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Many-Body Effects in Intermolecular Forces

Matthew J. Elrod[†] and Richard J. Saykally*

Department of Chemistry, University of California, Berkeley, California 94720

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Contents

I. Introduction

The investigation of many-body effects in intermolecular interactions has assumed increasing prominence as modern experimental and computational technology has progressed such that a detailed description of the condensed phases of matter is now possible through computer simulations. Indeed, these technologies have recently allowed great advances in the understanding of the binary interaction, such that many relevant pair potential energy surfaces are now obtainable by inversion of experimental data or by direct *ab initio* quantum chemical calculation. Paralleling these developments, many workers have attempted to extend this success to the construction of more general *many-body* potential energy surfaces, which are ultimately necessary to achieve the goal of describing macroscopic properties from a rigorous microscopic viewpoint. Consider a system of N identical atoms; the total potential energy function $V(r_1,r_2,...,r_N)$ is expanded as sum of n-body potentials:

$$V(r_1,r_2,...,r_N) = \sum_{i<j}^{N} V_2(r_i,r_j) + \sum_{i<j<k}^{N} V_3(r_i,r_j,r_k) + ... + \sum_{i<j<k,...,z}^{N} V_n(r_i,r_j,r_k,...,r_z) \quad (1)$$

It has been assumed that this series is rapidly convergent and in most relevant systems the pairwise additive approximation (inclusion of the V_2 term only) has been shown to be qualitatively valid for many measurable properties. An examination of higher order terms in this series usually requires an accurate knowledge of the V_2 term so that pairwise additive experimental properties may be calculated and compared to the actual many-body experimental result. Therefore, the study of many-body forces generally demands very accurate experimental and theoretical methods. Although evidence for deviations from simple pairwise additivity has existed for quite some time, difficulties in rationalizing the possible many-body effects and the relative ease of calculations based on pairwise additivity, such as statistical mechanical simulations of liquids, have led to an almost universal use of simple pairwise additive potentials in the calculation of properties for condensed-phase systems. However, as experimental and theoretical techniques continue to become more sophisticated, it is becoming clear that many-body effects cannot be neglected in quantitative treatments and may, in fact, play critical roles in determining many important physical properties. Perhaps the most important historic difficulty in the extraction of many-body effects has been the fact that most experiments sensitive to these effects were performed on macroscopic systems with the result that only the *total* many-body effect could be accessed. Condensed-phase properties have often been used to determine "effective" pair potentials, which actually include effects due to all of the terms in the many-body expansion. In contrast, the study of van der Waals molecules affords the ideal program of studying complexes of increasingly higher order, such that each successive many-body term may be extracted uniquely. It is crucial, however, that the documented successes and failures of other approaches to the many-body question are carefully studied, as it is unlikely that any single approach, experimental or theoretical, can be expected to solve this difficult problem. It is therefore the purpose of this review to provide a comprehensive survey (and list of references) of the most important approaches applied to the problem, dating back to its origin in the early 1940s and continuing to the present day. The first two sections of the review are devoted to a discussion of the experimental and theoretical techniques applied to the study of many-body forces. The discussion of results obtained by these methods are further subdivided into sections on atomic and molecular systems. The results for atomic systems are discussed chronologically, since the rate of evolution of the various techniques applied to the problem has had a significant impact on the difficulties in gaining a consensus description of the relevant many-body effects. In contrast, the much more recent study of many-body effects for molecular ensembles is discussed on a system-by-system basis.

Although many subfields implicitly encompassing many-body forces have been the subjects of previous reviews, there are only a few articles which directly address the many-body problem itself. An early review on the theoretical approach by Margenau and Stamper[1] provided the first systematic study of the possible many-body terms. Using results from their application of *ab initio* perturbation theory methods, Szczęśniak and Chałasiński[2] recently described a

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[†] Present address: Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 54-1312, Cambridge, MA 02139.

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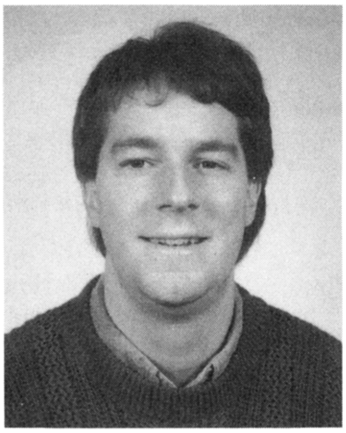
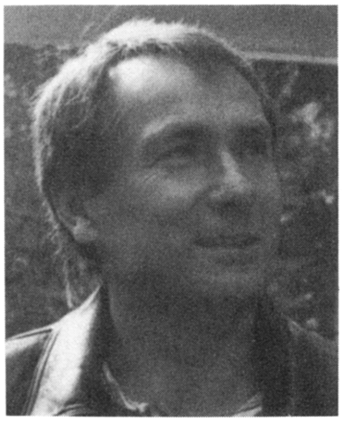


Matthew J. Elrod was born in 1967 in Clinton, IA. He graduated with a B.A. in chemistry from Grinnell College in 1989 and completed his Ph.D. in physical chemistry at University of California, Berkeley in May 1994. During his time in Professor Saykally's research group, he pursued projects concerning many-body effects in intermolecular forces and the determination of potential energy surfaces from spectroscopic data. He is currently a postdoctoral fellow in the Department of Earth, Atmospheric, and Planetary Sciences at the Massachusetts Institute of Technology.



Richard Saykally was born in 1947 in Rhinelander, WI. He graduated from the University of Wisconsin—Eau Claire in 1970, and received his Ph.D. from University of Wisconsin—Madison in 1977 under the direction of R. C. Woods. After spending two years at NIST in Boulder as a NRC postdoctoral fellow with K. M. Evenson, he was appointed Assistant Professor at University of California—Berkeley in 1979. Tenured in 1983, and promoted to Full Professor in 1986, he served as Vice-Chair of Chemistry from 1988 to 1991, and has been the thesis advisor for 22 Ph.D. candidates. Richard Saykally is a Professor in the Department of Chemistry at University of California—Berkeley. He has received numerous honors and awards for his work in laser spectroscopy, including the Harrison-Howe Award, the Lippincott Prize for Vibrational Spectroscopy, the Bomem Michelson Award in Spectroscopy, the E. K. Plyler Prize for Molecular Spectroscopy, and the Bourke Lectureship of the Royal Society of Chemistry. He has been a Presidential Young Investigator and a Dreyfus Scholar, and is a Fellow of the American Physical Society and The Royal Society of Chemistry. He serves on the editorial boards of *The Journal of Chemical Physics*, *Molecular Physics*, *Chemical Physics Letters*, *The Review of Scientific Instruments*, and *Spectroscopy*, and has published over 150 papers on applications ranging from intermolecular forces and molecular ions to astrophysics.

dissection of important three-body terms for several van der Waals trimer systems. The potential manifestation of many-body effects in the experimental results for the rare gases was first reviewed by Barker.[3] Two review articles by Meath and coworkers[4,5] represent a very well-balanced consideration of the problems of reconciling the available experimental and theoretical results for the rare gases.

