab Initio Calculations[†]

GRZEGORZ CHAŁASIŃSKI*,[‡] and MACIEJ GUTOWSKI[‡]

*Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland, and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112*

*Received November 4, 1987 (Revised Manuscript Received May 16, 1988)*

## Contents

## I. Introduction

The study of intermolecular forces is important for applications in many different branches of science. Crystallography, molecular biology, surface and colloid chemistry, molecular spectroscopy, molecular beam scattering, thermodynamics, and polymer science all benefit from knowledge as to the nature of intermolecular forces.

The foundations for a physical interpretation of intermolecular forces were laid in the first decades of this century.[1-5] Contributions to the interaction energy may be classified as having either a classical or quantum mechanical origin. It is important to distinguish between long-range (van der Waals) terms, vanishing as certain powers of $R^{-1}$ (where $R$ stands for the intermolecular separation), and short-range terms, which decay exponentially with $R$. Let us briefly recall the four most important contributions: the electrostatic, induction, dispersion, and exchange repulsion energies.

The electrostatic and induction energies are classical long-range contributions, first considered by Keesom[2] and Debye.[1] These terms are conceptually simple and are well described in standard physical chemistry textbooks.[6,7]

The dispersion energy, which was introduced by London,[3,4] has also the long-range character but requires a quantum mechanical interpretation. Most textbooks focus on the interpretation of the dispersion contributions as arising from the interaction of instantaneous induced multipole moments.[6,7] However, it is also im-

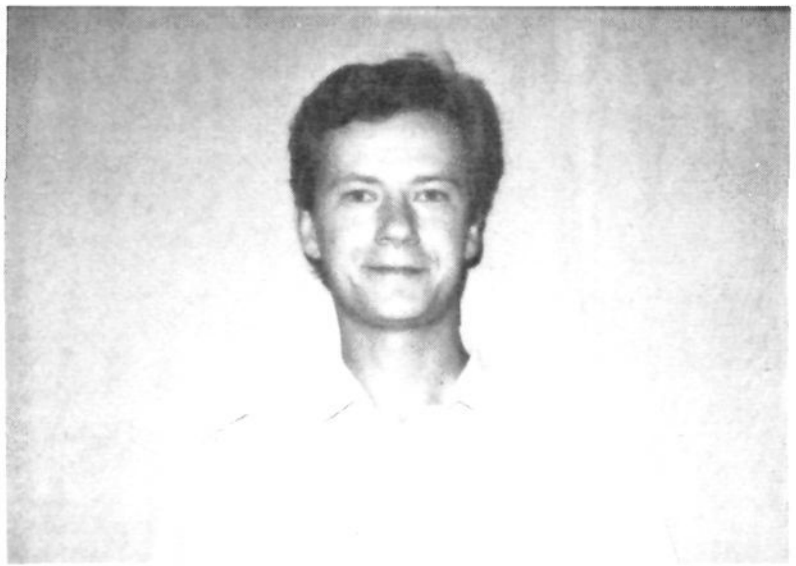
---

[†] Dedicated to Professor R. Zahradník on the occasion of his 60th birthday.

[‡] Permanent address: Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland.

0009-2665/88/0788-0943$06.50/0

Grzegorz Chałasiński was born in Warsaw, Poland, in 1948. He earned his M.S. degree in chemistry from the University of Warsaw in 1971. Since then he has been working in Wlodzimierz Kołos' group at the Department of Chemistry, University of Warsaw, where he collaborated closely with Bogumil Jeziorski. He received his Ph.D. degree in theoretical chemistry in 1977 for work on intermolecular interactions. In 1980 he spent one year as a visiting professor at the University of Utrecht collaborating with Frans van Duijneveldt. In 1985 he joined Jack Simons's group, Department of Chemistry, University of Utah, for two years. His research interests focus on ab initio investigations of intermolecular interactions.



Maciej Gutowski was born in Warsaw, Poland, in 1955. He received his M.S. degree in chemistry from the University of Warsaw in 1978. In 1979 he joined Wlodzimierz Kołos' group at the Department of Chemistry, University of Warsaw. He spent a brief period as a research associate with Frans van Duijneveldt at the University of Utrecht. In his research on intermolecular interactions and ionic crystals he collaborated closely with Grzegorz Chałasiński an Lucjan Piela. He earned his Ph.D. degree in theoretical chemistry from the University of Warsaw on exchange effects in intermolecular interactions. Recently, he joined the research group of Jack Simons at the Department of Chemistry, University of Utah. His research interests focus on ab initio investigations of intermolecular interactions.

portant to remember that the dispersion effect arises from the mutual correlation of electrons that belong to different monomers (intermonomer correlation effects).

Short-range effects appear because the electron clouds of the monomers penetrate each other and bring about charge overlap and exchange effects. Whereas charge overlap effects may be understood classically, the exchange effects originate from imposing the antisymmetry condition on the wave function of the whole complex. The antisymmetry principle forbids two electrons to have the same spatial and spin functions (Pauli exclusion principle). Therefore, when the monomer wave functions begin to overlap, the motion of the electrons becomes more constrained than in the isolated monomers. In the case of two closed-shell systems, which are of main interest to us in the context of weak interactions, this effect raises the energy of the complex and is often referred to as the exchange repulsion energy.

Eisenschitz and London[5] in 1930 were the first to show that the balance between long-range terms and the exchange repulsion energy leads to the appearance of the van der Waals minimum and is responsible for the shapes of potential energy curves. Since then the general interpretation of weak intermolecular interactions has not essentially changed. The main effort has been devoted to making this interpretation more rigorous and applicable to quantitative descriptions of intermolecular potential hypersurfaces. The ab initio studies of interactions between small monomers have been particularly useful in this respect because these systems may be treated at the highest level of theory and computational technology. The reason for such a highly accurate treatment is twofold. First, accurate calculations, unfeasible for larger systems, are necessary to enrich and refine our knowledge of the nature of intermolecular interactions. Second, they serve as standards to compare the results obtained by newly developed formalisms, both ab initio and semiempirical. Until the late 1970s accurate ab initio model studies of weak interactions were performed only on the ${}^2\Sigma_u^+$ state of $H_2^+$ ion and the ${}^3\Sigma_u$ state of $H_2$ molecule for which highly accurate potentials were calculated by Peek[8] and by Kołos and Wolniewicz,[9] respectively. The rapid development of computer technology over the past 10 years has made possible very advanced calculations of the interactions among slightly larger and more interesting monomers such as He, Be, $H_2$, $Li^+$, $H^-$, etc. In contrast to the ${}^3\Sigma_u$ $H_2$ and the ${}^2\Sigma_u^+$ $H_2^+$ systems, van der Waals complexes of these monomers are often accessible to experimental studies. On the other hand, small complexes of nonpolar monomers such as $He_2$, $HeH_2$, or $(H_2)_2$ are excellent "guinea pigs" for studies of electron correlation effects in intermolecular forces: the dispersion contribution and the intramonomer correlation corrections. The fact that the dispersion term is the dominant attractive term makes these complexes particularly challenging to ab initio calculations.

The above facts justify a special review article in this issue devoted to ab initio calculations of intermolecular interactions between small systems. We believe that such a review will be useful to all those in the chemical community who want to understand and use state-of-the-art ab initio methods and results in the field of intermolecular interactions. In general, we will restrict the presentation to the interactions of not more than four-electron monomers. However, since we are interested in these systems from the perspective of the general theory of intermolecular forces, we will not hesitate to refer to calculations for larger complexes as long as they are accurate enough to be useful in this respect. On the other hand, we will not dwell on the studies of ${}^2\Sigma_u^+$ $H_2^+$ and ${}^3\Sigma_u$ $H_2$ as such studies were thoroughly analyzed elsewhere.[10-14]

The present article focuses on the literature from 1980 until 1987. Over this period there have been at least four relevant review articles: by van der Avoird et al.,[15] by Jeziorski and Kołos,[16] by Kołos,[17] and by van

Lenthe et al.[18] The books by Arrighini[19] and Kaplan[20] should also be mentioned.

In section II we describe the present state of the perturbation theory of intermolecular forces. The perturbation method, despite problems with forcing proper symmetry and with convergence, still provides an irreplacable conceptual framework and tools for the calculation of individual contributions to the interaction energy.

In section III we discuss the supermolecular approach to ab initio calculations of interaction energies. The "brute force" flavor of this approach (Professor Coulson once remarked that such a procedure resembles obtaining the weight of a captain as the difference between the mass of the ship with and without the captain) has not prevented this method from becoming more and more useful. Our review focuses on post-Hartree–Fock ab initio methods with restriction to those which, in principle, can obtain the exact electronic wave function and energy. We discuss them from the perspective of their application to intermolecular forces calculations.

In section IV we give an account of basis set problems in ab initio calculations of weak interactions. In particular, basis set extension effects and the basis set superposition error are discussed.

In section V we collect the most accurate (to the best of our knowledge) calculations of small systems involving at most four-electron monomers. Calculations of both pair interactions and nonadditive effects are presented.

A short summary and the outline of perspectives are given in section VI.

## *II. Perturbation Theory of Intermolecular Forces*

In the classic application of the Rayleigh–Schrödinger perturbation theory (RSPT) to intermolecular interactions, the total Hamiltonian of a complex of two molecules, a and b, may be decomposed as

$$H = H^{\circ} + V \tag{1}$$

$$H^{\circ} = H_{\mathrm{a}} + H_{\mathrm{b}} \tag{2}$$

where $H_{\mathrm{a}}$ and $H_{\mathrm{b}}$ are the Hamiltonians of a and b, respectively, and $V$ collects the intermolecular interaction terms. We will further assume that $H_{\mathrm{a}}$ has orthonormal eigenfunctions $\phi(\mathrm{A})$ and eigenvalues $\epsilon(\mathrm{A})$ characterized by a set of quantum numbers denoted by A. Analogous notation will be used for molecule b. The RSPT expression for the total energy $E^{\mathrm{ab}}$ of the complex may be written as

$$E^{\mathrm{ab}} = E^{(\mathrm{o})} + \sum_{i=1} E^{(i)} \tag{3}$$

where $E^{(\mathrm{o})}$ is the sum of the unperturbed energies of the isolated monomers

$$E^{(\mathrm{o})} = \epsilon(\mathrm{A}) + \epsilon(\mathrm{B}) \tag{4}$$

and all corrections $E^{(i)}$ contribute to the interaction energy. The zeroth-order wave function has the form $\phi(\mathrm{A})\phi(\mathrm{B})$. Such a wave function is not antisymmetric with respect to intersystem exchange of electrons, and this property was termed by Hirschfelder the "polarization approximation" (PA).[21] This name reflects the fact that the electrons are assigned to individual monomers and hence the complex may be viewed as "polarized". Though the above assumption does not prevent PA RSPT from reproducing the long-range contributions (see Appendix 2 of ref 16), this formalism fails to predict the exchange effects and leads to convergence problems as pointed out by Claverie[22] and Kutzelnigg[23] (see section II.C.1).

**TABLE I. Contributions to the Interaction Energy Predicted by PA RSPT and Exchange Perturbation Theory through Second Order**

| order of PT | PA RSPT term$^{a}$ | exchange counterpart |
|---|---|---|
| first | electrostatic$^{c,l,a+r}$ | exchange repulsion$^{q,s,r}$ |
| second | induction$^{c,l,a}$ | exchange induction$^{q,s,r}$ |
| | dispersion$^{q,l,a}$ | exchange dispersion$^{q,s,r}$ |

[a] c = classic, q = quantum mechanical, l = long range, s = short range, a = attractive, r = repulsive.

Because of its success in the long-range region a great deal of effort has been devoted to generalizing the RSPT approach so that it would allow for exchange effects and circumvent convergence problems. Such studies, initiated by the classic paper of Eisenschitz and London,[5] culminated in the 1970s and brought about the formulation of exchange perturbation theories or symmetry-adapted perturbation theories (SAPT). These studies resulted in a deeper understanding of charge overlap and exchange contributions. Suitable methods for the calculation of these effects were developed; for relevant reviews see Chipman et al.[10,24] and Jeziorski and Kołos.[12] Since the late 1970s the accumulated knowledge has been used primarily for three purposes: (a) to explain the nature of the van der Waals bond in different complexes, (b) to infer the structure of interatomic and intermolecular potentials, and (c) to compute ab initio specific contributions to the interaction energy as well as the total interaction energy.

### A. Polarization Approximation

#### *1. Multipole Approximation*

PA RSPT as carried out through the second order predicts three familiar and well-defined components of the interaction energy. These are (a) the electrostatic (Coulomb) interaction energy in the first order, (b) the induction, and (c) dispersion energies in the second order (cf. Table I). The first-order energy corresponding to the interaction of molecule a in state $\phi(\mathrm{A})$ and molecule b in state $\phi(\mathrm{B})$ is given by

$$E^{(1)}_{\mathrm{elstat}} = \langle \phi(\mathrm{A})\phi(\mathrm{B}) | V | \phi(\mathrm{A})\phi(\mathrm{B}) \rangle \tag{5}$$

The second-order energy may be written in the form

$$\begin{aligned} E^{(2)} &= E^{(2)}_{\mathrm{ind}} + E^{(2)}_{\mathrm{disp}} \\ &= E^{(2)}_{\mathrm{ind}}(\mathrm{a}\rightarrow\mathrm{b}) + E^{(2)}_{\mathrm{ind}}(\mathrm{b}\rightarrow\mathrm{a}) + E^{(2)}_{\mathrm{disp}} \end{aligned} \tag{6}$$

where

$$E^{(2)}_{\mathrm{ind}}(\mathrm{a}\rightarrow\mathrm{b}) = -\sum_{\mathrm{B}'\neq\mathrm{B}} \frac{|\langle \phi(\mathrm{A})\phi(\mathrm{B}) | V | \phi(\mathrm{A})\phi(\mathrm{B}') \rangle|^2}{\Delta\epsilon(\mathrm{B}')} \tag{7}$$

$$E^{(2)}_{\mathrm{disp}} = -\sum_{\mathrm{B}'\neq\mathrm{B}} \sum_{\mathrm{A}'\neq\mathrm{A}} \frac{|\langle \phi(\mathrm{A})\phi(\mathrm{B}) | V | \phi(\mathrm{A}')\phi(\mathrm{B}') \rangle|^2}{\Delta\epsilon(\mathrm{A}') + \Delta\epsilon(\mathrm{B}')} \tag{8}$$

and $E^{(2)}_{\mathrm{ind}}(\mathrm{b}\rightarrow\mathrm{a})$ is given by an expression obtained from eq 7 by interchanging A and B. In these formulas

$\Delta\epsilon(A') = \epsilon(A') - \epsilon(A)$ is the excitation energy corresponding to the transition $A \rightarrow A'$ in molecule a. (This notation has been taken from Meath.[25])

The above terms have a clear physical interpretation if the multipole expansion approximation of $V$[26] is introduced. The electrostatic interaction collects the interactions among the permanent monomer multipole moments. The induction energy gives the interaction between permanent and induced multipole moments and is expressed through the monomer multipole moments and polarizabilities. The dispersion energy may be interpreted as the interaction between instantaneous multipole moments and, owing to the Casimir–Polder relation,[27] may be expressed through monomer dynamic polarizabilities. The multipole expansion of any energy contribution $E$ may be written in the general form

$$E = -\sum_{m=k} C_m X_m R^{-m} \qquad (9)$$

where $k$ depends on the nature of the particular interaction contribution $E$, $C_m$ are independent of $R$ and given in terms of the properties of the isolated monomers, and $X_m$ depend on mutual orientations of a and b. The most complete classification and analytical description of two- and many-body interaction energy contributions appearing in eq 9 from the first 3 orders of perturbation theory have been recently given by Piecuch.[28]

The multipole expansion of eq 9 is, however, strictly valid only asymptotically, i.e., for intersystem separation $R$ tending to infinity. For finite $R$ the expansion neglects short-range charge overlap effects and makes the second- and higher-order expressions for the interaction energy divergent,[29,30] although asymptotically convergent.[31]

### 2. Charge Overlap Effects

Charge overlap effects may be allowed for in the framework of PA RSPT if one uses the exact interaction operator rather than its multipole expansion form.[11,32,33] Moreover, it is possible to maintain the elegant physical picture of the interaction energy that is obtained in the multipole expansion approximation by employing the exact partial wave expansion (bipolar expansion) of the interaction operator.[11,26,34,35] The partial wave expansion of the energy contribution $E$, in the simplest case of two interacting atoms, may be written in the form

$$E = \sum_{l_a=0} \sum_{l_b=0} \sum_{m=-\min[l_a,l_b]}^{\min[l_a,l_b]} E_{l_a l_b m} \qquad (10)$$

where $l_a$ and $l_b$ are angular quantum numbers for monomers a and b, respectively, and $m$ is the magnetic quantum number. Individual terms predicted by the multipole expansion may be related to exact partial wave components by introducing appropriate ($R$- and orientation-dependent) scaling functions to the terms of eq 9. In the second and higher orders of PA RSPT, where the multipole expansion is divergent, they are referred to as "damping" functions.[36-38] Scaling functions may be calculated ab initio in the first[35] and second order.[14,39] It should be noted that the partial wave expansion predicts some extra, short-range, "spherical" terms ($E_{000}$, $E_{l_a00}$, and $E_{0l_b0}$ in eq 10).[33,40] Individual partial wave energies are often referred to as "nonexpanded" energies as opposed to the "expanded" energies arising in the multipole expansion.[11] Calculations of the first-order interaction energy by means of the partial wave expansion technique have been performed for the $H_2$ dimer[35] (with accurate $H_2$ wave functions at both the SCF and correlated levels) and larger systems[41-43] (with monomers described at the SCF level only). The most detailed analysis was performed for $(N_2)_2$.[43] It was shown that in the region of the van der Waals minimum the partial wave expansion was not rapidly convergent and that charge overlap effects were significant. In particular, the "spherical" terms turned out to be nonnegligible.

Effects of charge overlap on the second-order dispersion and induction contributions have been studied extensively for model systems: the $^2\Sigma_u^+$ state of $H_2^+$,[11,44,45] the $^3\Sigma_u$ state of $H_2$,[14] and the ground state of $He_2$[46] (in the last case only the dispersion was analyzed). These calculations have provided a rigorous insight into the nature of charge overlap effects in the second-order PA RSPT and have yielded an ab initio standard for semiempirical and model damping functions. Moreover, in the region of the van der Waals minimum, it was shown that the partial wave expansion was slowly convergent and again the "spherical" terms proved to be nonnegligible.[14,46] These conclusions were also confirmed for larger systems, $Ne_2$,[47] $Li_2$ and $Ar_2$,[39] and HeHF.[48]

## B. Application of the Polarization Approximation to Interactions of Many-Electron Systems

### 1. Double Perturbation Theory

Application of perturbation theory to intermolecular interactions requires knowledge of the isolated monomers' wave functions. However, exact or even accurately correlated wave functions are, in practice, seldom available or are too complicated to be used in solution of the perturbation equations. Only the fairly accurate SCF wave functions are easily accessible. Since the SCF level of the theory provides a good approximation to a plethora of chemical phenomena, it is natural to take it as a starting point in the studies of intermolecular interactions. To this end one may use double perturbation theory where the interaction operator represents one perturbation and the second perturbation (denoted by $W$) is the sum of the correlation or fluctuation potentials of the monomers as extracted from the monomer Hamiltonians. This partition is often referred to as the Møller–Plesset one.[49] For intermolecular interaction problems it has the form[50]

$$H = F^{\circ} + W + V \qquad (11)$$

and the total energy of the complex may be expanded in the perturbation series

$$E^{ab} = \sum_{i=0} \sum_{j=0} E^{(ij)} \qquad (12)$$

The zeroth-order Hamiltonian $F^{\circ}$ is then the sum of the monomer Fock operators, and the indicies $i$ and $j$ are related to the order in $V$ and $W$, respectively. The idea of double perturbation formalism dates back to the papers of Musher and Amos[51] and Broussard and Kestner.[52] The most complete presentation, which also includes exchange effects, can be found in the papers of Szalewicz and Jeziorski[53] and Jeziorski and Kołos[12] (see also Rybak et al.[54,55]).

**TABLE II. Comparison of van der Waals $C_6$ Coefficients Calculated at UCHF and CHF Levels of Theory with the Exact Ones ($C_6$ in $a_0{}^6E_h$)**

| system | $C_6{}^{\mathrm{UCHF}}$ | $C_6{}^{\mathrm{CHF}}$ | $C_6{}^{\mathrm{exact}}$ |
|---|---|---|---|
| $He_2$ | 1.12 (ref 99) | 1.38 (ref 70) | 1.46[a] (ref 273) |
| $Ne_2$ | 5.00 (ref 56) | 5.39 (ref 70) | 6.43[b] (ref 274) |
| $Ar_2$ | 73.6 (ref 275) | 61.5 (ref 39) | 64.2[b] (ref 274) |
| $Be_2$ | 256.6 (ref 276) | 284 (ref 277) | 213.5[a] (ref 85) |
| $(H_2)_2$[c] | 10.1[d] (ref 278) | 12.30 (ref 65) | 12.12[a] (ref 83) |
| $(N_2)_2$ | 94.99 (ref 83) | 71.46 (ref 83) | 73.8[b] (ref 279) |

[a] Ab initio result. [b] Semiempirical result. [c] $r_{HH} = 1.449a_0$. [d] The result of Mulder et al.[278] extrapolated to $r_{HH} = 1.449a_0$.

### 2. Interaction Energy between Hartree–Fock Systems

The interaction energy obtained by considering in eq 12 the corrections of the zeroth order in $W$ only may be termed "the interaction energy between Hartree–Fock systems".[56] The intramonomer correlation effects may be allowed for by calculating the remaining corrections.[12] However, in the second and higher orders with respect to $V$, some of the intramonomer correlation corrections can be obtained by using the time-dependent coupled Hartree–Fock[57] polarization propagator.[58] For this reason these corrections are sometimes termed the "apparent intramolecular correlation".[54,59] When considering the interaction energy between Hartree–Fock systems, it is important to recognize the uncoupled Hartree–Fock (UCHF) level (if all terms involving $W$ are discarded) and the coupled Hartree–Fock (CHF) level (if the $W$-dependent "apparent correlation" terms are included) of the perturbation theory.

**(a) UCHF Second-Order Energy.** Presently, the UCHF induction and dispersion energies can be routinely calculated.[47,50,60–62] The Hylleraas variational principle may be used, preferably in a pseudospectral form that is obtained if the basis sets for the monomers diagonalize the monomers' Fock Hamiltonians.[14,50] Calculations of the dispersion energy then reduce to the summation of $M_a{}^*M_b{}^*N_a{}^*N_b$ transformed two-electron Coulomb integrals (where $M$ and $N$ are the number of occupied and virtual orbitals, respectively). It should be noted that the variational character of the UCHF induction and dispersion energies[50] permits optimization of nonlinear parameters of the basis functions as well as the addition of functions centered at bonds or partner monomers.[46,63,64]

**(b) CHF Second-Order Energy.** Unfortunately, the UCHF calculations of induction and dispersion energies are often found to be insufficient. One can see this inadequacy from the comparison of the accurate and the UCHF $C_6$ dispersion van der Waals coefficients collected in Table II. Going to the CHF level of theory usually gives quite an improvement over the UCHF level (the exception is the atypical Be dimer). This is the reason why the CHF van der Waals dispersion coefficients have recently been the object of several studies.[65–68] van der Waals dispersion coefficients may be obtained from the Casimir–Polder relation,[27] where the product of the dynamic polarizabilities $\alpha$ of the monomers is integrated over imaginary frequency $\omega$. If $\alpha$ is the dipole dynamic polarizability, then

$$C_6 = \frac{3}{\pi}\int_0^\infty \alpha_a(i\omega)\alpha_b(i\omega)\,d\omega \qquad (13)$$

If the dynamic polarizabilities are calculated by the time-dependent CHF method, one obtains CHF dispersion coefficients.[65,69,70]

It is more involved to calculate dispersion energies at the CHF level without assuming the multipole approximation. Even then, however, it is possible to express the dispersion energy in terms of products of polarization propagators[71,72] (sometimes called generalized second-order response functions or generalized dynamic polarizabilities) integrated over imaginary frequency.[58,73,74] On employing the time-dependent CHF approximation to the polarization propagator, one obtains the CHF dispersion energies. Application of this technique has begun only recently.[39,73,75] Calculations of CHF dispersion energies are more involved than are UCHF calculations. The CHF calculations require the summation of $M_a{}^*M_b{}^*N_a{}^{2*}N_b{}^2$ terms along with the integration in the Casimir–Polder formula over the imaginary frequency.[75,58] Such calculations have been performed for $He_2$,[75,76] $(HF)_2$,[75,76] $Ar_2$ and $Li_2$,[39] HeHF,[48,76] NeHF,[76] and $Ne_2$.[76] For HeHF the nonexpanded CHF induction contribution was also calculated.[48,76]

Another approach is to calculate the CHF dispersion energies explicitly in the framework of the double perturbation theory by summing up all ring diagrams that originate from "bubble" diagrams of the time-dependent CHF theory for polarizabilities.[54,77]

### 3. Intramonomer Electron Correlation Effects

True intramonomer correlation effects are substantially more difficult to calculate than the apparent ones, and our knowledge about them is far from satisfactory. What we do know is that they modify various components of the interaction energy differently. The intramonomer electron correlation corrections to the electrostatic, induction, and dispersion contributions will be hereafter refered to as the electrostatic correlation, induction correlation, and dispersion correlation energies, respectively.

The electrostatic correlation term may be viewed as originating from two effects: (a) modification of the multipolar part by an alteration of the multipole moments, and (b) a change of the overlap effects. Estimates of the former modification are relatively simple since the problem reduces to the calculation of correlated monomer moments. Calculations of the modification of overlap effects are much more involved and have been carried out but for a few systems: $(H_2)_2$,[35,78] $He_2$,[79] and $Be_2$.[80]

As to the second-order induction correlation and dispersion correlation terms, only multipolar results are available. Static polarizabilities necessary to calculate multipolar induction energies may be routinely calculated by the finite-field method[81] and are fairly well known for small systems. It is much more difficult, however, to calculate correlated dynamic polarizabilities and van der Waals coefficients since a time-dependent formalism must be used and in general one should include in the monomer wave function the higher than two-electron clusters, of both the linked and unlinked type.[82] Accurate van der Waals coefficients have been calculated for $He_2$,[83,84] $HeH_2$,[83] $(H_2)_2$,[83] and $Be_2$.[85] For larger systems advanced calculations have only been performed for $Ne_2$.[82]

The only calculations of the dispersion energy with intramonomer correlation corrections and simultaneous inclusion of charge overlap effects are those of Rybak and Jeziorski[55] for $He_2$, $Be_2$, $(HF)_2$, and $(H_2O)_2$.

## C. Exchange Effects and Symmetry-Adapted Perturbation Theory

### *1. Symmetry Problem in Perturbation Theory*

The problem of intermonomer exchange of electrons in the perturbation theory of intermolecular forces may be formulated as the problem of the alteration of symmetry under the influence of a perturbation. The zeroth-order wave function of PA RSPT, since it is not fully antisymmetric, has lower symmetry than the exact perturbed wave function. Perturbation methods may be unable to account for a switch from lower to higher symmetry. As a consequence, the PA RSPT, if at all convergent, would converge toward a "mathematical" eigenstate (with partially bosonic character and artificially low energy) instead of the genuine physical ground state.[22,23] It has been shown that, at large distances, there may be first an apparent convergence toward an energy value lying between the mathematical and physical eigenstates, followed by an extremely slow convergence to the mathematical eigenstate.[86,87] It is important to stress that the energy difference between the physical and mathematical state may not, in general, vanish when $R$ tends to infinity.

Incorporation of "symmetry forcing" or "adaptation of symmetry" in the perturbation theory of intermolecular forces was addressed by many outstanding theoreticians in the 1970s. Excellent reviews of these studies have already appeared;[10,12,24] hence we need to recall the most important points only briefly and comment on the latest works.

There are essentially two types of exchange perturbation or symmetry-adapted perturbation theories: (a) those that are based on a zeroth-order wave function that has the correct symmetry of the perturbed system (cf. references in ref 12 and more recent works, ref 88 and 89) and (b) those that are based on the zeroth-order wave function of the PA RSPT form and that force the required symmetry in consecutive orders or iterations; cf. ref 10, 12, and 24. The basic problems of the exchange perturbation theory formulation are (a) the possibility of an infinite number of formalisms,[10] (b) a nonunique definition of the order,[21] (c) the ensurance of the convergence of the perturbation expansion,[87] and (d) the treatment of degeneracy.[90,91] Recent criticism[91] of all symmetry-adapted perturbation theory formalisms set forth so far should be mentioned in this context.

It is important to stress that the great majority of symmetry-adapted perturbation theories predict the same first-order energy

$$E^{(1)}_{\mathrm{SAPT}} = \frac{\langle \phi(\mathrm{A})\phi(\mathrm{B}) | V\mathcal{A} | \phi(\mathrm{A})\phi(\mathrm{B}) \rangle}{\langle \phi(\mathrm{A})\phi(\mathrm{B}) | \mathcal{A} | \phi(\mathrm{A})\phi(\mathrm{B}) \rangle} \tag{14}$$

where $\mathcal{A}$ is the total antisymmetrizer for the complex. Equation 14 includes the electrostatic interaction energy of PA RSPT and the exchange repulsion energy. This first-order term is closely related to the Heitler–London first-order interaction energy[92] (to which it is identical if the monomer wave functions are obtained with the same basis set[79a]).

### *2. Exchange Repulsion and Exchange Polarization*

Adding only the exchange repulsion term to the PA RSPT contributions is often sufficient to obtain a reliable estimate of the interaction energy curve in the region of the van der Waals minimum. However, to obtain a result that is quantitatively accurate, one has to allow for second- and perhaps higher-order exchange effects. The definition of the second-order exchange contribution depends strongly on the manner in which symmetry is forced in a particular perturbation formalism.[12] Not dwelling upon the intricacies in the comparison of different second-order energy definitions, we should say only that three of the formalisms—the symmetrized Rayleigh–Schrödinger formalism, the Jeziorski–Kołos intermediate symmetry forcing formalism,[12,93] and the Murrell–Shaw–Musher–Amos formalism[51,94]—give the same second-order energy. This second-order energy reproduces the long-range PA contributions, and its exchange component proved to be very efficient in the calculations on the $^2\Sigma_u^+$ $H_2^+$ model system[12,93] (in $H_2^+$ the exchange of protons rather than electrons must be allowed for). To calculate this second-order energy one begins with the evaluation of the first-order PA wave function and then forces the proper symmetry in the expression for the second-order energy. Such an approach was termed the "weak symmetry forcing" because the symmetry is introduced *after* the electrostatic deformation has been carried out.[12] This feature leads to two important consequences. First, it gives rise to an appealing physical interpretation of the exchange counterparts of the dispersion and induction terms. They are termed "exchange dispersion" and "exchange induction" contributions, respectively, and their sum is referred to as the "exchange polarization".[95,96] Second, the algorithm for exchange polarization energy is tractable for many-electron systems.[96,97]

### *3. Problems with the Exchange Induction Term*

For the $H_2^+$ ion the exchange induction term efficiently approximated second- and higher-order exchange effects.[98] Later, however, it was found that the sum of the induction and exchange induction contributions failed to reproduce the mutual deformation effect arising at the SCF level between closed-shell atoms.[56,96,99,100] This fact was attributed to the weak symmetry forcing applied in the exchange polarization term.[101,102] It turned out that exchange effects are crucial in the mutual deformation of closed-shell atoms and ions.[102,103] These effects can be accounted for only by an exchange perturbation formalism with strong symmetry forcing.[101] (Strong symmetry forcing, as opposed to weak symmetry forcing, considers symmetry constraints and electrostatic effects *simultaneously*.[12]) It is still not clear whether the exchange dispersion term suffers from the same problem.