II. Experimental Methods

In a consideration of the experimental methods which have been applied to the problem, it is important to evaluate both the sensitivity of the approach to the existence of many-body forces and the overall accuracy of the approach (so as to be able to confidently distinguish many-body effects from pairwise additive effects). There are basically two kinds of experiments: (1) those which probe macroscopic properties and therefore are influenced by all terms in the many-body expansion and (2) those which probe microscopic properties (usually gas phase interactions) which, under controlled circumstances, are influenced only by identifiable low-order terms in the many-body expansion.

In the first category, measurements of crystal structures[6] and binding energies[7] have been particularly important in studies of the rare gases. Crystal lattice structures are usually determined unambiguously from X-ray diffraction methods and predictions of these structures from pairwise additive potential functions are straightforward for these simple systems. As will be explained in more detail in section IV, one of the first experimental indications of the possible effects of many-body forces was that the measured crystal structures of the rare gases (with the exception of helium) were not in agreement with predictions from pairwise additive potentials.[8] Crystal binding energies (extrapolated to 0 K) have also indicated the existence of many-body forces in the rare gases. These experiments have indicated a deviation from pairwise additivity of about 10%, which is much larger than the uncertainties associated with these experiments (0.1−0.4%). Since interatomic distances in crystals closely correspond to the position of the minimum in the pair potentials, these results contain information from both the repulsive and attractive portions of the many-body potential.

The structure of liquids have also been the subject of much experimental scrutiny. X-ray and neutron-scattering techniques[9] have been used to determine experimental radial distribution functions which can be directly calculated from pairwise additive surfaces using statistical mechanical techniques. These experiments are difficult to perform with a high level of accuracy and tend to contain information only on the hard-sphere repulsive part of the potential, but have found useful application to the problem of many-body forces.

The absorption and scattering of light by dense media due to many-body induced dipole moments or polarizability tensors have been the subject of experimental study.[10] In particular, the far infrared translational absorption spectrum of mixed rare gases has been studied extensively. The total absorption cross section and the wavelength dependence of the spectrum have been shown to be sensitive to the possible influence of many-body forces.[11,12] In fact, the observation of an absorption spectrum due to a *pure* rare gas medium would be direct information on many-body forces, since the two-body induced dipole moment in such systems is exactly zero by symmetry.[13]

There are also a number of standard macroscopic properties (other than energy) that are, in principle, sensitive to many-body forces. For example, viscosity, thermal conductivity, and diffusion in gases are all dependent on many-body forces, but in general it is not possible to measure these quantities sufficiently accurately or to easily calculate their values from pairwise additive potentials.[14] Some condensed-phase properties, such as surface tension,[15] have been investigated in connection with many-body forces.

Among those experiments of the second category—those which probe only low-order terms in many-body expansion—gas imperfections (pressure—volume relations) were the first to be extensively studied. The results from these experiments[16] are usually fit to the virial equation of state:[17]

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \ldots \qquad (2)$$

where B and C, the second and third virial coefficients, are functions only of temperature and the intermolecular potential, and represent, respectively, binary and ternary molecular interactions. The third virial coefficient contains contributions from both two- and three-body terms in the potential. Given a potential function that contains two- and three-body terms, it is straightforward to calculate the three-body contribution to the third virial coefficient (ΔC) for an atomic system:

$$\Delta C = \frac{1}{3}(8\pi^2 N_0{}^2) \times$$

$$\int\int\int \exp\left(\frac{-\sum V_2}{kT}\right)\left[\exp\left(\frac{-V_3}{kT}\right)\right] \times$$

$$R_{12}R_{13}R_{23}\,\mathrm{d}R_{12}\,\mathrm{d}R_{13}\,\mathrm{d}R_{23} \qquad (3)$$

where N_0 is Avogadro's number and V_2 and V_3 are the two- and three-body potential functions, respectively. This direct connection to the total potential allows easy comparison with experiment and the ability to test various proposed three-body terms. Although third virial coefficients can be measured with an accuracy of only about 10%, it has been estimated that ΔC accounts for up to 50% of the value of the experimental $C(T)$ for the rare gases.[18]

Molecular beam scattering techniques, which have played an important role in the determination of pair potential energy surfaces, have also been applied to the many-body problem. Although three crossed beam scattering experiments are not feasible, gas—surface interactions have been investigated using a rare gas surface which has been absorbed onto a graphite substrate.[19,20] A molecular beam of another rare gas is then used to probe the surface. This technique is primarily sensitive to the repulsive part of the many-body potential, but its main limitation seems to be due to the difficulties in obtaining sufficiently accurate pairwise additive potential surfaces.[21] Because the total pairwise additive surface requires at least three constituent pair potentials (substrate rare gas—graphite, substrate rare gas—substrate rare gas, and substrate rare gas—impinging rare gas) which are not all well determined, the results from these experiments are difficult to interpret.