### *4. Calculations of Exchange Terms for Many-Electron Systems*

The exchange contributions for many-electron systems may be analyzed in terms of symmetry-adapted double perturbation theory[12,53] in a manner parallel to that described in section II.B.1. At the lowest level of the theory, the exchange repulsion between Hartree–Fock systems may be easily calculated.[22b,104] Several well-defined approximations are possible (e.g., expansion in terms of the intersystem overlap integral[22b,104] or many-orbital cluster expansion[105]).

Second-order exchange terms (exchange induction and exchange dispersion) are more difficult to treat. An algorithm at the UCHF level and through the square terms in the intersystem overlap integral has been derived[96] and applied to $He_2$,[53,99] $Be_2$,[80,96] $Ne_2$,[56] and $(HF)_2$.[106] Exchange dispersion at the incomplete CHF level was calculated for $He_2$[54] as was the exchange induction at the CHF level for $Be_2$.[100] Exchange dispersion three-body terms were derived and calculated for $He_3$[107] and $Be_3$.[108]

Calculations of intramanomer electron correlation effects on the exchange repulsion energy ("exchange repulsion correlation") have been carried out only for the interaction of two-electron systems, $He_2$,[79,109] $Be_2$ (outer-shell approximation),[80] and $(H_2)_2$.[78] This effect proved to be more important than the exchange dispersion term. Unfortunately, at this time the nonorthogonality problem has prohibited calculation of the exchange repulsion correlation for complexes composed of more than two-electron monomers.

No calculations of true intramonomer electron correlation effects on the second-order exchange effects have been reported.

## *III. Supermolecular Approach*

In the supermolecular approach the interaction energy is calculated directly from its definition as

$$\Delta E = E^{ab} - (\epsilon(A) + \epsilon(B)) \qquad (15)$$

Formally, the dimer and monomer energies may be obtained by any ab initio quantum mechanical method. The benefits of this approach are as follows: (a) Convergence problems in the perturbation expansion of the interaction energy are avoided. (b) Intermolecular exchange effects are automatically incorporated. (c) The whole interaction energy hypersurface is uniformly treated. (d) Since electronic energy and structure calculations are a "major industry" of contemporary quantum chemistry, one can use many advanced methods and highly efficient codes.

However, the supermolecular approach has its flaws, too. The apparently simple and straightforward eq 15, when applied to weak intermolecular interactions, requires subtraction of energies that are several orders of magnitude larger than the interaction energy. In most cases it is impossible to obtain $E^{ab}$, $\epsilon(A)$, and $\epsilon(B)$ with an error smaller than $\Delta E$. The only thing one can do is to evaluate $E^{ab}$, $\epsilon(A)$, and $\epsilon(B)$ in a manner that is consistent methodologically and numerically.

Methodological consistency means that both the monomer and the dimer are treated at the same level of theory. Not only should the method be size extensive[110] (to ensure proper scaling with size in a homogeneous system) but it also has to be size consistent[111] (to ensure correct separation of a supermolecule into its fragments). Note that in general size consistency is a stronger requirement than size extensivity but they are equivalent for the interaction of closed-shell systems.[110]

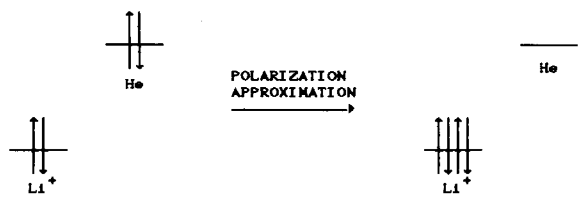


**Figure 1.** Unphysical transfer of electrons from He to $Li^+$. It may occur in calculations that neglect the Pauli exclusion principle during deformation of interacting species. Actually, during deformation of the He monomer the occupied, low-lying 1s energy level of $Li^+$ is available for the electrons of He and the unphysical charge transfer takes place.

For finite basis set calculations the problem of numerical consistency appears. It arises from the fact that in the dimer energy calculations the individual monomer takes advantage of the basis set of the whole dimer rather than of just "its own" basis set centered at this monomer. The related lowering in the monomer energies is called basis set superposition error (BSSE).[112] In section IV.B we discuss how to deal with BSSE.

A serious drawback of the supermolecular approach is that eq 15 provides us with a single number, the decomposition of which into physically meaningful contributions is difficult. Not only is such a decomposition important for an interpretation of the results but the simultaneous calculation of all interaction energy contributions has the drawback of requiring a large, often prohibitively large, versatile basis set.

At the SCF level the interaction energy may be decomposed into electrostatic, exchange repulsion, and deformation energies.[113,114] The last term collects what is left after separation of electrostatic and exchange repulsion terms. Furthermore, the deformation term is sometimes split into polarization, charge transfer, and (hopefully) a small remainder.[115] There are a few problems with such a decomposition. First, separation of individual terms requires proper consideration of basis set extension effects[114,116-118] (see section IV.B). Second, charge-transfer terms are not defined in a basis set independent manner.[50,101,103] Third, rigorous calculation of polarization contribution through infinite order may lead to unphysical charge transfer because of the incorrect symmetry of PA.[23,103] It has recently been shown on the $HeLi^+$ model system[103] that if PA is introduced into the Hartree–Fock dimer calculations (the method terms by Sadlej the Hartree–Hartree–Fock approximation[119]) then the procedure leads to unphysical transfer of electrons from He to $Li^+$ due to the convergence to a nonphysical, mathematical eigenstate;[23] see Figure 1.

The problem of physical decomposition is even more difficult at the correlated level. Some insight into this decomposition may be acquired, however, by means of localized orbitals.[120] Similarly, as in the perturbation theory, different types of excitations in the wave functions may be interpreted as arising from intra, inter, and coupled inter–intramonomer electron correlation effects.[121-123] Restricting the wave function to contain only certain kinds of excitations permits calculations of separate interaction energy contributions. Simultaneous single excitations localized on different monomers provide the intermolecular correlation (dispersion) term. Excitations from localized orbitals on one monomer only give the intramonomer electron correlation contribution. The usefulness of such an approach depends rather strongly on the specific method of calculating the correlation energy.

There are three principal methods used for correcting the SCF wave function for the effect of electron correlation: (a) configuration interaction (CI) methods, (b) coupled cluster (CC) methods, and (c) many-body perturbation theory (MBPT), also termed Møller–Plesset perturbation theory (MPPT).

### A. Configuration Interaction Methods

Of all CI-type methods only the full CI expansion, which may also be realized in the form of the complete active-space SCF formalism,[124] is size consistent. Truncated CI expansions, as, e.g., single and double excitation CI, are not size consistent. Since the size-inconsistency error is not negligible, one has to correct for it when using eq 15. One way is to replace the sum of $\epsilon(A)$ and $\epsilon(B)$ in eq 15 by $E^{ab}$ evaluated at such a large distance that the $E^{ab}$ energy is numerically constant.[125] However, simultaneous correcting for BSSE is then a problem.[126-128] Alternatively, one may use Davidson's correction[129] or one of several variations of this formula, recently reviewed by Shavitt et al.,[130] to correct all energies in eq 15. Such an approach has been used[128] but its performance has not been sufficiently analyzed as yet. One should keep in mind that size-consistency corrections are not exact.[130]

An interesting and very effective modification of the CI approach, specifically designed for weakly interacting systems, has been set forth by Liu and McLean.[131] It is termed the interacting correlated fragments (ICF) method. Accurate potential energy curves were obtained for the ground states of $He_2$,[131] $Be_2$,[131,132] $Mg_2$,[131] and the excited states arising from $Mg(^3P)$ interacting with $He(^1S)$.[133] According to the authors, this method establishes a series of wave functions that correspond to increasing levels of electronic correlation in the separated fragments. At each level, the complete one-particle basis set limit for the interaction potential is computed to within a known tolerance, giving a rapid convergence of potentials. A large Slater-type basis set is used and the valence space of the subsystem is spanned by localized orbitals obtained from the MCSCF orbitals. All calculations performed so far by this method are characterized by a very small BSSE, probably due to the high degree of localization of orbitals and the use of extended STO bases. Unfortunately, the ICF results are insufficiently documented to make precise evaluation of their accuracy possible. Only recently it has been disclosed that the accuracy of the $He_2$ potential curve was fortuitous.[134] It is also not clear how serious the lack of size consistency is. No separation into physically meaningful contributions has been carried out in this method.

A promising method in the context of the supermolecular approach is the valence bond (VB) method.[135] This method permits separation of the interaction energy into perturbation components as described in section II,[136] particularly so, if no orthogonalization between the interacting systems' occupied orbitals is performed.[89,137-141] It is also capable of providing high-quality results as was shown for HeHF[142] and for $He_2$.[143] For the latter a very accurate estimate of the exchange repulsion correlation effects was obtained. Proponents of the VB method emphasize that the nonorthogonal VB does not suffer from the BSSE problem[144] but this seems to be true only as long as no charge-transfer structures are included.[136,145] Moreover, the VB method is not size consistent.

Methods based on the CI expansion, despite problems of size inconsistency and BSSE, are expected to be very useful for the accurate calculation of intermolecular forces. This is because the multiconfiguration reference state CI (MR CI) is the most accurate and versatile of all ab initio methods and, as pointed out by Handy,[146] is capable of describing bond-breaking and curve-crossing situations and is applicable to open-shell systems, excited states, and degenerate and quasi-degenerate states.

### B. Coupled Cluster Methods

The CC method should be regarded as the method of first choice in all cases where it can be employed due to its size-consistent behavior and balanced treatment of inter- and intramonomer correlation effects.[147]

Let us start with the related family of coupled electron pair approximation (CEPA) methods which may be viewed as approximations to the coupled clusters singles and doubles (CCSD) scheme.[110] An important feature of CEPA methods is that, after Boys[120] (or other) localization of orbitals on monomers, separation of inter- and intramonomer correlation may be performed. One of the first applications of CEPA to intermolecular interactions was the study of the HF dimer by Lischka.[121] Very extensive CEPA calculations have recently been performed for interactions of two-electron monomers.[148-151] Although the CEPA methods, and in particular a very promising variational variant, the coupled pair functional method,[152] may give very valuable results, they are not suitable for highly accurate calculations because of their approximate treatment of electron pairs and complete neglect of linked triple-electron clusters. Moreover, a potentially serious feature of the CEPA approximations (except for CEPA0) is that they are not invariant with respect to a unitary transformation from canonical to localized orbitals.[153] To achieve rigorous insight into the roles of single, double, and higher many-electron clusters one should use the hierarchy of CC methods: CCD, CCSD, and CCSDT. This has been done for the Be dimer[154] and the water dimer[155] but the basis sets were not good enough to provide definite conclusions and further studies are necessary. Moreover, it seems that for $Be_2$ a multiconfiguration reference state is necessary. One can only look forward to further activity in the application and extension of the CC method.

### C. Many-Body Perturbation Theory

MBPT seems to be particularly attractive because it is size-consistent and because it is straightforward to apply without introducing arbitrary choices or approximations.[156] Due to the analysis of the convergence as carried out by Handy et al.[157] (cf. also Laidig et al.[158]), one can use this method with much greater confidence while at the same time being aware that it may fail if curve crossing or degeneracy appears. The second-order level, MBPT(2) (MP2), may be programmed very efficiently,[159,160] also using symmetry,[161] and provides the bulk of the electron correlation contribution for a majority of cases. Substantial quantitative improvement is obtained by a calculation through the third order, MBPT(3) (MP3), and through the fourth order with linked triple-electron clusters, MBPT(4) (MP4). The efficacy of this level of theory is very competitive to CI and CC types of calculations. Moreover, Chałasiński and Szczęśniak[162] have recently shown that, for large *R*, the interaction energies obtained at the MBPT(2) and MBPT(3) levels may be related to contributions predicted by the double perturbation theory of intermolecular interactions as described in section II.B. MBPT(2) includes the electrostatic correlation term of the second order in *W* (the $E^{(11)}_{\text{elstat}}$ term vanishes for the Hartree–Fock zero-order Hamiltonian[53]) and the UCHF dispersion contribution (see also ref 163). Induction correlation terms are also present:

$$\Delta E^{(2)}_{\text{MBPT}} \cong E^{(12)}_{\text{elstat}} + E^{(20)}_{\text{disp}} + \text{induction correlation} \quad (16)$$

MBPT(3) includes the electrostatic correlation term (third order in *W*), the third-order UCHF dispersion term, the CHF dispersion term (first order in *W*), and induction correlation terms:

$$\Delta E^{(3)}_{\text{MBPT}} \cong E^{(13)}_{\text{elstat}} + E^{(30)}_{\text{disp}} + E^{(21)}_{\text{disp}} + \text{induction correlation} \quad (17)$$

In the region of the van der Waals minimum the accompanying exchange terms should be also considered.

Whereas MBPT(2) calculations of intermolecular forces are relatively simple and very popular, the MBPT(4) level of theory has only recently become easily accessible (GAUSSIAN 82 and 86[159] and GRNFNC[160] codes). One can expect in the near future extensive application of this method to intermolecular interaction problems.

### D. "Piecewise" Approach

By the "piecewise" approach we mean an approach that builds the potential energy surface as a sum of different contributions calculated by different methods and often with different basis sets. Calculations combining the supermolecular SCF method and perturbation theory of intermolecular forces to calculate the dispersion contribution (SCF + DISP model)[36,50,56,61] serve as good examples of such an approach. The SCF + DISP model may be further refined by adding corrections for electrostatic and exchange correlation.[54,78,80]

Another example may be the evaluation of the potential for $HeH_2$ by Meyer et al.[122] where different correlated methods and basis sets were used for different contributions to the interaction energy. A piecewise approach must be based on a deep understanding of the nature of intermolecular interactions and requires thorough experience in the theory and technology of ab initio calculations. The accuracy of a particular piecewise potential may be quite good but it is often partly due to the more or less obscure cancellation of errors.

## *IV. Basis Sets*

The requirements that must be met by a basis set are different for the different components of the interaction energy and in general do not depend on the method (supermolecular or perturbational) by which a given contribution is obtained. Consequently, the choice of the basis set should be preceded by recognition of the dominant contributions to the interaction energy in the system under consideration. In the case where the interaction energy is calculated without separation into different terms, as it often happens in the supermolecular approach, a crucial difficulty is to achieve a reasonable compromise between the size and versatility of the basis set.

### A. Basis Sets for Calculations of Different Interaction Energy Contributions

Various strategies of basis set selection for individual contributions have recently been discussed by van Lenthe et al.;[18] cf. also Hobza and Zahradník.[164] Here we will give only general guidelines and focus on extended basis sets that are appropriate for accurate calculations.

Reliable calculations of long-range interaction energy contributions, i.e., electrostatic, induction, and dispersion, require basis sets suitable for the calculation of monomer electric properties: multipole moments and polarizabilities (static and dynamic). Appropriate basis sets for these properties have been extensively studied (see, for example, ref 165 and 166 and reviews 18, 167 and 168). Since the calculations of multipole moments and polarizabilities are sensitive to the accuracy of the wave function both close and far from the nuclei, in addition to the energy-optimized part of the basis set (of double-$\zeta$ or better quality) supplemental diffuse and diffuse polarization functions are necessary.

For dipole properties a basis set composed of a double-$\zeta$ core plus two polarization functions per atom (two d's for atoms C, N, O, and F and two p's for H) is satisfactory.[166] Calculation of electrostatic, induction, and dispersion contributions that are related to the dipole electric properties may be sufficient to obtain qualitative results. However, a more accurate treatment of the interaction requires calculations of the terms that are related to higher multipole properties. Higher multipoles require higher polarization functions and are also affected more seriously by the basis set truncation error within a particular symmetry of the basis set.[168–170] Moreover, with increasing order in the multipole property, the charge overlap effects become very important.[14,46] Consequently, the relationship between higher multipole properties and the interaction energy is not so transparent. In this case, the partial wave expansion for the leading components of the interaction energy is very useful to efficiently design the polarization part of the basis. In particular, it is important to recall that the partial wave expansion for the dispersion energy is slowly convergent[14,46] and the convergence is worse for species with p-symmetry occupied orbitals.[47]

Unfortunately, inclusion of higher than f-symmetry basis functions is difficult. Although there are integral codes that can handle g- and higher-symmetry functions,[171] the dimension of the basis set soon becomes prohibitively large. Furthermore, whereas to obtain fairly accurate van der Waals coefficients two exponents per symmetry are often enough, accurate calculations of accompanying charge overlap effects require more basis functions per symmetry.[46,172] Optimization of induction-type and dispersion-type exponents may be carried out by means of the Hylleraas variational principle.[46,50]

Currently there is a growing interest in different well-tempered[173] and even-tempered[174] basis sets. There is no doubt that for s and p symmetry they are both optimal and practical.[116,175] The polarization part of the basis set cannot, however, be made large and, unless the bases are prepared with the reproduction of the interaction contributions in mind,[46,151] a tempered basis may not be efficient.[176]

To reproduce exchange and overlap effects, a basis must be able to describe faithfully the electron distribution not only close to the nuclei but also at large distances from the nuclei—in the so-called "tail" region.[116] The great majority of ab initio calculations use Gaussian orbitals that have the incorrect long-range behavior. A Gaussian orbital dies off too quickly, as $\exp(-\alpha r^2)$ rather than as the correct $\exp(-\alpha r)$ function. This fact may cause severe underestimation of exchange and charge overlap contributions. Adding functions with diffuse exponents to an energy-optimized basis set helps, but to achieve a uniformly accurate result over a large interval of $R$, one should switch to large even- or well-tempered basis sets. It is particularly important to cover the low-exponent region regularly, rather than to add a few randomly selected diffuse orbitals.[18,116]

In conclusion, an efficient basis set for accurate calculations of interaction energies should be comprised of an energy-optimized well- or even-tempered set supplemented with interaction-energy-oriented polarization and diffuse sets, also prepared in a "tempered" manner. Since the monomer wave functions are not highly deformed in the intermolecular interaction problems treated here, a large part of the basis involving larger exponents may be kept contracted. This offers the possibility of reducing the size of a basis set. It seems particularly convenient to represent the occupied orbitals of atoms in the form of single contractions obtained within Raffenetti's scheme.[177] This approach turned out to be very efficient for computing interatomic interactions.[56,175] Contraction schemes specifically designed for intermolecular interactions should be further investigated.

The above discussion of basis sets would be incomplete if we did not mention attempts to use basis functions that are not located on the nuclei of the monomers but situated in the region between the interacting monomers. Such functions have been shown to be quite efficient if their exponents and locations are optimized.[46,134,148–150]

## B. Dimer-Centered Basis Set and Basis Set Extension Effects

A peculiar feature of the supermolecular approach is that in calculations of the dimer energy, each monomer and the interaction energy automatically take advantage of the basis set of the whole dimer. If the separation of the interaction energy and a comparison with the perturbational approach (eq 3) are to be meaningful, modification of the occupied and virtual orbital space of the monomer by the basis functions centered at the partner has to be considered. The basis set of the whole dimer may be called the dimer-centered basis set as opposed to the monomer-centered basis set.[116] As a measure of this basis set extension (BSE) effect one may use the differences between the values of a quantity $X$ (which may be a monomer energy or a component of the interaction energy) calculated with the dimer- and the monomer-centered basis sets.

### *1. Basis Set Superposition Error in Supermolecular Interaction Energy Calculations*

BSSE is usually defined as the BSE effect for the monomer energies (so-called higher-order BSSE will be discussed in section IV.B.2). It must not be included in the interaction energy. It is a matter of controversy whether full or somehow restricted dimer basis is accessible to the monomer in the dimer calculations.[114,128,151,178–180] The problem of BSSE is of the utmost practical importance, and much effort has been devoted to explaining its origin as well as to proposing methods of circumventing it. An excellent review of these efforts has recently been published by van Lenthe et al.;[18] therefore we will limit the presentation to the most important points and the most recent studies.

At the SCF level of theory, avoiding or considerably reducing BSSE by saturation of the monomer basis sets seems to be possible although rather expensive.[64,112,181,182] At the correlated level, BSSE appears extremely resilient to such tactics.[64,151,182] Basis functions with diffuse exponents as well as higher polarization functions, necessary to reproduce induction and dispersion energies, are readily used by all monomers in the complex and yield BSSE often of the size of the interaction energy correlation contribution.[134,151,155,175,183]

Two general approaches have been proposed to eliminate BSSE from the interaction energy calculations. In the first approach, the dimer calculations are performed in such a manner that BSSE is avoided by eliminating or by separating BSE terms. Elimination is possible in the VB theory if nonorthogonal basis sets are used,[144] but then charge-transfer configurations must be neglected.[183] Separation of the BSE effects may be achieved in the "chemical Hamiltonian approach".[184] In this approach the total Hamiltonian is partitioned into "physical" and "basis extension" components. Next, the "physical" component may be separated into effective intramolecular Hamiltonians and the interaction energy operator. Some supermolecular[185] and perturbation[89] schemes of the interaction energy calculations have been proposed, which neglect the basis extension component. The above partitioning of the Hamiltonian is basis set dependent and because of the singularities of the overlap matrix becomes ill-defined when the monomer bases tend to completeness. This seems to be the main formal flaw of the chemical Hamiltonian approach.

The second approach to circumvent BSSE problems consists in the application of the counterpoise method (CP). In the Boys and Bernardi CP method[186] the monomer energies to be used in eq 15 are calculated with the full dimer basis. A common objection against this method has been the following: in the dimer calculation, the monomers cannot take advantage of the full dimer basis as the Pauli principle prevents the monomer from using the occupied orbitals of the partner.[187,188] In support of this philosophy there have been presented numerical examples in which results obtained by the Boys and Bernardi CP method were too repulsive in comparison with experimental or basis-set-saturated results.[128,187,189–191] In view of this objection, Daudey et al.[188] proposed to calculate the energy of each monomer with a monomer-centered basis set augmented only by the virtual orbitals of the partner. In contrast to the "full" CP (FCP) method of Boys and Bernardi, this scheme is referred to as the "virtual" CP (VCP) method.

The recent discussion of BSSE has been focused on two issues: (a) Is it really worth the effort to remove BSSE? (b) Which procedure, FCP or VCP, is correct? The first question is still being asked despite a number of well-documented cases reported in the literature that show that uncorrected interaction energies yield nonsensical values as the result of the contamination of $\Delta E$ with monomer energy terms.[113,192-197] The recently raised doubts originate from the fact that there have also been reported some cases where the uncorrected values of the interaction energy, if compared to the experimental or more accurate results, look reliable enough and after using FCP or VCP method do not apparently improve or even seem to deteriorate.[190,198] In particular, in intermolecular correlation energy calculations with small or medium bases the correlation contribution may be so drastically reduced that it seems "unbelivable" that the CP method does not overcorrect for BSSE.[155,182,183,199] However, in the cases where basis set effects were carefully studied, this reduction was fully rationalized by an analysis of other basis set effects.[64,151,178,196,197,200,201] Indeed, the above arguments against the CP method overlook the fact that it does not make and is not intended to make a basis set better suited for intermolecular interactions calculations.[113,186,202] Neither is the magnitude of the CP correction useful in estimating the error of the interaction energy. Its only role is to remove the monomer energies' contamination from the interaction energy. To rationalize the value of the interaction energy corrected for the BSSE, one should analyze the accuracy of the dominant components of the interaction energy for a given basis set.

A second question has also been discussed recently.[18,114,128,151,179,180] It has been pointed out that the interpretation of the Pauli principle which leads to the VCP method does not make sense if extrapolated to the complete basis set limit.[114,151] Moreover, for basis sets ranging from minimal to complete there is good reason to consider the effect of the Pauli principle as inherent to the interaction, which is the assumption of the FCP method. Extended calculations for $He_2$[114,151] have demonstrated that the VCP method does not seem to remove the whole monomer energy contamination. Indeed, the VCP results have shown strange behavior, similar to uncorrected results and in contrast to the FCP results. The recent proof of Collins and Gallup[179] that the FCP method overcorrects interaction energies has been also questioned by Gutowski et al.,[180] who pointed out that the authors tacitly assumed that the Heitler–London interaction energy is not affected by the BSE effect. Several other papers have recently come up with support of FCP vs VCP.[178,200,201]

To summarize: although it is not yet possible to prove rigorously what is the correct CP method, it seems that (1) the VCP method should be rejected and (2) the FCP method has, in general, a very beneficial effect.

It should be noted that gradient optimizations of the complex geometry,[203] based on minimization of the dimer energy, are affected by the BSSE. The example of the linear $H_2$–$H^-$ complex proved that BSSE, at the MBPT(4) level of theory, shortens the intersystem distance by 0.1 Å, for a relatively large spd basis set.[204] A similar effect has been observed for $(H_2)_2$ at the MBPT(2) level.[205] Incorporation of the FCP method to gradient optimizations is of great interest; cf. also van Lenthe et al.[18]

### *2. Basis Set Extension Effects on Different Components of the Interaction Energy*

Basis set extension effects on individual contributions to the interaction energy are sometimes referred to as higher-order basis set superposition errors.[117,206] The name "error" is unfortunate since BSE effects may be beneficial for some components of the interaction energy and do not cause any basis set inconsistency when eq 15 is used. There have been several attempts to remove higher-order BSSE.[89,185,207,208] Below we will discuss how BSE effects affect various interaction energy terms.

The electrostatic interaction may be severely contaminated by BSE effects.[206] This is due to the artificial deformation of the electronic charge clouds of the isolated monomers. Although the same is true for polarizabilities,[206] if induction and dispersion are calculated from variational principles, any enlargement of the basis almost always gives better values for these terms. The dimer-centered basis set was proposed for induction and dispersion calculations by Jeziorski and van Hemert.[50] In fact, BSE may partly make up for the lack of higher symmetry polarization functions, which is a very desirable effect.[46,56] The role of the partner orbitals ("ghosts") will be greater the more the monomer charge cloud penetrates the vicinity of the partner. The relative role of ghosts may thus serve as a measure of the "charge-transfer" effects but this role depends strongly on a basis set. In a basis set independent treatment this term eludes rigorous definition since only the total electron density is well defined.

Use of the dimer-centered basis set seems to be beneficial in calculations of first-[79a,116] and crucial for the second-order exchange effects[56,209] and may be a remedy for the too fast decay of Gaussian wave functions. Moreover, the use of the dimer basis in calculations of the first-order interaction energy ensures vanishing of the dominant components of the zeroth-order exchange term,[79a,116] which is an unwanted and unphysical contribution.

Proper consideration of BSE effects on the supermolecular interaction energy is particularly important if one wants to split the interaction energy into different contributions. The popular decomposition of Kitaura and Morokuma[115,210] does not take into account this problem. Sokalski et al.[117] and Cammi et al.[118] attempted to correct this drawback but did not use the same basis set for all components of the interaction energy. This does not seem to be consistent in view of the recent studies.[103,114,151]

## *V. Ab Initio Calculations for Small van der Waals Complexes*

### A. Two-Body Potentials

At present, for small dispersion bound systems, not only are the ab initio potentials far from the Kołos–Wolniewicz standard[9] but they are rarely of spectroscopic quality (1% error). In fact, an error in the interaction energy up to 10% or larger is not uncommon. This total error in the potential is in general the result of a balance of several methodological and numerical errors that may either enhance or fortuitously cancel each other. To trace the origin and to estimate the magnitude of this error are extremely difficult, particularly in the case of supermolecular calculations. In general, all results reported below suffer primarily from (a) lack of high polarization functions (g, h, i, ...), (b) nonnegligible BSSE, and (c) neglect or too approximate treatment of higher than two-electron clusters.

With regards to the comparison with experimental data, two facts should be kept in mind. First, the relationship between the potential and the experiment is never straightforward.[211] (For instance it requires inversion of scattering cross-section data or transport and virial coefficients.) Second, different experiments probe only certain regions of the total potential. Third, quite different potentials may be equally good from the point of view of agreement with available experimental data; therefore such a comparison may not be discriminating enough.

In Table III we have collected references (basically since 1980 but important earlier papers are also included) to ab initio calculations of small systems along with the information on the basis sets and methods used. The theoretical values of the depth of the van der Waals minimum, $D_e$, and its position, $R_e$, are also given and compared with the experimental values.

### 1. Ground State of $He_2$

The ground state of $He_2$ is one of the most studied van der Waals systems. $He_2$ is the smallest system easily accessible to experiments; therefore it has been the object of numerous ab initio calculations which can be compared with a great deal of precise experimental data. It has also been widely used to analyze different contributions to the interaction energy and to verify the efficiency of ab initio quantum mechanical methods designed to study weak intermolecular forces. Interestingly, the He dimer is also one of the more difficult systems to treat accurately because the interaction energy is very small (of the order of 10 K) and attraction is almost entirely determined by the dispersion energy.

For more than 10 years, the potential of Liu and McLean[212] has been considered to be the best ab initio potential for $He_2$. It has never been published by the authors although it has been made available to experimental groups who have compared it to several other potentials.[213] This potential was shown to nearly coincide with the empirical HFIMD potential of Feltgen et al.[213] The former predicted $D_e$ of 10.76 K and the latter $D_e$ of 10.74 K. In the short range ($R = 1.0$–$3.0a_0$) the best ab initio potential is that of Ceperley and Partridge,[214] obtained by the Monte Carlo method.

Recently, the best experimentally determined potentials of Feltgen et al.[213] and Aziz et al.[215] as well as the ab initio calculation by Liu and McLean have been challenged. The new empirical work of Aziz et al.[216] predicted a larger $D_e$ of 10.948 K, and van Lenthe et al.[134] in ab initio MR CI calculations, with a basis set including functions through h symmetry, obtained a $D_e$ of 10.86 K. Interestingly, the BSSE would lower this result by 12.5 K! This fact illustrates both the practical inability of "killing" BSSE by saturation of the basis set (at the present state of the art) as well as the adequacy of the FCP method which was used by the authors.

Several other calculations are reported in Table III, some of which are less accurate than those discussed above, although they are also of interest. In particular, one can see that the pair electron correlation level of theory leads approximately to 10% error in the potential (cf. the results in Table III).

An interesting perturbation study of the interaction energy in $He_2$ has been published by Rybak et al.[54] The interaction energies were obtained at a few points and agree very well with the HFIMD potential[213] (at $5.6a_0$ $D_e = 10.56$ K). Strictly speaking, the interaction energies were obtained in a piecewise manner as the sum of the interaction energy at the SCF level from Liu and McLean,[112] the exchange repulsion correlation contribution from Chałasiński and Gutowski,[79a] the dispersion term calculated with the explicitly correlated extended Gaussian basis set at the incomplete CHF level, the exchange dispersion, and third-order interaction energy terms. The last three terms were obtained by the authors of ref 54.

### 2. Ground State of $HeH_2$

The potential energy surface of $HeH_2$ provides the simplest example of an anisotropic interaction between two neutral closed-shell systems and has therefore received considerable attention from theoreticians[122,149,217] (for earlier references, see Burton and Senff[149]). The He atom is attracted to the $H_2$ molecule at the SCF level by the quadrupole-induced dipole interaction, but the dominant attractive contribution is due to the dispersion energy. Until now, the best ab initio potential energy surface is that reported by Meyer et al.[122] This potential has recently been found[218] to reproduce a variety of the measurement of scattering cross sections and bulk properties and its anisotropic part seems to be better than that of the highly regarded semiempirical potential of Schafer and Gordon.[219] Yet, the best experimental $D_e$ of 49 μhartrees[220] differs from the ab initio value by more than 10%.