Finally, the spectroscopy of van der Waals molecules has recently become a very important tool in the study of many-body forces. The measurement of high-resolution spectra for binary van der Waals complexes formed in molecular beams, coupled with theoretical advances in the treatment of the associated quantum dynamics problem, have led to the determination of anisotropic intermolecular pair potentials[22-25] of unprecedented detail and accuracy during the last decade. As mentioned in the introduction, the study of van der Waals molecules is ideal for a systematic examination of many-body terms, and when coupled with high-resolution spectroscopy, provides extremely accurate data (~1 ppm accuracy) which is very rich in detail. Like the other techniques outlined above, extension of this approach to the study of many-body forces is nontrivial since the experiments are limited by the existence of decreased numbers of higher order complexes in the molecular beams used to generate them and dynamics calculations used to predict spectra from pairwise additive potentials are taxed by the corresponding increased number of intermolecular degrees of freedom.[26] However, high-resolution microwave[27] and laser-based far infrared,[28] near infrared,[29,30] and visible[31] spectra of ternary and higher-order clusters have been obtained and the observed rotational energy level spacings have been used to determine structures and possible many-body effects on those structures. Measurement of the intermolecular vibrational modes in the determination of pair potentials provided extremely valuable information, as these vibrational states sample a much larger range of the multidimensional potential energy surface in a very direct manner.[22-25] These measurements will be even more important in the determination of many-body forces since these systems contain even more degrees of freedom that may not be sampled by the complex in its ground vibrational state. Although all of the high-resolution techniques listed above are capable, in principle, of measuring the low frequency intermolecular vibrational modes indirectly, the direct transitions lie in the far infrared region of the spectrum and it is results from these rapidly evolving experiments that provide motivation for this review.

III. Theoretical Methods

In terms of the desired information on many-body forces, theoretical methods are easier to categorize into the microscopic (quantum mechanics) and the macroscopic (statistical mechanics) domains. Transcending the obvious connection between the two methods, it is important to note that statistical mechanical simulations require microscopic intermolecular potential functions which are either obtained directly from quantum mechanical calculations or semiempirical formulations. In the examination of many-body forces themselves, quantum mechanical calculations are therefore more directly informative. On the other hand, it is the macroscopic manifestations of many-body forces that are of the ultimate interest, and statistical mechanical calculations allow this connection to be made explicit.

Ab initio quantum mechanical methods have been applied to the many-body problem since the 1940s.

There are two common approaches to the *ab initio* calculation of weakly interacting systems: supermolecular and perturbation theory techniques. It should be noted that both methods are susceptible to basis set superposition errors (BSSE), which occur due to the use of incomplete basis sets.[32] These effects are often larger enough to completely invalidate quantitative results for weakly interaction systems. Although modern methods now use some form of "counterpoising" to remove the unphysical effects of BSSE, quantitative agreement between similar *ab initio* methods can be limited by these considerations. In the supermolecular method, the total energy of the system is calculated and the van der Waals interaction is obtained by subtracting the energies of the constituent monomers. The perturbation theory method treats the infinitely separated monomers as the zero-order situation, and the van der Waals interaction is obtained through successive order perturbations. The supermolecular technique is relatively easy to apply, but careful and accurate calculations must be made, since the van der Waals interaction energy is much smaller than the energies of the monomers. In addition, the supermolecular approach does not allow the potential energy to be separated into exchange, electrostatic, induction, and dispersion contributions as is commonly done in the theory of intermolecular forces. The perturbation theory technique does allow such a physically sensible partitioning of the energies, but it is often more difficult to implement and can suffer from a slow convergence that can render it less efficient than the supermolecular approach in the calculation of the *total* energy. Of course, since the investigation of many-body forces is essentially the systematic study of each term in the perturbation series expansion, "slow convergence" is not a relevant criticism. As will be discussed in detail later in this review, the perturbation theory approach has provided the most useful theoretical insight into the problem of many-body forces of any *ab initio* method[2] such that a more extensive discussion of the approach is warranted.

The most mature application of the perturbation theory method is actually a simultaneous implementation of supermolecular Møller–Plesset perturbation theory (MPPT) and intermolecular MPPT.[33] This double perturbation expansion allows the decomposition of the interaction energy into the usual terms of the theory of intermolecular forces: exchange, induction, electrostatic, and dispersion. The following discussion of the method is directly taken from the excellent review of Szczęśniak and Chałasiński.[2] The zeroth- and first-order terms are usually considered together as the self-consistent field (SCF) energy, which may be further decomposed in the Heitler–London and SCF deformation interactions:

$$\Delta E^{(0)} + \Delta E^{(1)} = \Delta E^{\mathrm{SCF}} = \Delta E^{\mathrm{HL}} + \Delta E^{\mathrm{SCF\text{-}def}} \quad (4)$$

Table 1. Many-Body Effects in Supermolecular Møller–Plesset Perturbation Theory[2]

perturbation theory order	perturbation theory many-body term	asymptotic connection to theory of intermolecular forces
ΔE_{SCF}	$\epsilon_{\mathrm{exch}}^{\mathrm{HL}}$	many-body exchange repulsion
	$\Delta E_{\mathrm{def}}^{\mathrm{SCF}}$	many-body classical polarization
$\Delta E^{(2)}$	$\Delta E_{\mathrm{def}}^{(2)}$	
	$\Delta E_{\mathrm{exch}}^{(2)}$	
$\Delta E^{(3)}$	$\Delta E_{\mathrm{def}}^{(3)}$	
	$\epsilon_{\mathrm{disp}}^{(30)}$	three-body dispersion
	$\Delta E_{\mathrm{exch}}^{(3)}$	
$\Delta E^{(4)}$	$\Delta E_{\mathrm{def}}^{(4)}$	
	$\epsilon_{\mathrm{disp}}^{(40)}$	four-body dispersion
	$\Delta E_{\mathrm{exch}}^{(4)}$	

The ΔE^{HL} term represents the interaction energy between mutually undeformed SCF subsystems, while $\Delta E^{\mathrm{SCF\text{-}def}}$ represents effects due to relaxation of the orbitals under the restrictions imposed by the Pauli exclusion principle. At long range, the $\Delta E^{\mathrm{SCF\text{-}def}}$ term can be asymptotically described by a classical polarization model for systems which contain subunits with permanent multipole moments. The ΔE^{HL} term may be further subdivided:

$$\Delta E^{\mathrm{HL}} = \epsilon_{\mathrm{elec}}^{(10)} + \Delta E_{\mathrm{exch}}^{\mathrm{HL}} \quad (5)$$

The first term is the electrostatic energy and the second term is the exchange interaction. All components of ΔE^{SCF} are non-pairwise additive, with the exception of the electrostatic term. The second-order term, $\Delta E^{(2)}$, contains the second-order analogues of the ΔE^{SCF} components already discussed and the dispersion component, $\epsilon_{\mathrm{disp}}^{(20)}$, which is pairwise additive. The third order interaction, $\Delta E^{(3)}$, again incorporates third-order effects of terms already present in ΔE^{SCF} as well as $\epsilon_{\mathrm{disp}}^{(30)}$, the three-body dispersion component which asymptotically correlates to the well-known triple-dipole term. Therefore, many-body induction (polarization) and exchange forces appear immediately in the perturbation expansion, while the many-body dispersion terms appear with each corresponding perturbation order. This information is summarized in Table 1.

Approximate electronic structure methods have also been used in connection with many-body models. These techniques have been used both to simplify few atom many-body calculations and to make possible the calculation of relatively large systems. The Gaussian effective-electron model approximates all exchange effects by placing one "effective" electron (with a Gaussian charge distribution) on each atom, thus making the associated exchange integrals much easier to evaluate.[34] This approximation has also been used to directly express the interaction in a multipole series, therefore making many-body exchange calculations on larger scale systems even more tractable.[35] Because a Gaussian description of the electron distribution is not very accurate, a careful reparameterization of the model must be made to obtain reasonable results.[36] Another approach (the Gordon–Kim model[37]), which incorporates both the repulsive and attractive regions of the potential well, also uses the electron density as the fundamental physical quantity. The atomic electron densities are obtained by Hartree–Fock calculations and assumed to be strictly additive (no electron distortion as the atoms are brought close together) and the interaction energies are calculated by a Coulombic sum over charges, while the other effects (electron kinetic energy, exchange, and correlation) are evaluated through a simple free electron gas approximation. This method also suffers from an inaccurate description of the true electronic distribution because of the imposition of charge density additivity. Variations of the Gordon–Kim model have also been applied to large systems such as rare gas–graphite systems[38] and rare gas crystals.[39] In the latter application, the crystal electron density is calculated via a perturbation theory approach starting from the free atomic states (obtained from Hartree–Fock calculations). The interatomic interaction *within* the crystal is then computed via the Gordon–Kim approach. Many-body dispersion forces have also been estimated for rare gas–graphite systems using an image charge approach (in which the solid is treated as a continuous dielectric medium)[40] and via quantum mechanical third-order perturbation theory.[41]

There are two general classes of statistical mechanical simulations. The molecular dynamics method[42] uses a classical dynamical model for atoms and molecules and the trajectory is determined by integrating Newton's equations of motion. This method provides dynamical information as well as the standard equilibrium statistical properties. The Monte Carlo[43] method employs a random walk approach to obtain the equilibrium ensemble averages. Although it is not possible to directly obtain time-dependent information with the Monte Carlo approach, this method is more generally applicable in that it can be applied to quantum systems and lattice models. Both of these methods have found widespread use in the study of many-body forces, providing the connection between the microscopic potential energy function and the related macroscopic equilibrium properties which can be measured by condensed phase experimentalists. The rapidly increasing availability of supercomputer resources has made these approaches much more valuable, as workers in this field have been able to carry out realistic investigations (with respect to ensemble size and complexity of the many-body potential function) on important systems such as liquid water.

IV. Many-Body Effects in Atomic Systems

Due to the existence of accurate pair potentials, atomic systems, particularly the rare gases, have been the primary focus in the investigation of many-body forces. For all practical purposes, the study of many-body forces began in 1943 when Axilrod and Teller[44] and Muto[45] used third-order perturbation theory to calculate the three-body triple-dipole dispersion energy for atoms with a spherical charge distribution. The so-called triple-dipole (or ATM, or DDD) term has the following functional form:

$$E_{\mathrm{DDD}} = C_9 \frac{3 \cos \gamma_1 \cos \gamma_2 \cos \gamma_3 + 1}{{R_{12}}^3 {R_{23}}^3 {R_{31}}^3} \qquad (6)$$

where $C_9 \approx {}^9/_{16} V\alpha^3$ (V and α are the atomic ionization potential and polarizability); R_{12}, R_{23}, and R_{31} are the lengths of the sides; and γ_1, γ_2, and γ_3 are the angles of the triangle formed by the atoms. Examination of the angular part of the term reveals that E_{DDD} is negative for collinear geometries and positive for equilateral triangle geometries. As was mentioned earlier, the heavy rare gases crystalize in a face-centered cubic (fcc) lattice, although calculations using pairwise additive potentials predict a hexagonally close packed (hcp) lattice. In the first practical application of the ATM term, Axilrod examined the dependence of preferred lattice structures for the rare gases.[46] Although it was found that the cohesive energy of the crystals was between 2 and 9% less than in the pairwise additive approximation, the preferred calculated crystal structure was still the hcp lattice. More accurate estimates for the C_9 coefficient have appeared in the literature since the original work.[47–51] In 1970, Bell generalized the long-range nonadditive third-order interaction,[52] of which the ATM expression is the leading term:

$$E_{\text{three-body}}^{\text{long-range}} = \mathrm{DDD} + \mathrm{DDQ} + (\mathrm{DQQ} + \mathrm{DDO}) + (\mathrm{QQQ} + \mathrm{DQO} + \mathrm{DDH}) + \ldots \qquad (7)$$

where D, Q, O, and H represent dipole, quadrupole, octopole and hexadecapole, respectively. Subsequently, Doran and Zucker used third-order terms (DDD, DDQ, DQQ, QQQ, and DDO) and the fourth-order DDD term to calculate preferred lattice structures for the rare gases.[53] Once again, the lattice structures showed a surprising insensitivity to these highly anisotropic terms, as was later more extensively discussed by Bell and Zucker.[54] Fowler and Graben investigated the sensitivity of third virial coefficients to these terms and found that only the first few terms in the series were important.[55] Etters and Danilowicz used a Monte Carlo method to address the contribution of these terms to the bulk properties of the rare gases.[56] They found that the third-order DDQ and the fourth-order DDD terms are both about 20% of the third-order DDD (ATM) term at equilibrium interatomic distances. Extrapolating their results for smaller clusters, they found that the many-body contribution to the bulk crystal binding energy for argon was about 8%, in qualitative agreement with the experimental result of 10%. McGinnies and Jansen investigated possible exchange effects on the ATM term (just as it is necessary to damp the two-body long-range dispersion expression at short intermolecular distances) using an approximate model and second-order perturbation theory.[57,58] Although the use of a multipole expansion made this approach too approximate to be predictive, the results did indicate that these effects should not be neglected. O'Shea and Meath investigated the effects of charge overlap on the ATM term at relevant interatomic distances using a partial wave analysis.[59,60] They found that these effects led to a damping of the ATM term of between 15 to 40% at typical interatomic distances, indicating that previous studies probably overestimated the influence of these many-body forces. Although these theoretical results seemed to establish the reasonably rapid convergence of the long-range third-order expansion, they also called into question the validity of the long-range expressions at relevant interatomic distances. Unfortunately, rigorous comparison with experimental properties had to await the generation of accurate and realistic pair potential functions.