The potential of Meyer et al.[122] was obtained in a piecewise manner. All calculations were done starting from occupied Hartree–Fock MOs localized according to the Boys criterion,[120] to distinguish between intramonomer and intermonomer correlation effects. The intermonomer correlation (dispersion) was calculated by the pseudo natural orbital CI method with carefully chosen configurations corresponding to the asymptotically most important single–single and single–double excited configurations. To evaluate the intramonomer correlation energy, the CEPA method was used and the result was corrected by means of the FCP method. Different basis sets were used for intermonomer and intramonomer correlation contributions.

Recently, Senff and Burton[149] carried out CEPA2 calculations for this system with a large, carefully selected basis set. Their potential is even shallower than that of Meyer et al., which may be partly due to the pair electron correlation approximation. They also pointed out that the potential of Meyer et al. may benefit to some extent from the fortuitous cancellation of errors.

### 3. Ground State of $(H_2)_2$

Although quadrupole–quadrupole interaction is not negligible in $(H_2)_2$, the dominant attractive contribution is due to the dispersion term.

Until now, the most accurate potential for $(H_2)_2$ is the improved version of the work of Schaefer and Meyer[221] by Meyer and Schaefer[222] and Schaefer and Liu.[223] Some results of these unpublished calculations were disclosed in the paper of Buck et al.[224] When compared with the experimental data, this potential is too shallow by 5%.[224] Because the details of these calculations have not been published, it is difficult to assess the actual error of the results.

Recently, CEPA2 calculations with a relatively large basis set have been reported.[148] The resulting well depth turned out to be too small by 30%, probably due to the pair electron correlation approximation and unsaturation of the basis set.

Stationary points on the MBPT(2) surface have recently been investigated by Schneider et al.[205] The T-shaped structure has been established as a minimum.

$(H_2)_2$ has been used as a model testing system for computational methods. In these cases the calculations are limited to the T-configuration at an $H_2$–$H_2$ distance of $6.5a_0$. At this geometry full CI calculations were carried out[225] with the basis of Burton and Senff,[148] which led to the conclusion that, at the CEPA2 level, 10% of the potential well is missing with respect to full CI level. At the same geometry but with poorer basis sets, the MBPT theory was tested by Hobza et al.[197]

### 4. Ground State of $Li^+He$

Compared with $He_2$ this is a farily strong complex (100 times stronger) and is bound already at the SCF level by 2600 $\mu$hartrees, primarily due to the charge-induced dipole interaction. The best potential to date was calculated at the CEPA2 level with a large basis set by Senff and Burton.[150] The calculations were much more extensive than the previous ones of Hariharan and Staemler[226] but a comparison with the experimental data of Viehland[227] has revealed that the potential is too deep by 10%. The origin of this discrepancy is not clear.

### 5. Ground State of $Li^+H_2$

To the best of our knowledge, the potential hypersurface of Kutzelnigg et al.[123] from 1973 is still the best ab initio potential for this system. The complex is bound by ca. 5 kcal/mol[123] at the SCF level due to charge-quadrupole and charge-induced dipole interactions which favor the T-shaped configuration. Correlation effects in these calculations do not exceed 5% of the total $D_e$. Consequently, both the SCF and correlated curves were found satisfactory in theoretical studies of inelastic scattering of $H_2$ by $Li^+$.[228]

### 6. Ground State of LiHe

This is one of the weakest complexes studied: an order of magnitude weaker than $He_2$. The fact that mixed alkali metal–rare gas dimers are weaker than both the alkali metal dimers and the rare gas dimers is well known.[229] At long range the LiHe potential must fall at a greater rate than the $He_2$ potential because of greater polarizability of Li. However, the exchange repulsion is also much stronger due to the very diffuse character of the 2s orbital of Li, virtually undeformed by the He atom. An early potential was obtained by Das and Wahl using the MCSCF method,[230] but the well depth was 3 times as deep as that predicted by the experimental work of Dehmer and Wharton.[231] The discrepancy may be attributed to BSSE. The VB calculations of Cremaschi et al.[137] (though not very extensive) predicted a value of the well depth 30% larger than the experimental value.

### 7. Ground State of $HeH^-$

Only a very approximate estimate of the potential energy curve was calculated by Olson and Liu using the MCSCF and CI methods.[232] These calculations indicate $R_e \sim 15a_0$ and $D_e \sim 13$ $\mu$hartrees but the basis set was not appropriate for dispersion calculations and hence these values are probably not highly reliable.

### 8. Ground State of HeH

There is a surprising lack of information on the ground state of this molecule. The only ab initio potential for HeH is that of Das et al. obtained by the MCSCF method.[233] It is 1.5 times as deep as the semiempirical HFD potential of Scoles.[234]

### 9. Ground State of $H_2H^-$

There is no experimental evidence on this system, only suspicion that it may exist in the interstellar space.[235] The best potential for the linear optimal geometry has been obtained at the MBPT(4) level of theory by Chałasiński et al.[204] The attraction is primarily due to charge-quadrupole and charge-induced dipole interactions already at the SCF level.[204,236] Correlation effects are, however, also important. They shift the position of the minimum by 0.4 Å and yield 30% of the $D_e$, which equals 1.2 kcal/mol.

### 10. Ground State of BeHe

There are no experimental data for this system. The only ab initio calculations with a rather limited basis set and without correction for BSSE are those of Chiles and Dykstra.[237] The van der Waals minimum is shallower and the internuclear distance longer than in the case of $He_2$: $D_e$ and $R_e$ amount to 25 $\mu$hartrees and $9a_0$, respectively.

### 11. Ground State of $Be_2$

The ground state of the Be dimer has for some time been the subject of a great deal of theoretical interest and calculations (cf. the recent review by Harrison and Handy[238]). The origin of the difficulty is the 2s,2p near degeneracy of Be, which makes linked triple and quadruple electron clusters unusually important.[239] If treatment of correlation is inadequate and/or the basis set is not extended enough, a shallow well at $8$–$9a_0$ is observed.[239] In particular, single-configuration reference pair theories are not appropriate[239] despite the good performance of MBPT(4).[181] The high-accuracy study of Lengsfield et al.[132] predicted a potential well of 1.87 kcal/mol with a minimum at $4.73a_0$. This result was later confirmed by Harrison and Handy,[225] who also predicted nine bound vibrational levels.[238] The first spectroscopic measurements of laser-induced fluores-

**TABLE III. Ab Initio Calculations of Weak Interactions between Small (up to Four-Electron) Monomers ($D_e$ = van der Waals Minimum Depth, $R_e$ = Equilibrium Distance)**

| authors, basis set[a] | method[b] | $D_e$,[c] μhartrees | $R_e[a_0]$[d] |
|---|---|---|---|
| | $He_2$ | | |
| Liu and McClean,[212] STO | ICF | 34.07 | 5.62 |
| Lowther and Coldwell,[280] | variational Monte Carlo | 35 | 5.60 |
| Chiles and Dykstra,[281] CGTO [6s2p2d] | CEPA0 | 29.00 | 5.94 |
| | CEPA1 | 27.89 | 5.99 |
| | CEPA2 | 28.45 | 5.99 |
| | CCSD | 27.27 | 5.74 |
| Collins and Gallup,[138] CGTO [2s3p1d] | VB | 31.13 | 5.6[u] |
| Tatewaki et al.,[282] STO [3s2p2d1f] | CI | 29–30 | 5.6[u] |
| Senff and Burton,[150] CGTO [8s5p3d2f + (1s1p)*] | CEPA2 | 29.75[c] | 5.67 |
| Gutowski et al.,[151] CGTO [7s3p2d1f1g1h] | CEPA1 | 28.98[c] | 5.6[u] |
| Sauer et al.,[196] CGTO [7s4p3d] | MBPT(2) | 16.9[c] | 5.6[u] |
| Chałasiński,[283] CGTO [4s3p2d1f] | MBPT(2) | 18.4[c] | 5.6[u] |
| | MBPT(3) | 26.6[c] | 5.6[u] |
| | MBPT(4)-DQ | 26.6[c] | 5.6[u] |
| | MBPT(4)-SDQ | 27.0[c] | 5.6[u] |
| | MBPT(4) | 29.8[c] | 5.6[u] |
| | CCD | 25.4[c] | 5.6[u] |
| Rybak et al.,[54] ECG | picewise approach | 33.00 | 5.6[u] |
| van Lenthe et al.,[134] CGTO [7s4p4d2f1g1h + (2s2p1d)*] | MR CI | 34.39[c] | 5.6[u] |
| | empirical[215] | 34.20 | 5.61 |
| | empirical[213] | 34.01 | 5.62 |
| | empirical[216] | 34.67 | 5.60 |
| | $HeH_2$, Isotropic[e] | | |
| Meyer et al.,[122] CGTO | | | |
| dispersion: He[7s4p2d1f], H[6s3p1d(2d1f)*] | CI + CEPA + RSPT | 42.26[c] | 6.43 |
| SCF, intra: He[10s4p2d], H[6s3p1d(1p1d)*] | | | |
| Senff and Burton,[149] CGTO | | | |
| He[8s4p3d1f(1s1p)*], H[6s4p1d(1d1f)*] | CEPA2 | 39.75[c] | 6.46 |
| | empirical[220] | 49 | 6.33 |
| | semiempirical[284] | 43.3 | 6.38 |
| | semiempirical[284] | 39.3 | 6.48 |
| | $(H_2)_2$, Isotropic[e] | | |
| Schaefer and Meyer[221] unpublished results, see ref 224 | | 102 | 6.5 |
| Meyer and Schaefer[222] unpublished results, see ref 224 | | 105 | 6.69 |
| Schaefer and Liu[223] unpublished results, see ref 224 | | 105 | 6.69 |
| Burton and Senff,[148] CGTO [4s3p(1s1p)*(1d)] | CEPA2 | 76.8[c] | 6.50 |
| Chałasiński[78] | piecewise approach | 107 | 6.50[u] |
| Lavendy et al.,[285] CGTO [4s3p] | CI | 75 | 6.50 |
| | empirical[224] | 110 ± 5.5 | 6.50 ± 0.05 |
| | $(H_2)_2$, T-Configuration | | |
| Schaefer and Meyer[221] unpublished results, see ref 224 | | 178 | 6.25 |
| Burton and Senff,[148] CGTO [4s3p(1s1p)*(1d)] | CEPA2 | 148.6[c] | 6.5 |
| Harrison and Handy,[225] as in ref 148 | full CI | 165 | 6.5 |
| Chałasiński[78] | piecewise approach | 176 | 6.50[u] |
| Hobza et al.,[197] CGTO [5s4p1d] | MBPT(2) | 119[c] | 6.5 |
| | MBPT(3) | 138[c] | 6.5 |
| | MBPT(4) | 139[c] | 6.5 |
| Lavendy et al.,[285] CGTO [4s3p] | CI | 120 | 6.50 |
| | $HeLi^+$ | | |
| Senff and Burton[150] CGTO [8s5p3d2f(1s1p)*] | CEPA2 | 2955[c] | 3.58 |
| Tatewaki et al.,[282] STO [3s2p2d1f] | CI | 2646 | 3.63 |
| | empirical[227] | 2680 | 3.75 |
| | $Li^+H_2$, T-Configuration | | |
| Kutzelnigg et al.,[123] CGTO Li[6s4p] | | | |
| H[3s1p] | IEPA | 8089 | 3.75 |
| | HeLi | | |
| Das and Wahl,[230] STO Li[3s2p1d1f1h] | | | |
| He[2s2p] | MCSCF | 7.5 | 11.6 |
| Cremaschi et al.,[137] Li[4s1p1d] | | | |
| He[1s1p] | VB | 3.6 | 12.75 |
| | empirical[231] | 2.7 | 12 |
| | $HeH^-$ | | |
| Olson and Liu,[232] STO H[5s3p2d] | | | |
| He[5s5p1d] | CI | 13 | 15 |
| | HeH | | |
| Das and Wahl,[233] STO H[3s1p1d] | | | |
| He[2s1p] | MCSCF | 32.3 | 10 |

**TABLE III** (Continued)

| authors, basis set[a] | method[b] | $D_e$,[c] μhartrees | $R_e[a_0]$[d] |
|---|---|---|---|
| $H_2H^-$, Linear[e] | | | |
| Rayez et al.,[235b] CGTO [5s3p] | CI | 797 | 6.94 |
| Hirao and Yamabe,[236] CGTO [4-31G + 2s + 1p] | CI | 940 | 6.94 |
| Michels and Montgomery,[286] CGTO [7s4p1d] | MBPT(4) | 1760[c] | 6.13 |
| Chałasiński et al.,[204] CGTO [5s4p3d1f] | MBPT(4) | 1850[c] | 5.95 |
| HeBe | | | |
| Chiles and Dykstra,[237] CGTO He[5s2p1d] | CEPA0 | 24.4 | 9.00 |
| Be[7s3p1d] | CEPA2 | 25.1 | 9.01 |
| | approx CCD | 20.8 | 9.14 |
| $Be_2$ | | | |
| Blomberg et al.,[239] CGTO [7s3p2d] | MRCI | 1430 | 4.9 |
| | ICF | 2230 | 4.8 |
| Chiles and Dykstra,[281] CGTO [7s3p1d] | CEPA0 | 5900 | 4.62 |
| | CEPA2 | 5300 | 4.89 |
| | CCSD | 70 | 9.13 |
| Liu and McLean,[131] Lengsfield et al.,[132] STO [6s4p2d1f] | ICF | 2980 | 4.73 |
| Harrison and Handy,[225] CGTO [8s5p2d1f] | full CI | 2960 | 4.75 |
| Lee and Bartlett,[154] CGTO [7s3p1d] | MBPT(4) | 1390 | 5.5 |
| | CCSD | 110 | 9.5 |
| | CCSDT-1 | 70 | 8 |
| Diercksen et al.,[181] CGTO [7s3p2d2f] | MBPT(2) | 1510 | 5.35 |
| | MBPT(3) | 2340 | 5.10 |
| | MBPT(4) | 2920 | 4.87 |
| | empirical[240] | 3600 | 4.63 |

[a] CGTO = contracted Gaussian-type orbitals, STO = Slater-type orbitals, ECG = explicitly correlated Gaussians. Number of individual CGTO or STO are given in square brackets; bond functions are indicated by asterisk. [b] For the sake of comparison the best empirical results are also given and indicated by "empirical". [c] Results obtained by means of the CP method (BSSE removed) are indicated by superscript "c". [d] If the equilibrium distance has not been optimized, it is indicated by superscript "u". [e] The $R_e$ distance is measured from the midpoint of the $H_2$ bond.

cence appeared a year later.[240] These results show $D_e = 2.25 \pm 0.08$ kcal/mol at $R_e = 4.63a_0$, in fairly good agreement with the theoretical calculations.

The interpretation of the origin of the well for $Be_2$ has also been a subject of interest. Chałasiński attributed the small-$R$ well to unusually strong (for a closed-shell neutral system) mutual polarization of Be atoms (due to exchange deformation effects and large polarizability of the Be atom) and the importance of the exchange repulsion correlation effects, which are attractive in this case.[80] Gerratt proposed that the qualitative nature of the ground-state curve may be accounted for by an avoided crossing between two states of $^1\Sigma_g^+$ symmetry correlating with two $^1S(1s^22s^2)$ atoms and with two $^3P(1s^22s2p)$ atoms.[241] The role of the core–valence shell interatomic correlation effects was analyzed by Roeggen et al.[242]

Ab initio calculations of the ground state of $Be_2$ were aptly described by Harrison and Handy[238] as "a success story for those who perform high accuracy quantum chemistry". However, in order not to be carried away by the enthusiasm we should remember that $Be_2$ is a very small, model system and the highest level of theory and technology was necessary to obtain a not very accurate result that is still not fully understood.