Although much of the early work on atomic systems centered on the nonadditive long-range terms, many-body contributions to the short-range potential were also investigated, albeit at a much more approximate level. In 1953, Rosen used the valence bond method to calculate the short-range energy of three helium atoms, and determined functional forms for the three-body interaction for both the linear and equilateral triangle geometries.[61] By using these formulas and the helium pair potential minimum separation (5.6 a_0), the three-body contribution was estimated to be negative (attractive) for the triangular geometry, but small in magnitude (0.4% of the sum of the two-body terms). Shostak also investigated nonadditivity in linear He_3 using the molecular orbitals formed from linear combinations of atomic orbitals (MO-LCAO) approach.[62] In 1962, Jansen introduced the Gaussian effective-electron model in order to simplify the calculation of many-body exchange effects, and found that first-order three-body exchange effects for the rare gases could be as large as 20% (negative for triangular geometries) of the two-body exchange energies.[34] Jansen later extended the method to second-order three-body effects and found that these corrections were very large. In reference to the crystal structure paradox, Jansen also claimed that these second-order interactions were sufficient to stabilize the fcc lattice vs the hcp lattice.[63] Lombardi and Jansen also extended the approach to four-body effects, but found that for most relevant geometries, these effects were negligible.[64] Murrell and co-workers used a perturbation theory approach to approximate exchange effects in the small overlap region.[65] In contrast to Jansen's results, they found the three-body exchange effect to be relatively small (only 10% of the ATM term) at the equilibrium separation for triangular He_3. In addition, they also found this term to be positive (repulsive), in opposition to all previous work. Clearly, the early results on possible short-range many-body effects were far from a consensus conclusion.

In 1971, *ab initio* self-consistent field (SCF) methods were first applied to the many-body problem in the calculation of many-body effects for helium.[66,67] For equilateral He_3, it was found that the total three-body effect was negative and about 5% of the two-body effect. It was also found that the four-body term for square He_4 was approximately the same magnitude as the three-body term, implying that the many-body series was not very rapidly convergent. Musso *et al.* showed that these nonadditive effects were most likely due to charge penetration effects, and that the contradictory results by Murrell and co-workers (positive three-body contribution for triangular He_3) were due to approximations inherent in their perturbation theory approach.[68] Novaro and co-workers extended their SCF approach to nonadditivity in Ne_3 and found relatively smaller three-body effects than had been the case for helium.[69,70] Kołos and Leś showed that the Gaussian effective electron method could produce much more reliable results if the Gaussian orbitals were modified to fit the SCF charge distribution of the atoms.[36] Using this approach, Kołos and Leś calculated two-, three-, and four-body effects to first-order for helium and argon. The resulting three-body effects were found to be much smaller than with Jansen's unmodified model, and basically agreed with the SCF results of Novaro *et al.* for helium. Thus, some of the early contradictions were simply identified as resulting from the effects of poor approximations within the various theoretical models.

Summarizing the theoretical situation for the period up to the early 1970s, the question of the importance of many-body effects remained unanswered. Although the nature of the long-range interaction was well-known, its applicability at typical interatomic separations had been questioned. *Ab initio* configuration interaction (CI) calculations had not yet been applied to the problem to address this concern. Moreover, the importance of nonadditive short-range forces was camoflaged by contradictory results from approximate models, and although the early SCF methods would eventually prove to be at least qualitatively correct, a consensus as to the proper treatment of these effects seemed far off.

During this same period, experimental manifestations of nonadditive effects were becoming more numerous and certain. In addition to the rare gas crystal structure paradox,[71] the measured crystal binding energies were not in agreement with simple pairwise additive sums, showing many-body effects as large as 10%.[72] Since the manifestations of nonadditive forces in the solid could be quite complicated in the case of slow convergence of the many-body expansion, a consideration of the effects of three-body forces on third virial coefficients presented itself as a more tractable problem. Graben and Present[73] showed that experimental third virial coefficients[74,75] were sensitive to three-body forces by performing pairwise additive calculations with and without the ATM term. Dymond *et al.* showed that inclusion of the ATM term gave better agreement with the experimental virial coefficients than the results from the pairwise additive potential alone.[76] Sherwood and Prausnitz studied the effects of the ATM term and a model three-body exchange repulsion term for helium on the third virial coefficient and found that both were necessary to achieve agreement with the experimental results.[77,78] However, Sherwood *et al.* concluded later that since the third virial coefficient is also sensitive to the two-body potential, it was difficult to make definitive conclusions about the influence of three-body forces.[79] Stogryn studied the specific orientation dependence of three-body induction and dispersion and the resulting effects on third virial coefficients.[80] He concluded that the dispersion effects were fairly isotropic, indicating that the atomic expression should be qualitatively valid for molecular systems.

In 1968, Barker and Pompe reported the first argon pair potential which satisfactorily fit all experimental data and had the theoretically correct long-range functional form.[18] In addition to the obvious benefit of an accurate pair potential to the solution of the many-body problem, Barker and Pompe also showed that the inclusion of the ATM term greatly enhanced the agreement of the potential with experimental third virial coefficients *and* crystal binding energies. Johnson and Spurling later extended the calculation

Table 2. Comparison of Experimental and Theoretical Crystal Binding Energies (J/mol) for the Rare Gases

rare gas	E_{exp}	$E_{\text{pw-add}}$	$E_{\text{exp}} - E_{\text{pw-add}}$	DDD[4]
Ne	−1933 ± 8[a]	−2008.2[b]	75 ± 8	63 ± 1.5
Ar	−7726 ± 13[c]	−8327.2[d]	601 ± 13	571 ± 11
Kr	−11192 ± 17[c]	−12187.1[e]	987 ± 17	1000 ± 20
Xe	−15851 ± 25[c]	−17321.9[f]	1471 ± 25	1686 ± 34

[a] McConville, G. T. *J. Chem. Phys.* **1974**, *60*, 4093. [b] Aziz, R. A.; Meath, W. J.; Allnatt, A. R. *Chem. Phys.* **1983**, *78*, 295. [c] Tessier, C.; Terlain, A.; Larher, Y. *Phys. A* **1982**, *113*, 286. [d] Aziz, R. A.; McCourt, F. R. W.; Wong, C. C. *Mol. Phys.* **1986**, *58*, 679. [e] Dham, A. K.; Alnatt, A. R.; Meath, W. J.; Aziz, R. A. *Mol. Phys.* **1989**, *67*, 1291. [f] Dham, A. K.; Meath, W. J.; Allnatt, A. R.; Aziz, R. A.; Slaman, M. J. *Chem. Phys.* **1990**, *142*, 173.

of third virial coefficients to include the third-order expansion up to QQQ terms and the fourth-order DDD term.[81,82] They found even better agreement with the experimental values when using the full expansion rather than just the ATM term alone. Although the early success of the pair + ATM term many-body potential was rather casually explained as a "fortuitous cancellation" of higher-order effects, extension of this approach to other rare gas systems and comparison to other properties was to prove surprisingly effective.

Following the initial success of the pair + ATM potential in the description of third virial coefficients and crystal binding energies for argon, Bobetic and Barker presented a slightly modified version of this pair + ATM potential which showed excellent agreement with experimental measurements of the specific heat, thermal expansion coefficient and the bulk modulus of crystalline argon.[83,84] Barker and co-workers later carried out Monte Carlo and molecular dynamics simulations using another slightly modified pair + ATM potential and found excellent agreement with all measured gas, liquid, and solid properties of argon.[85] In 1974, accurate pair potentials were determined for the krypton and xenon systems, and the inclusion of the ATM term was found to be necessary to achieve agreement with experimental crystal binding energies.[86] Pair potentials were also determined for the argon−krypton and krypton−xenon systems, and calculations of the excess thermodynamic properties of mixing revealed the necessity of the ATM term to reconcile the computed values with the experimentally determined ones.[87] Barker summarized the remarkable success of the pair + ATM approach in his 1976 review of the subject.[3]

By the mid 1970s, an impressive number of experimental properties for several of the rare gases had been well-described by the pair + ATM potential approach. Table 2 shows the remarkable agreement obtained for the crystal binding energies using the pair + ATM method. Although a rigorous theoretical justification for these results was lacking, the success of this procedure encouraged other workers to apply the simple model to other chemically different systems, such as metals.[88] At that time, Bulski and co-workers published work describing their application of *ab initio* first-order perturbation theory to the problem of *short-range* nonadditive forces. In a study of Be_3, Bulski found very large three-body exchange repulsion forces: negative and about 20% of the magnitude of the two-body exchange term at the potential minimum,[89] which later SCF calculations also revealed.[90,91] Three-body exchange effects were also calculated for the helium system and significant discrepancies with respect to the earlier SCF results of Novaro and Beltran-Lopez[67] were discovered, although the relative magnitude of the three-body effects with respect to two-body effects was roughly the same (~2% at the potential minimum).[92] It is important to stress that the first-order three-body exchange energies were calculated here to be almost precisely equal to those estimated from the ATM term, but of *opposite* sign.

Bulski and co-workers later extended their *ab initio* first-order perturbation theory calculations to Ne_3 and found results similar to those for helium, although the magnitude of the three-body exchange term was only about one-third that of the ATM term.[93] Bulski also performed SCF calculations (including corrections for basis set superposition error) on Ne_3 in order to compare with the perturbation theory findings and determine the total three-body induction + second and higher order exchange contributions.[94] At the potential minimum, the sum of these terms was found to be more than 1 order of magnitude smaller than either the first-order three-body exchange or ATM terms. Bulski and Chałasiński determined the first-order three-body exchange term for Ar_3 and again found near cancellation with the ATM term at the potential minimum.[95] In summary, the *ab initio* perturbation theory results clearly indicated that the first-order three-body exchange term could not be neglected for the helium, neon, and argon systems. In fact, the theoretical results seemed to indicate that a pairwise additive potential should be a better approximation than the empirically established pair + ATM model!

Thus far, only short-range *ab initio* calculations on the atomic systems have been discussed. In order to determine the full potential surface at all interatomic separations via *ab initio* methods, configuration interaction (CI) methods must be used to treat the dispersion energy as this contribution arises entirely from electron correlation. Although the rare gas systems possess other properties that make them excellent prototypes for the study of many-body forces, Wells and Wilson showed that careful attention must be paid to both electron correlation and basis set superposition error (BSSE) effects in order to accurately determine the full many-body potential energy surface. Reinvestigating the He_3 system, Wells and Wilson[96] found that the consequences of BSSE had badly affected the results of Novaro and Beltran-Lopez.[67] However, the new calculations confirmed the short-range picture that was emerging from the perturbation theory findings and provided one of the first *ab initio* CI estimates of the magnitude of the ATM term. The results indicated that the three-body exchange term was *twice* as big (and opposite in sign) as the three-body dispersion (ATM) term near the potential minimum. Wells and co-workers applied a similarly thorough treatment to the neon[97] and argon[98] systems, concurring with the perturbation theory conclusions about the near can-

Table 3. Comparison of Three-Body Dispersion and Exchange–Repulsion Terms (Energies in Microhartrees)

molecule	DDD[4]	E_{exchange} (perturbation order)	E_{SCF}
He_3 (R = 5.6 a_0)	0.3737	−0.7999[92,100] (E_1) 0.1804 (E_2)	−0.85[96]
Ne_3 (R = 5.96 a_0)	1.732		−0.681[98]
(R = 6.0 a_0)	1.631	−0.5951[93] (E_1)	
Ar_3 (R = 7.0 a_0)	17.66	−14.6[101] (E_1) 9.2 (E_2) −1.9 (E_3)	−12.13[98]
Kr_3 (R = 7.0 a_0)	53.56		−90.4[a]
Xe_3 (R = 8.0 a_0)	57.09		−59.0[a,b]

[a] Radzio, E.; Andzelm, J. *Chem. Phys.* **1987**, *117*, 105.
[b] Corrected for relativistic effects.