## B. Nonadditive Effects

To characterize complexes composed of more than two monomers one has to account for all pair interactions as well as to allow for nonpairwise additive effects. Although nonadditive effects are in general much smaller than the additive part of the interaction energy, they can be significant when considering the properties of bulk matter and molecular clusters.

Because nonadditive effects are usually 1 or 2 orders of magnitude smaller than additive effects, only when the pair potential is known precisely at all distances can serious work on the problem of nonadditive effects be started. This has, however, not been achieved yet, except for the $^3\Sigma_u^+$ state of $H_2$ and the ground state of $He_2$. Consequently, reliable ab initio calculations of nonadditive effects are still rare even for small systems. On the other hand, there is a great need for such calculations. Let us mention in this context the recent unresolved discrepancy between theoretical and experimental estimates of many-body effects in rare gas crystals.[243,244] The necessity of an incorporation of reliable nonadditive terms into model potentials has also been shown.[245–247]

Basic classification and understanding of nonadditive effects can be achieved by means of perturbation theory (cf. Margenau and Kestner[248] and Piecuch[249]). It turns out that the first-order electrostatic and second-order dispersion effects are pairwise additive. Nonadditive effects appear in (a) the second- and higher-order induction energy, (b) the third- and higher-order dispersion energy, and (c) all exchange effects. In the interactions of polar species the nonadditivity of induction effects is very important. The dominant component of the third-order dispersion nonadditivity is the so-called Axilrod–Teller–Muto triple-dipole nonadditivity.[250,251] The dominant exchange nonadditivity resides in the first-order exchange energy.[107,108]

### 1. Spin-Parallel States of $H_3$ and $H_4$

The first-order exchange nonadditivity for three $^2S$ hydrogen atoms in the quartet state was calculated by Kołos and Leś.[252] A partial wave analysis of the nonexpanded induction and third-order dispersion nonadditive effects was carried out by O'Shea and Meath.[253,254] They also compared these terms to the nonadditive exchange term for the equilateral triangle configuration. The conclusion was the following: for distances smaller than $R_e$ (the position of the van der Waals minimum in the two-body potential), the attractive exchange nonadditivity dominates and, for distances larger than $R_e$, the repulsive third-order dispersion nonadditivity prevails. For $R \sim R_e$ both the effects cancel to a large extent. Second-order exchange terms (exchange induction and exchange dispersion) were found to be of secondary importance.[255] A more detailed analysis of these results has been done by Meath and Aziz.[243]

Although the above results shed new light on the origin and importance of various nonadditive terms, they are still not complete enough. First, higher than triple-dipole terms in the partial wave expansion of dispersion nonadditivity were neglected. Second, it is extremely difficult to obtain accurate estimats of second- and higher-order nonadditive exchange effects.

The first-order exchange nonadditivity has also been studied in the quintet state of $H_4$.[252] The four-body effect proved to be repulsive and to amount to a few percent of the three-body exchange term in tetrahedral and square configurations.

### 2. $He_3$ and $He_4$

An analysis of the total nonadditive effect in the equilateral triangle configuration of $He_3$ has recently been given by Bulski and Chałasiński.[107] The first-order exchange nonadditivity obtained by Jeziorski et al.[107] was compared to the exchange-dispersion nonadditivity and to the approximate nonexpanded triple-dipole nonadditivity.[107] The relative role of those terms was found to be very similar to the $H_3$ case. The two dominant nonadditive effects (first-order exchange and triple-dipole) have opposite signs and tend to cancel for $R \sim R_e$ (this trend is in fact observed for all rare gas trimers[243,256,257]), and the exchange dispersion term (in general, of secondary importance only) may be significant in this particular region. The results of the supermolecular MBPT(3) calculations of Wells and Wilson[258] obtained at $R = 5.6a_0$ agree fairly well with the perturbational results. The total nonadditivity amounts at $R_e$ to $-0.15$ K, which is ca. 1% of $D_e$ for $He_2$.

The first-order exchange term was studied in $He_4$ by means of the effective electron model.[259] As in the $H_4$ case the four-body effect was repulsive and amounted to a few percent of the three-body first-order exchange term.

### 3. $Be_3$ and $Be_4$

The important role of three- and four-body nonadditive effects in beryllium clusters is a very intriguing phenomenon as $Be_3$ and $Be_4$ were found to be relatively much more stable than $Be_2$. A number of calculations on beryllium clusters have been recently published[108,260–266] and recently reviewed by Harrison and Handy.[238] So far Harrison and Handy have obtained the most accurate results.[238] $Be_3$ ($D_{3h}$) turns out to be bound only at the correlated level ($D_e = 24 \pm 2$ kcal/mol, $R_e = 4.22a_0$).[238] $Be_4$ ($T_d$) is bound already at the SCF level (this unusual fact was first noted by Brewington et al.[267]) and the minimum becomes deeper at the correlated level ($D_e = 75 \pm 5$ kcal/mol, $R_e = 3.9 \pm 0.1a_0$).[238] Enhanced stability of $Be_4$ ($T_d$) was attributed to significant sp hybridization.[260,266–268]

Unfortunately, a consistent evaluation of all two-, three-, and four-body terms, not contaminated by the basis set and methodological artifacts, has not been yet accomplished. Perturbation[108,269] and SCF[270] calculations of nonadditive effects in $Be_3$ proved the unusual importance of the first-order exchange and the exchange deformation nonadditivities. However, because of large exchange effects and the 2s,2p near degeneracy of the Be atom, the perturbation approach is not appropriate in the region of the minimum.

### 4. $(H_2)_3$

The first-order three-body contribution to the interaction energy of three hydrogen molecules, for intermolecular distances close to $R_e$, has been calculated and analyzed by Leś and Radzio.[271] The effect was found to be almost equal but of opposite sign to the Axilrod–Teller–Muto contribution.

### 5. $H^-(H_2)_2$

This system has been investigated as a model of anion–solvent molecule interaction. There is no experimental evidence on this system, only the suspicion that it may exist in the interstellar space.[235] Its structure and energy have been recently investigated.[235,236,272] So far Kendall et al. have obtained the most accurate results.[272] At the MBPT(2) level of theory they found the global minimum of the potential surface for the V-shaped geometry of the complex, with the hydride at the base of the V. The supermolecular MBPT(4) calculations gave interaction energy −2.75 kcal/mol. The three-body contribution to the interaction energy was found to be large (16.5%) and cause the geometry of the complex to be nonlinear. The thermodynamic stability of $H^-(H_2)_2$ cluster was predicted to be unlikely, but a few of the isotopically substituted complexes were predicted to be stable.

## VI. Summary and Outlook

In the preceding sections the current state of ab initio investigations of intermolecular interactions from the perspective of small van der Waals complexes has been presented. There are a few conclusions that are important to stress when discussing the future of such studies.

The perturbation approach has provided and will continue to provide the basic conceptual framework for our understanding of the nature of intermolecular forces. This approach yields not only expressions for the dominant interaction energy contributions but also valuable interpretations. This knowledge is important both in ab initio studies and for building empirical, semiempirical, and model potentials. Recently, calculations of the dispersion term and related damping functions have been of great interest to both experimentalists and theoreticians. We should mention, however, the problems with convergence of the perturbation expansion, which are related to the exchange (symmetry) effects, discussed in section II.C.. These problems still need to be solved in a fully satisfactory way.

At present and in the nearest future, the bulk of numerical information on intermolecular interactions is expected to be provided by the supermolecular approach. In this context the MR CI method has proven to be the most accurate and versatile, although the most expensive. It provides results that often explain the experimental data but it does not bring about much of the physical and chemical "understanding". The CC approach in its numerous variants is expected to become an important alternative approach. In many cases the electron-pair correlated level of theory may give very useful and reliable results. It should be stressed, however, that in the case of dispersion-bound complexes this approximation is sometimes insufficient (for example when a higher accuracy is required or if one deals with a difficult case such as the alkaline earth metal complexes) and one should recourse to the CCSDT method or even to the multiconfiguration reference CC method. These higher levels of the CC approach have recently been rapidly developing.

The VB and MBPT methods seem well suited for approximate treatments. The latter method is particularly attractive because it is uniquely defined, size consistent, facile to apply, and efficient. Not surprisingly, one already witnesses a boom of MBPT calculations. One should, however, be even more conscious of the limitations of this method.

It should be noted here that ab initio quantum chemistry codes, over the past few years, have been becoming more and more easily accessible to a wide chemical community. However, whereas the codes are "user friendly" (e.g., GAUSSIAN 86), to select the proper method and the basis set for a particular intermolecular interactions problem remains far from trivial. Moreover, the basis sets available in many libraries and collections need, at least, supplemental functions and modifications of the contraction schemes.

The basis set saturation problem in the case of intermolecular interactions calculations persists and is found to be very difficult. It is still very expensive to avoid BSSE directly, even at the SCF level. At the correlated level BSSE is frequently hopelessly large, and it seems that present ab initio quantum chemical codes and state-of-the-art computers are not capable of using basis sets that are big enough to guarantee negligible BSSE. Therefore, at least for some time, we will have to work with basis sets producing BSSE that must subsequently be removed by means such as the CP method. A number of valuable results have already been obtained in this way. For complexes that are bound by dispersion forces, an extra difficulty arises from the fact that accurate intermonomer correlation calculations require higher symmetry polarization functions. Whereas the role of these functions has already been elucidated in the case of closed-shell atoms, there is practically no experience for molecules.

Calculations for small systems are not likely to be abandoned in the near future since the interplay between theory and experiment demands further refinements of theory and more and more accurate experimental data. In particular, small systems may serve as good models for the studies of two difficult aspects of intermolecular interactions: (a) the effects of the anisotropy of interactions and (b) the nonadditive effects. Rigorous studies of these effects have barely started.

## VII. Acknowledgments

We thank Prof. J. P. Simons for his kind hospitality during our stay in Salt Lake City and for numerous helpful discussions as well as reading and commenting on the manuscript. Profs. W. Kołos and F. B. van Duijneveldt and Drs. M. Bulski, D. Funk, B. Jeziorski, P. Piecuch, K. Szalewicz, and M. Szczęśniak are greatly acknowledged for their helpful remarks on the manuscript. This work was supported by the National Science Foundation (Grant CHE-8511307), the U.S. Army Research Office (Contract DAAG-2984K0086), and the Polish Academy of Sciences (Grant CPBP.01.12).

## VIII. Abbreviations

| | |
|---|---|
| BSE | basis set extension |
| BSSE | basis set superposition error |
| CC | coupled cluster |
| CCSDT | coupled cluster singles, doubles, and triples |
| CEPA | coupled electron pair approximation |
| CHF | coupled Hartree–Fock |
| CI | configuration interaction |
| CP | counterpoise procedure |
| FCP | full counterpoise procedure |
| HF | Hartree–Fock |
| ICF | interacting correlated fragments |
| IEPA | independent electron pair approximation |
| MBPT | many-body perturbation theory |
| MCSCF | multiconfiguration self-consistent field |
| MPPT | Møller–Plesset perturbation theory |
| MR CI | multiconfiguration reference state configuration interaction |
| PA | polarization approximation |
| PA RSPT | polarization approximation Rayleigh–Schrödinger perturbation theory |
| PT | perturbation theory |
| RSPT | Rayleigh–Schrödinger perturbation theory |
| SAPT | symmetry-adapted perturbation theory |
| SCF | self-consistent field |
| UCHF | uncoupled Hartree–Fock |
| VB | valence bond |
| VCP | virtual counterpoise procedure |

## IX. References

(1) Debye, P. *Phys. Z.* **1920**, *21*, 178.
(2) Keesom, W. H. *Phys. Z.* **1921**, *22*, 129.
(3) London, F. *Z. Phys. Chem.* (*B*) **1930**, *11*, 222.
(4) London, F. *Trans. Faraday Soc.* **1937**, *33*, 8.
(5) Eisenschitz, R.; London, F. *Z. Phys.* **1930**, *60*, 491.
(6) Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Co.: San Francisco, 1982.
(7) Fried, V.; Hameka, H. F.; Blukis, U. *Physical Chemistry*; Macmillan: New York, 1977.
(8) Peek, J. M. Sandia Laboratory Research Report SC-RR-65-77, 1965.
(9) Kołos, W.; Wolniewicz, L. *Chem. Phys. Lett.* **1974**, *24*, 457.
(10) Chipman, D. M.; Hirschfelder, J. O. *J. Chem. Phys.* **1973**, *59*, 2838.
(11) Kreek, H.; Meath, W. J. *J. Chem. Phys.* **1969**, *50*, 2289.
(12) Jeziorski, B.; Kołos, W. *Int. J. Quant. Chem.* **1977**, *XII, Suppl 1*, 91.
(13) Kołos, W. *Int. J. Quant. Chem.* 1974, *S8*, 241.
(14) Koide, A.; Meath, W. J.; Allnatt, A. R. *Chem. Phys.* **1981**, *58*, 105.
(15) van der Avoird, A.; Wormer, P. E. S.; Mulder, F.; Berns, R. M. *Top. Curr. Chem.* **1980**, *93*, 1.
(16) Jeziorski, B.; Kołos, W. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1982; Vol. 3.
(17) Kołos, W. In *New Horizons of Quantum Chemistry*; Lowdin, P.-O., Pullman, B., Eds.; D. Reidel: Dordrecht, 1983.
(18) van Lenthe, J. H.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Adv. Chem. Phys.* **1987**, *69*, 521.
(19) Arrighini, P. *Intermolecular Forces and Their Evaluation by Perturbation Theory*; Springer-Verlag: Berlin, 1981.