cellation of the three-body exchange term with the ATM term. The convergence of the many-body expansion for helium was also considered by Wells and Wilson.[99] Although four-body effects were found to be very sensitive to geometry, these forces were determined to be less than 1% of the three-body contribution near the potential minimum. Bulski and Chałasiński extended their perturbation theory approach to second order for He_3,[100] and explicitly showed what the general agreement between the first-order perturbation theory results and the SCF results implied: second-order three-body exchange effects are small (although they can be relevant where the first-order exchange–ATM cancellation is nearly exact). This finding indicated that Jansen's earlier warning[63] about the possibility of very large higher-order exchange effects was not warranted. However, in their first many-body forces application of supermolecular Møller–Plesset theory linked to the perturbation theory of intermolecular forces,[33] Chałasinşki *et al.* did show that second-order exchange effects were important to obtain the total three-body effect in Ar_3 near the potential minimum.[101]

Therefore, by the end of the 1980s, the combined and consistent results from the SCF/CI approach and the perturbation theory method provided a very serious theoretical objection to the empirically successful pair + ATM many-body approach. Meath's reviews provide excellent in-depth discussions of the relevant points of contention for the two contradictory positions.[4,5] Although the *ab initio* results seemed to indicate that the many-body expansion was rapidly convergent (four-body terms found to be relatively unimportant), the convergence of the perturbation theory expansion (especially for Ar_3) remained an important question to address. Table 3 contains a comparison of the most accurate DDD, exchange and SCF values for the rare gases, and it is readily seen that the theoretical position suggests a much more complicated picture than that of the empirical pair + ATM approach.

During the period in the 1980s when the *ab initio* methods firmly established the importance of the short-range many-body terms, some experimental results (which probed properties more directly influenced by short-range forces) began to indicate inconsistencies with the pair + ATM model. Molecular beam scattering experiments on rare gases absorbed onto graphite substrates had been performed for some time, and although the early studies had indicated that "surface-mediated" many-body effects were substantial,[19,20,38,40] the lack of adequate pair potentials prevented a detailed analysis. Then in 1985, Jonsson and Weare claimed that pairwise additive potentials could not reproduce the scattering results for helium impinging on a Kr–graphite surface.[102] In fact, they found that inclusion of the ATM term corrected the results in the *wrong* direction. This paper was the subject of an interesting debate recorded during a Faraday Society Discussion in 1985 (during which the salient arguments of the theoretical argument with the pair + ATM empirical rule were heatedly and revealingly discussed).[103] Cole and co-workers challenged the work summarized above, claiming that the Jonsson and Weare's He–graphite potential was not well-determined and that their own results on that system indicated that the pair + ATM potential was successful in reproducing the experimental results.[104] Subsequently, Jonsson and Weare used an improved He–graphite pair potential and found that a model that consisted of a pair + ATM + small exchange repulsion term reproduced the experimental results.[105] In a thorough experimental/theoretical study of helium scattering from a Xe–graphite surface, Aziz *et al.* concluded that the ATM correction did improve agreement with experiment. However, they strongly demonstrated that the agreement was not perfect and that improvements in the knowledge about many-body forces from these kind of experiments would require very accurate pair potentials or "future workers in this area should be prepared to be disappointed".[21] The purpose of providing a detailed account of the history of the study of many-body forces for the rare gas–graphite systems is to emphasize the crucial importance of the relative sensitivity and accuracy of an approach and the absolutely critical requirement of accurate pair potentials. The conclusions from Hutson and Schwartz's 1983 close-coupling calculations on the He–Xe/graphite system were thus proven to be prophetic: "Three-body forces have a considerable influence on the resonant scattering, but experimentally it may be difficult to distinguish the effects of three-body effects from those of uncertainties in the atom–substrate interaction".[106]

The study of many-body effects on collision-induced spectra also provided some insight on the possible role of many-body exchange interactions. In the mid 1970s, theoretical workers had looked into the possibility of absorption of light by *pure* rare gases due to many-body induced dipole moments, as was first suggested by Buckingham[107] and van Kranendonk.[108] Since the two-body dipole moments exactly cancel in a pure rare gas medium, this effect is one of the only proposed experiments that does not require knowledge of the corresponding pair potential in order to extract many-body information. Weiss used a simplified induction model to estimate the long-range induced dipole moment,[109] while Adam and Katriel attempted to model the short-range contribution to the induced dipole moment.[110] While several workers improved on these approaches,[111–113] these methods were remained quite approximate and the lack of experimental results hindered the utility of this method in the study of many-body forces.

In 1988, Guillot *et al.* introduced a modified Gaussian effective-electron model (in the spirit of Jansen[34] and Kołos and Leś[36]) to calculate three-body induced dipole moments for identical atoms using the exchange-quadrupole induced dipole (EQID) mechanism.[13] In this formalism, the effective charge redistribution resulting from the effects of the two-body exchange repulsion interaction is expressed as in a multipole series (the quadrupole is the lowest order moment allowed by symmetry for identical atoms). This quadrupole moment can then induce a *three-body* dipole moment on the third atom, resulting in an allowed, albeit weak, absorption spectrum. Krauss and Guillot later showed that the EQID model provided estimates similar to the results from SCF calculations for the three-body dipole moment.[114] Although an absorption spectrum for a pure rare gas system has yet to be observed, the application of this model to the analysis of spectra for rare gas *mixtures* has proved important. In a systematic analysis of short-range contributions to three-body dipole moments for several mixed systems, Guillot *et al.* showed that there are three important contributions: (1) three-body exchange effects, (2) the EQID mechanism, and (3) a dipole-induced dipole (DID) mechanism, occurring when a colliding pair of dissimilar atoms induces, via its two-body overlap dipole, an induced dipole on a nearby atom.[12] Molecular dynamics calculations of the induced far infrared spectrum showed that for krypton–argon mixtures, the three-body contribution to the absorption cross section was relatively large, due to near cancellation of the two-body dipoles. For mixtures consisting primarily of argon, the three-body exchange mechanism was the major contributor to the three-body spectrum. However, for mixtures consisting primarily of krypton, the larger polarizability of the krypton atom resulted in a much larger EQID contribution. In both cases, the DID mechanism was found to be unimportant. For the light H_2–helium system, only the three-body overlap mechanism was found to be important, and inclusion of this term improved agreement with the experimentally measured induced infrared spectrum.[115,116] Guillot also investigated the long-range contributions to the three-body induced dipole moment using a simple theory based on classical electrostatics.[12] For the previously mentioned krypton–argon system, Guillot found a near cancellation of exchange effects with the long-range effects near the equilibrium interatomic separation, although the two-plus three-body calculation better reproduced the experimental results.[117]

Three-body dipole polarizabilities, which may influence results from light scattering experiments of dense fluids, have also been investigated theoretically via SCF methods[118] and a classical dipole induced dipole model.[119] On the basis of calculations using pair polarizabilities,[120] Bafile *et al.* inferred that collision-induced depolarization light scattering experiments on compressed H_2 indicated temperature-dependent many-body effects.[121] At low temperatures, the experimental and theoretical results implied contributions from long-range three-body contributions, while the high temperature results implied contributions from exchange-dependent interactions. Therefore, theoretical and experimental investigations of induced absorption and scattering of light by dense media provided several counterexamples to the pair + ATM model.