(20) Kaplan, I. G. *Theory of Molecular Interactions*; North-Holland: Amsterdam, 1986.
(21) Hirschfelder, J. O. *Chem. Phys. Lett.* **1967**, *1*, 325.
(22) (a) Claverie, P. *Int. J. Quant. Chem.* 1971, *5*, 273. (b) Claverie, P. In *Intermolecular Interactions: From Diatomics to Biopolymers*; Pullman, B., Ed.; Wiley: New York, 1978.
(23) Kutzelnigg, W. *J. Chem. Phys.* **1980**, *73*, 343.
(24) Chipman, D. M.; Bowman, J. D.; Hirschfelder, J. O. *J. Chem. Phys.* **1973**, *59*, 2830.
(25) Meath, W. J. *Am. J. Phys.* **1972**, *40*, 21.
(26) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1964.
(27) Casimir, H. B. G.; Polder, D. *Phys. Rev.* **1948**, *73*, 360.
(28) Piecuch, P. In *Topics in Molecular Organization and Engineering*; Maruani, J., Ed.; D. Reidel: Dordrecht, 1988; Vol. 2.
(29) Dalgarno, A.; Lewis, J. T. *Proc. R. Soc. London, Ser. A* **1955**, *A233*, 70.
(30) Young, R. H. *Int. J. Quant. Chem.* **1975**, *9*, 47.
(31) Ahlrichs, R. *Theor. Chim. Acta* **1976**, *41*, 7.
(32) Longuet-Higgins, H. C. *Proc. R. Soc. London, Ser. A* **1956**, *A235*, 537.
(33) Murrell, J. N.; Shaw, G. *J. Chem. Phys.* **1968**, *49*, 4731.
(34) Buehler, R.; Hirschfelder, J. O. *Phys. Rev.* **1951**, *83*, 628; **1952**, *85*, 149.
(35) Ng, K. C.; Meath, W. J.; Allnatt, A. R. *Mol. Phys.* **1976**, *32*, 177.
(36) Ahlrichs, R.; Penco, R.; Scoles, G. *Chem. Phys.* **1977**, *19*, 119.
(37) Koide, A. *J. Phys. B* **1976**, *9*, 3173.
(38) Feltgen, R. *J. Chem. Phys.* **1981**, *74*, 1186.
(39) Knowles, P. J.; Meath, W. J. *Chem. Phys. Lett.* **1986**, *124*, 164.
(40) Cusachs, L. C. *J. Chem. Phys.* **1963**, *38*, 2038.
(41) Ng, K. C.; Meath, W. J.; Allnatt, A. R. *Mol. Phys.* **1977**, *33*, 699.
(42) Ng, K. C.; Meath, W. J.; Allnatt, A. R. *Mol. Phys.* **1979**, *38*, 449.
(43) Koide, A.; Proctor, T. R.; Allnatt, A. R.; Meath, W. J. *Mol. Phys.* **1986**, *57*, 491.
(44) Varandas, A. J. C. *Mol. Phys.* **1987**, *60*, 527.
(45) Magnasco, V.; Figari, G. *Mol. Phys.* **1987**, *60*, 625.
(46) Gutowski, M.; Verbeek, J.; van Lenthe, J. H.; Chałasiński, G. *Chem. Phys.* **1987**, *111*, 271.
(47) Chałasiński, G.; van Lenthe, J. H.; Groen, T. P. *Chem. Phys. Lett.* **1984**, *110*, 369.
(48) Knowles, P. J.; Meath, W. J. *Mol. Phys.* **1986**, *59*, 965.
(49) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
(50) Jeziorski, B.; van Hemert, M. *Mol. Phys.* **1976**, *31*, 713.
(51) Musher, J. I.; Amos, A. T. *Phys. Rev.* **1967**, *164*, 31.
(52) Broussard, J. T.; Kestner, N. R. *J. Chem. Phys.* **1970**, *53*, 1507; **1973**, *58*, 3593.
(53) Szalewicz, K.; Jeziorski, B. *Mol. Phys.* **1979**, *38*, 191.
(54) Rybak, S.; Szalewicz, K.; Jeziorski, B.; Jaszuński, M. *J. Chem. Phys.* **1987**, *86*, 5652.
(55) Rybak, S.; Jeziorski, B., to be published. Rybak, S. Ph.D. Thesis, University of Warsaw, 1988.
(56) Chałasiński, G. *Mol. Phys.* **1983**, *49*, 1353.
(57) Langhoff, P. W.; Epstein, S. T.; Karplus, M. *Rev. Mod. Phys.* **1972**, *44*, 602 and references therein.
(58) McWeeny, R. *Croat. Chim. Acta* **1984**, *57*, 865.
(59) Sadlej, A. *J. Chem. Phys.* **1981**, *75*, 320.
(60) Cole, S. J.; Szalewicz, K.; Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1986**, *84*, 6833.
(61) Kochanski, E. *J. Chem. Phys.* **1973**, *58*, 5823.
(62) Groen, T. P. Program INTACT, Internal Report, Utrecht, 1975. van Lenthe, J. H. INTACT-ATMOL version, 1983.
(63) Roszak, S.; Sokalski, W. A.; Hariharan, P. C.; Kaufman, J. J. *Theor. Chim. Acta* **1986**, *70*, 81.
(64) Szalewicz, K.; Cole, S. J.; Kołos, W.; Bartlett, J. *J. Chem. Phys.*, in press.
(65) Visser, F.; Wormer, P. E. S.; Stam, P. *J. Chem. Phys.* **1983**, *79*, 4973.
(66) Visser, F.; Wormer, P. E. S. *Mol. Phys.* **1984**, *52*, 923.
(67) Visser, F.; Wormer, P. E. S. *Chem. Phys.* **1985**, *92*, 129.
(68) Amos, R. D.; Handy, N. C.; Knowles, P. J.; Rice, J. E.; Stone, A. J. *J. Phys. Chem.* **1985**, *89*, 2186.
(69) Dalgarno, A.; Davison, W. D. *Adv. Atom. Mol. Phys.* **1966**, *2*, 1.
(70) Kaneko, S. *J. Chem. Phys.* **1972**, *56*, 3417.
(71) Jørgensen, P.; Simons, J. *Second Quantization-Based Methods in Quantum Chemistry*; Academic: New York, 1981.
(72) Oddershede, J. *Adv. Chem. Phys.* **1987**, *69*, 201.
(73) Claverie, P. In *Structure and Dynamics of Molecular Systems*; Daudel et al., Eds.; D. Reidel: Dordrecht, 1986; Vol. II.
(74) Dmitriev, Y.; Peinel, G. *Int. J. Quant. Chem.* **1981**, *19*, 763.
(75) Jaszuński, M.; McWeeny, R. *Mol. Phys.* **1985**, *55*, 1275.
(76) Knowles, P. J.; Meath, W. J. *Mol. Phys.* **1987**, *60*, 1143.
(77) Moszyński, R.; Rybak, S.; Jeziorski, B., to be published.
(78) Chałasiński, G. *Mol. Phys.* **1986**, *57*, 427.
(79) (a) Chałasiński, G.; Gutowski, M. *Mol. Phys.* **1985**, *54*, 1173. (b) Chałasiński, G.; van Smaalen, S.; van Duijneveldt, F. B. *Mol. Phys.* **1982**, *45*, 1113.
(80) Chałasiński, G. *Chem. Phys.* **1983**, *82*, 207.
(81) Cohen, H. D.; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, S34.
(82) Wormer, P. E. S.; Rijks, W. *Phys. Rev.* **1986**, *A33*, 2928.
(83) Meyer, W. *Chem. Phys.* **1976**, *17*, 27.
(84) Thakkar, A. J. *J. Chem. Phys.* **1981**, *75*, 4496.
(85) Maeder, F.; Kutzelnigg, W. *Chem. Phys. Lett.* **1976**, *37*, 285.
(86) Chałasiński, G.; Jeziorski, B.; Szalewicz, K. *Int. J. Quant. Chem.* **1977**, *11*, 247.
(87) Jeziorski, B.; Schwalm, W. A.; Szalewicz, K. *J. Chem. Phys.* **1980**, *73*, 6215.
(88) Wormer, P. E. S.; Bernards, J. P. C.; Gribnau, M. C. M. *Chem. Phys.* **1983**, *81*, 1.
(89) Surjan, P. R.; Mayer, I.; Lukovits, I. *Chem. Phys. Lett.* **1985**, *119*, 538. Surjan, P. R.; Poirier, R. A. *Chem. Phys. Lett.* **1986**, *128*, 358.
(90) Chałasiński, G.; Szalewicz, K. *Int. J. Quant. Chem.* **1980**, *18*, 1071.
(91) Klein, D. J. *Int. J. Quant. Chem.* **1987**, *32*, 377.
(92) Conway, A.; Murrell, J. N. *Mol. Phys.* **1972**, *23*, 1143.
(93) Jeziorski, B.; Szalewicz, K.; Chałasiński, G. *Int. J. Quant. Chem.* **1978**, *14*, 271.
(94) Murrell, J. N.; Shaw, G. *J. Chem. Phys.* **1967**, *46*, 1768.
(95) Murrell, J. N.; Randic, M.; Williams, D. R. *Proc. R. Soc. London, Ser. A* **1965**, *A284*, 566.
(96) Chałasiński, G.; Jeziorski, B. *Theor. Chim. Acta* **1977**, *46*, 277.
(97) van Duijneveldt, F. B. Ph.D. Thesis, Utrecht, 1969.
(98) Chałasiński, G.; Jeziorski, B. *Int. J. Quant. Chem.* **1973**, *7*, 745.
(99) Chałasiński, G.; Jeziorski, B. *Mol. Phys.* **1976**, *32*, 81.
(100) Jaszuński, M. *Mol. Phys.* **1980**, *39*, 77.
(101) Jeziorska, M.; Jeziorski, B.; Čížek, J. *Int. J. Quant. Chem.* **1987**, *32*, 149.
(102) Gutowski, M.; Kąkol, M.; Piela, L. *Int. J. Quant. Chem.* **1983**, *23*, 1843.
(103) Gutowski, M.; Piela, L. *Mol. Phys.* **1988**, *64*, 337.
(104) Jeziorski, B.; Bulski, M.; Piela, L. *Int. J. Quant. Chem.* **1976**, *10*, 281.
(105) Bulski, M.; Chałasiński, G.; Jeziorski, B. *Theor. Chim. Acta* **1979**, *52*, 91.
(106) Chałasiński, G. *Chem. Phys. Lett.* **1982**, *86*, 165.
(107) Bulski, M.; Chałasiński, G. *J. Chem. Phys.* **1987**, *86*, 937.
(108) Bulski, M.; Chałasiński, G. *Chem. Phys. Lett.* **1986**, *128*, 25.
(109) van Duijneveldt-van de Rijdt, J. G. C. M.; Gutowski, M.; van Lenthe, J. H.; van Duijneveldt, F. B., to be published.
(110) Bartlett, R. J. *Annu. Rev. Chem.* **1981**, *32*, 359.
(111) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quant. Chem.* **1976**, *S10*, 1.
(112) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1973**, *59*, 4557.
(113) Urban, M.; Hobza, M. *Theor. Chim. Acta* **1975**, *36*, 207, 215.
(114) Gutowski, M.; van Duijneveldt, F. B.; Chałasiński, G.; Piela, L. *Mol. Phys.* **1987**, *61*, 233.
(115) Kitaura, K.; Morokuma, K. *Int. J. Quant. Chem.* **1976**, *10*, 325.
(116) Gutowski, M.; Chałasiński, G.; van Duijneveldt-van de Rijdt, J. G. C. M. *Int. J. Quant. Chem.* **1984**, *26*, 971.
(117) Sokalski, W. A.; Roszak, S.; Hariharan, P. C.; Kaufman, J. J. *Int. J. Quant. Chem.* **1983**, *23*, 847.
(118) (a) Cammi, R.; Bonaccorsi, R.; Tomasi, J. *Theor. Chim. Acta* **1985**, *68*, 271. (b) Cammi, R.; Tomasi, J. *Theor. Chim. Acta* **1986**, *69*, 11.
(119) Sadlej, A. *Mol. Phys.* **1980**, *39*, 1249.
(120) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.
(121) Lischka, H. *J. Am. Chem. Soc.* **1974**, *96*, 4761.
(122) Meyer, W.; Hariharan, P. C.; Kutzelnigg, W. *J. Chem. Phys.* **1980**, *73*, 1880.
(123) Kutzelnigg, W.; Staemmler, V.; Hoheisel, C. *Chem. Phys.* **1973**, *1*, 27.
(124) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.
(125) Ahlrichs, R. *Theor. Chim. Acta* **1974**, *35*, 59.
(126) Dacre, P. D. *Chem. Phys.* Lett. **1977**, *50*, 147.
(127) Price, S. L.; Stone, A. J. *Chem. Phys. Lett.* **1979**, *65*, 127.
(128) van Lenthe, J. H.; van Dam, T.; van Duijneveldt, F. B.; Kroon-Batenburg, L. M. J. *Faraday Symp., Chem. Soc.* **1984**, *19*, 125.
(129) Langhoff, S. R.; Davidson, E. R. *Int. J. Quant. Chem.* **1974**, *8*, 61. Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; D. Reidel: Dordrecht, 1983.
(130) Shavitt, I.; Brown, F. B.; Burton, P. G. *Int. J. Quant. Chem.* **1987**, *31*, 507.

(131) Liu, B.; McLean, A. D. *J. Chem. Phys.* **1980**, *72*, 3418.

(132) Lengsfield, B. H.; McLean, A. D.; Yoshimine, M.; Liu, B. *J. Chem. Phys.* **1983**, *79*, 1891.

(133) Pouilly, B.; Lengsfield, B. H.; Yarkony, D. R. *J. Chem. Phys.* **1984**, *80*, 5089.

(134) van Lenthe, J. H.; Vos, R. J.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *Chem. Phys. Lett.* **1988**, *143*, 435.

(135) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Adv. Chem. Phys.* **1987**, *69*, 319.

(136) Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **1975**, *62*, 3326.

(137) Cremaschi, P.; Morosi, G.; Raimondi, M.; Simonetta, M. *Mol. Phys.* **1979**, *38*, 1555.

(138) Collins, J. R.; Gallup, G. A. *Mol. Phys.* **1983**, *49*, 871.

(139) Gallup, G. A. *Mol. Phys.* **1983**, *49*, 865.

(140) Stone, A. J.; Hayes, I. C. *Faraday Discuss. Chem. Soc.* **1982**, *73*, 19.

(141) Gerratt, J.; Papadopoulos, M. *Mol. Phys.* **1980**, *41*, 1071. Gallup, G. A.; Gerratt, J. *J. Chem. Phys.* **1985**, *83*, 2316. Gallup, G. A.; Gerratt, J. *J. Chem. Phys.* **1985**, *83*, 2322.

(142) Raimondi, M. *Mol. Phys.* **1984**, *53*, 161.

(143) Cremaschi, P.; Morosi, G.; Raimondi, M.; Simonetta, M. *Chem. Phys.* Lett. **1984**, *109*, 442.

(144) Raimondi, M. In *Gen. Discuss., Faraday Symp. Soc.* **1984**, *19*, 196.

(145) van Lenthe, J. H.; van Duijneveldt, F. B. In *Gen. Discuss., Faraday Symp. Soc.* **1984**, *19*, 196.

(146) Handy, N. C. *The Lennard-Jones Lecture*, 1984.

(147) Hoffmann, M. R.; Schaefer, H. F. *Adv. Quantum Chem.* **1986**, *18*, 207.

(148) Burton, P. G.; Senff, U. E. *J. Chem. Phys.* **1982**, *76*, 6073; **1983**, *79*, 526.

(149) Senff, U. E.; Burton, P. G. *J. Phys. Chem.* **1985**, *89*, 797.

(150) Senff, U. E.; Burton, P. G. *Mol. Phys.* **1986**, *58*, 637.

(151) Gutowski, M.; van Lenthe, J. H.; Verbeek, J.; van Duijneveldt, F. B.; Chałasiński, G. *Chem. Phys. Lett.* **1986**, *124*, 370.

(152) Ahlrichs, R.; Scharf, P.; Ehrhardt, C. *J. Chem. Phys.* **1985**, *82*, 890. Bohm, H.-J.; Ahlrichs, R. *Mol. Phys.* **1985**, *55*, 1159.

(153) Koch, S.; Kutzelnigg, W. *Theor. Chim. Acta* **1981**, *59*, 387.

(154) Lee, Y. S.; Barlett, R. J. *J. Chem. Phys.* **1984**, *80*, 4371.

(155) Harrison, R. J.; Bartlett, R. J. *Int. J. Quant. Chem.* **1986**, *S20*, 437.

(156) Wilson, S. *Diagrammatic Many-Body Perturbation Theory of Atomic and Molecular Electronic Structure*; North-Holland: Amsterdam, 1985.

(157) (a) Handy, N. C.; Knowles, P. J.; Somasundram, K. *Theor. Chim. Acta* **1985**, *68*, 87. (b) Knowles, P. J.; Somasundram, K.; Handy, N. C. *Chem. Phys. Lett.* **1986**, *113*, 8.

(158) Laidig, W. P.; Fitzgerald, G.; Barlett, R. J. *Chem. Phys. Lett.* **1985**, *113*, 151.

(159) (a) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1983**, *13*, program 406. (b) Frish, M. J.; Binkley, J. S.; Schlegal, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN 86, Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984.

(160) (a) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910 and references therein. (b) Lee, Y. S.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *81*, 5906.

(161) Dupuis, M.; Rys, J.; King, H. F.; Čársky, P.; Hess, B. A.; Schaad, L. J.; Urban, M.; Kellö, V. *QCPE Bull.* **1984**, *4*, 84. Čársky, P.; Fabian, J.; Hess, B. A.; Schaad, L. J. *J. Comput. Chem.* **1985**, *6*, 429.

(162) Chałasiński, G.; Szczęśniak, M. *Mol. Phys.* **1988**, *63*, 205.

(163) Szabo, A.; Ostlund, N. S. *J. Chem. Phys.* **1977**, *67*, 4351.

(164) Zahradník, R.; Hobza, P. *Chem. Rev.*, thematic issue.

(165) Werner, H.-J.; Meyer, W. *Mol. Phys.* **1976**, *31*, 855.

(166) van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. *J. Mol. Struct.* **1982**, *89*, 185.

(167) Davidson, E. R.; Feller, D. *Chem. Rev.* **1986**, *86*, 681.

(168) Wilson, S. *Adv. Chem. Phys.* **1987**, *64*, 439.

(169) Bishop, D. M.; Maroulis, G. *J. Chem. Phys.* **1985**, *82*, 2380.

(170) Bounds, D. G.; Wilson, S. *Mol. Phys.* **1985**, *54*, 445.

(171) (a) Saunders, V. R. In *Methods of Computational Molecular Physics*; Diercksen, G. H. F., Wilson, S., Eds.; D. Reidel: Dordrecht, 1983. (b) Saunders, V. R.; Guest, H. F. ATMOL3 Program System, 1976.

(172) Bukta, J. F.; Meath, W. J. *Int. J. Quant. Chem.* **1972**, *6*, 1045.

(173) Huzinaga, S.; Klobukowski, M.; Tatewaki, H. *Can. J. Chem.* **1985**, *63*, 1812.

(174) Schmidt, M. W.; Ruedenberg, K. *J. Chem. Phys.* **1979**, *71*, 3951.

(175) Chałasiński, G.; Funk, D.; Simons, J.; Breckenridge, W. H. *J. Chem. Phys.* **1987**, *87*, 3569.

(176) Wells, H. B.; Wilson, S. *Mol. Phys.* **1985**, *54*, 787.

(177) Raffenetti, R. C. *J. Chem. Phys.* **1973**, *58*, 4452.

(178) Szczęśniak, M.; Scheiner, S. *J. Chem. Phys.* **1986**, *84*, 6328.

(179) (a) Collins, J. R.; Gallup, G. A. *Chem. Phys. Lett.* **1986**, *123*, 56. (b) Collins, J. R.; Gallup, G. A. *Chem. Phys. Lett.* **1986**, *129*, 329.

(180) Gutowski, M.; van Duijneveldt, F. B.; Chałasiński, G.; Piela, L. *Chem. Phys. Lett.* **1986**, *129*, 325.

(181) Diercksen, G. H. F.; Kellö, V.; Sadlej, A. J. *Chem. Phys.* **1985**, *96*, 59.

(182) (a) Diercksen, G. H. F.; Kellö, V.; Sadlej, A. J. *Chem. Phys.* **1986**, *103*, 55. (b) Diercksen, G. H. F.; Sadlej, A. *Mol. Phys.* **1986**, *59*, 889.

(183) Wormer, P. E. S.; van Berkel, T.; van der Avoird, A. *Mol. Phys.* **1975**, *29*, 1181.

(184) Mayer, I. *Int. J. Quant. Chem.* **1983**, *23*, 341. Mayer, I. In *Modelling of Structure and Properties of Molecules*; Maksic, Z. B., Ed.; Ellis Horwood: Chichester, 1987; p 145.

(185) (a) Mayer, I.; Vibok, A. *Chem. Phys. Lett.* **1987**, *136*, 115; *Chem. Phys. Lett.* **1987**, *140*, 558. (b) Mayer, I. *Theor. Chim. Acta* **1987**, *72*, 207.

(186) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(187) Johansson, A.; Kollman, P.; Rothenberg, S. *Theor. Chim. Acta* **1973**, *29*, 167.

(188) Daudey, J. P.; Claverie, P.; Malrieu, J. P. *Int. J. Quant. Chem.* **1974**, *8*, 1.

(189) Kocjan, D.; Koller, J.; Azman, A. *J. Mol. Struct.* **1976**, *34*, 145.

(190) Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *82*, 2418.

(191) Olivares del Valle, F. J.; Tolosa, F.; Esperilla, J. J.; Ojalvo, E. A.; Requena, A. *J. Chem. Phys.* **1986**, *84*, 5077.

(192) Ostlund, N. S.; Merrifield, D. L. *Chem. Phys. Lett.* **1976**, *39*, 612.

(193) Bulski, M.; Chałasiński, G. *Theor. Chim. Acta* **1977**, *44*, 399.

(194) Kurdi, L.; Kochanski, E.; Diercksen, G. H. F. *Chem. Phys.* **1985**, *92*, 287.

(195) Kołos, W. *Theor. Chim. Acta* **1979**, *51*, 219.

(196) Sauer, J.; Hobza, P.; Carsky, P.; Zahradník, R. *Chem. Phys. Lett.* **1987**, *134*, 553.

(197) Hobza, P.; Schneider, B.; Sauer, J.; Carsky, P.; Zahradník, R. *Chem. Phys. Lett.* **1987**, *134*, 418.

(198) Frisch, M. J.; del Bene, J. E.; Binkley, J. S.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 2279.

(199) Hobza, P.; Schneider, B.; Carsky, P.; Zahradník, R. *J. Mol. Struct.* **1986**, *138*, 377.

(200) Alagona, G.; Ghio, C.; Cammi, R.; Tomasi, J. *Int. J. Quant. Chem.* **1987**, *32*, 207, 227.

(201) Sokalski, W. A.; Roszak, S. *Int. J. Quant. Chem.* **1987**, *32*, 279.

(202) Kołos, W. *Theor. Chim. Acta* **1979**, *51*, 219.

(203) Pulay, P. *Adv. Chem. Phys.* **1987**, *69*, 241.

(204) Chałasiński, G.; Kendall, R. A.; Simons, J. *J. Phys. Chem.* **1987**, *91*, 6151.

(205) Schneider, B.; Hobza, P.; Zahradník, R. *Theor. Chim. Acta* **1986**, *73*, 201.

(206) Karlstrom, G.; Sadlej, A. *Theor. Chim. Acta* **1982**, *61*, 1.

(207) Loushin, S. K.; Liu, S.; Dykstra, C. E. *J. Chem. Phys.* **1986**, *84*, 2720.

(208) Buckingham, A. D.; Fowler, P. W. *Mol. Phys.* **1983**, *50*, 1349.

(209) Chałasiński, G.; Jeziorski, B.; Andzelm, J.; Szalewicz, K. *Mol. Phys.* **1977**, *33*, 971.

(210) Morokuma, K.; Kitaura, K. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1982; Vol. 1.

(211) *Structure and Dynamics of Weakly Bound Molecular Complexes*; Weber, A., Ed.; D. Reidel: Dordrecht, 1987.

(212) Liu, B.; McLean, A. D., quoted by: Barker, A.; Henderson, D. *Rev. Mod. Phys.* **1976**, *48*, 593.

(213) Feltgen, R.; Kirst, H.; Kohler, K. A.; Pauly, H.; Torello, F. *J. Chem. Phys.* **1982**, *76*, 2360.

(214) Ceperley, D. M.; Partridge, H. *J. Chem. Phys.* **1986**, *84*, 820.

(215) Aziz, R. A.; Nain, V. P. S.; Carley, J. S.; Taylor, W. L.; McConville, G. T. *J. Chem. Phys.* **1979**, *70*, 4330.

(216) Aziz, R. A.; McCourt, F. R. W.; Wong, C. C. K. *Mol. Phys.* **1987**, *61*, 1487.

(217) Olivares del Valle, F. J.; Tolosa, S.; Ojalvo, E. A.; Esperilla, J. J. *J. Chem. Phys.* **1986**, *85*, 3448.

(218) Schafer, J.; Koehler, W. E. *Physica A* **1985**, *129*, 469.

(219) Shafer, R.; Gordon, R. G. *J. Chem. Phys.* **1973**, *58*, 5422.

(220) Gengenbach, R.; Hahn, C. *Chem. Phys. Lett.* **1972**, *15*, 604.

(221) Schaefer, J.; Meyer, W. *J. Chem. Phys.* **1979**, *70*, 344.
(222) Meyer, W.; Schaefer, J., to be published, quoted in ref 224.
(223) Schaefer, J.; Liu, B., to be published, quoted in ref 224.
(224) Buck, U.; Huisken, F.; Kolhase, A.; Otten, D.; Schaefer, J. *J. Chem. Phys.* **1983**, *78*, 4439.
(225) Harrison, R. J.; Handy, N. C. *Chem. Phys. Lett.* **1983**, *98*, 97.
(226) Hariharan, P. C.; Staemler, V. *Chem. Phys.* **1976**, *15*, 409.
(227) Viehland, L. A. *Chem. Phys.* **1983**, *78*, 279.
(228) Schaefer, J.; Lester, W. A. *J. Chem. Phys.* **1975**, *62*, 1913.
(229) Winn, J. S. *Acc. Chem. Res.* **1981**, *14*, 341.
(230) Das, G.; Wahl, A. C. *Phys. Rev.* **1971**, *A4*, 825.
(231) Dehmer, P.; Wharton, L. *J. Chem. Phys.* **1972**, *57*, 4821.
(232) Olson, R. E.; Liu, B. *Phys. Rev.* **1978**, *A22*, 1389.
(233) Das, G.; Wagner, A. F.; Wahl, A. C. *J. Chem. Phys.* **1978**, *68*, 4917.
(234) Scoles, G., as quoted in ref 38b,d of: Huxley, P.; Knowles, D. B.; Murrell, J. N.; Watts, J. D. *J. Chem. Soc., Faraday Trans.* **1984**, *80*, 1349.
(235) (a) Sapse, A. M.; Rayez-Meaume, M. T.; Rayez, J. C.; Massa, L. J. *Nature (London)* **1979**, *278*, 332. (b) Rayez, J. C.; Rayez-Meaume, M. T.; Massa, L. J. *J. Chem. Phys.* **1981**, *75*, 5393.
(236) Hirao, K.; Yamabe, S. *Chem. Phys.* **1983**, *80*, 237.
(237) Chiles, A. R.; Dykstra, C. E. *Chem. Phys. Lett.* **1982**, *85*, 447.
(238) Harrison, R. J.; Handy, N. C. *Chem. Phys. Lett.* **1986**, *123*, 321.
(239) Blomberg, M. R. A.; Siegbahn, P. E. M.; Roos, B. O. *Int. J. Quant. Chem.* **1980**, *S14*, 229.
(240) Bondybey, V. E.; English, J. H. *J. Chem. Phys.* **1984**, *80*, 568. Bondybey, V. E. *Chem. Phys. Lett.* **1984**, *109*, 436.
(241) Gerratt, J., private communication quoted in ref 238.
(242) Roeggen, I.; Morokuma, K.; Yamashita, K. *Chem. Phys. Lett.* **1987**, *140*, 349.
(243) Meath, W. J.; Aziz, R. A. *Mol. Phys.* **1984**, *52*, 225.
(244) Baker, J. A. *Mol. Phys.* **1986**, *57*, 755.
(245) Cieplak, P.; Lybrand, T. P.; Kollman, P. A. *J. Chem. Phys.* **1987**, *86*, 6393.
(246) Lybrand, T. P.; Kollman, P. A. *J. Chem. Phys.* **1985**, *83*, 2923.
(247) Varandas, A. J. C. *Mol. Phys.* **1983**, *49*, 817.
(248) Margenau, H.; Kestner, N. R. *Theory of Intermolecular Forces*; Pergamon: New York, 1969; Chapter 5.
(249) Piecuch, P. *Mol. Phys.* **1986**, *59*, 1067, 1085, 1111.
(250) Axilrod, B. M.; Teller, E. *J. Chem. Phys.* **1943**, *11*, 299.
(251) Muto, Y. *Proc. Phys. Soc. Jpn.* **1953**, *17*, 629.
(252) Kołos, W.; Leś, A. *Chem. Phys. Lett.* **1972**, *14*, 167.
(253) O'Shea, S. F.; Meath, W. J. *Mol. Phys.* **1974**, *28*, 1431.
(254) O'Shea, S. F.; Meath, W. J. *Mol. Phys.* **1976**, *31*, 515.
(255) Jeziorski, B. Ph.D. Thesis, Warsaw, 1974.
(256) Bulski, M.; Chałasiński, G. *Theor. Chim. Acta* **1980**, *56*, 199.
(257) Bulski, M.; Chałasiński, G. *Chem. Phys. Lett.* **1982**, *89*, 450.
(258) Wells, B. H.; Wilson, S. *Mol. Phys.* **1985**, *55*, 199.
(259) Kołos, W.; Leś, A. *Int. J. Quant. Chem.* **1972**, *6*, 1101.
(260) Whiteside, R. A.; Krishnan, R.; Pople, J. A.; Krogh-Jesperson, M.; von Schleyer, P. v. R.; Wenke, G. *J. Comput. Chem.* **1980**, *1*, 307.
(261) Stoll, H.; Flack, J. F.; Golka, E.; Krüger, T. *Surf. Sci.* **1981**, *106*, 251.
(262) Pacchioni, G.; Koutecký, J. *Chem. Phys.* **1982**, *71*, 181. Pacchioni, G.; Koutecký, J. *J. Chem. Phys.* **1982**, *77*, 5850. Pacchioni, G.; Plavsic, D.; Koutecký, J. *Ber. Bunsenges. Phys. Chem.* **1983**, *87*, 503. Pacchioni, G.; Pewestorf, W.; Koutecký, J. *J. Chem. Phys.* **1984**, *83*, 261.
(263) Bauschlicher, C. W.; Bagus, P. S.; Cox, B. N. *J. Chem. Phys.* **1982**, *77*, 4032.
(264) Bauschlicher, C. W.; Pettersson, L. G. M. *J. Chem. Phys.* **1986**, *84*, 2226.
(265) Marino, M. M.; Ermler, W. C. *J. Chem. Phys.* **1987**, *86*, 6283.
(266) Koutecký, J.; Fantucci, P. *Chem. Rev.* **1986**, *86*, 539.
(267) Brewington, R. B.; Bender, C. F.; Schaefer, H. F. *J. Chem. Phys.* **1976**, *64*, 905.
(268) Jordan, K. D.; Simons, J. *J. Chem. Phys.* **1977**, *67*, 4027.
(269) Bulski, M. *Mol. Phys.* **1975**, *29*, 1171.
(270) Kołos, W.; Nieves, F.; Novaro, O. *Chem. Phys. Lett.* **1976**, *41*, 431.
(271) Leś, A.; Radzio, E. *Acta Phys. Polon.* **1979**, *A55*, 351.
(272) Kendall, R. A.; Simons, J.; Gutowski, M.; Chałasiński, G. *J. Phys. Chem.*, in press.
(273) Glover, P. M.; Weinhold, F. *J. Chem. Phys.* **1977**, *66*, 191.
(274) Leonard, P. J.; Barker, J. A. *Theor. Chem. Adv. Perspect.* **1975**, *1*, 117.
(275) Andzelm, J.; Huzinaga, S.; Klobukowski, M.; Radzio, E. *Mol. Phys.* **1984**, *52*, 1495.
(276) Arrighini, G. P.; Biondi, F.; Guidotti, C. *Chem. Phys.* **1973**, *2*, 85.
(277) Stewart, R. F. *J. Phys. B* **1975**, *8*, 1.
(278) Mulder, F.; van der Avoird, A.; Wormer, P. E. S. *Mol. Phys.* **1979**, *37*, 159.
(279) Zeiss, G. D.; Meath, W. J. *Mol. Phys.* **1977**, *33*, 1155.
(280) Lowther, R. E.; Coldwell, R. L. *Phys. Rev.* **1980**, *A22*, 14.
(281) Chiles, R. A.; Dykstra, C. E. *J. Chem. Phys.* **1981**, *74*, 4544.
(282) Tatewaki, H.; Tanaka, K.; Ohno, Y.; Nakamura, T. *Mol. Phys.* **1984**, *53*, 233.
(283) Chałasiński, G., unpublished results.
(284) Rodwell, W. R.; Scoles, G. *J. Phys. Chem.* **1982**, *86*, 1053.
(285) Lavendy, H.; Robbe, J. M.; Chambaud, G.; Levy, B. *Chem. Phys.* **1987**, *116*, 11.
(286) Michels, H. H.; Montgomery, J. A. *Chem. Phys. Lett.* **1987**, *139*, 535.