The study of the structure of the solid and liquid phases of the rare gases also provided some objections to the pair + ATM rule. Kalos *et al.* showed that the experimental results for liquid and solid ^{4}He did not agree with Monte Carlo calculations using the pair + ATM models, but did agree with calculations from the simple pairwise additive model.[122] Measurements of the structure factor for krypton gas by neutron diffraction techniques indicated discrepancies with the pair + ATM model at short range that was attributed to the effects of three-body exchange repulsion.[123] Egelstaff *et al.* later performed Monte Carlo calculations to simulate their results for krypton and found that the ATM term should have little effect at higher densities, lending credence to their suggestion of possible three-body exchange effects.[124] Further study of the comparison of the theoretical and experimental results led Tau *et al.* to conclude that the short-range nonadditive term for krypton was positive,[125] a surprising result since all modern theoretical studies agree that the first-order three-body exchange contribution is negative for the rare gases. However, more recent work on liquid krypton has subsequently indicated that the experimental data may only be sufficiently accurate to suggest the applicability of the pair + ATM model, rather than to actually provide definitive identification of the various many-body forces.[126] Brillouin scattering techniques in a diamond anvil cell of argon were used to determine elastic constants up to 33 GPa and self-consistent phonon calculations were performed using the pair and pair + ATM potential models.[127] It was found that the high-pressure data could not be explained by either model, which led the authors to attribute the experimental findings to effects of many-body exchange repulsion. Loubeyre used self-consistent phonon calculations and Monte Carlo techniques with a pair + ATM model which included an approximate expression for the effects of three-body exchange repulsion to compare to high pressure experimental results for helium.[128] Although the exchange term was fit to the inaccurate SCF results of Novaro and Beltran-Lopez,[67] good agreement with experiment was achieved with this method. This approach was extended to argon using the perturbation theory results of Bulski and Chałasiński[95] to model the exchange repulsion term and a scaling procedure was used to estimate this term for krypton and xenon.[129] Once again, good agreement with experiment was obtained only upon inclusion of the three-body exchange term. However, McLean *et al.*[130] and Barker[131] later showed that inaccuracies in the repulsive part of the pair potentials could be responsible for part or all of the disagreement with the pair + ATM model. It should also be noted that the pair + ATM model continued to enjoy empirical success during this same period for a number of other properties, such as surface tension in rare gas liquids.[132]

Therefore, by the end of the 1980s, the theoretical position held that many-body exchange repulsion effects were very important in a full many-body description of the rare gas systems and some experimental methods also tentatively identified the manifestations of these effects. Although these experimental challenges to the pair + ATM model were perhaps to be expected eventually, the remarkable success of this model in describing the crystal binding energies remained an enigma. An interesting explanation for this phenomenon was put forward by LeSar in his crystal perturbation theory approach.[39] In this method, the atoms in the crystal environment constitute the zeroth-order solution, rather than the usual gas-phase convention. In the language of the usual many-body expansion, the zeroth-order solution in LeSar's method is itself explicitly many-body inclusive, due to the nature of the crystal lattice. The atomic wave functions are obtained by performing Hartree–Fock calculations on the atoms in a crystal field using local density functionals, and the interatomic interaction is handled via the Gordon–Kim[37] electron gas model. LeSar noted that the atomic orbitals in the crystal contract relative to those of the gas-phase atoms, resulting in less exchange repulsion. Therefore, the symmetry of the crystal environment serves to restrict extensive electron density redistribution.[133,134] The analogous gas-phase many-body explanation of this effect would be that the higher order exchange repulsion terms cancel each other to some extent and the total short-range many-body effect is actually quite small. McLean *et al.* carried out explicit calculations for the argon system using a pair + ATM + crystal perturbation model and obtained excellent agreement with the experimental solid-state results.[130] This conclusion is very interesting, since it represents the only theoretical explanation of the success of the pair + ATM model that does not contradict the results from *ab initio* studies of small clusters. These findings also imply that although the higher order terms in the many-body series describing the interactions of rare gases may fortuitously cancel to give a much lower order effective series, the existence of significant high-order terms serves as a caution for the study of other, more complicated, systems where the cancellation may not be so "fortuitous".

The influence of many-body effects on the formation mechanisms of rare gas clusters has been extensively studied. Polymeropoulos and Brickmann investigated argon cluster formation via molecular dynamics techniques using a Lennard-Jones pair potential + ATM potential model.[135] They found that three-body forces were indeed important at low temperatures for determining relative cluster stabilities and size distributions, confirming the role of the ATM term in the destabilization of clusters of higher order dimensionality (close-packed structures). Later, they extended this approach to xenon clusters and found that 13-atom xenon clusters were unusually stable using the many-body model, while no such "magic numbers" were observed for simulations using the pair potential alone.[136,137] Garźon and Blaisten-Barojas investigated both the ATM and three-body exchange repulsion effects on cluster formation by systematically varying the magnitude of both terms in their simulations.[138] Since the exchange term favors higher dimensional structures (triangular geometries are favored), it was found that the relative magnitudes of the two terms was crucial in determining relative structure stabilities. Chartrand *et al.* studied the formation and dynamics of small rare gas clusters via molecular dynamics and Monte Carlo simulations using the pair + ATM model.[139] For argon and krypton clusters, they concluded that although higher dimensional structures were relatively more destabilized by the ATM term, the qualitative structural trends remained unchanged. Wales studied clusters up to 55 atoms and concluded that the ATM term led to a larger number of low-energy structures than for systems with only pairwise additive potentials.[140,141] Halicioglu and White investigated similar effects in the determination of structures for small metal clusters and also found that three-body effects tend to destabilize the three-dimensional structures favored by pairwise additive potentials.[88] Although these simulations are interesting as an indicator to the possible effects of many-body forces on small clusters, detailed experimental measurements of these clusters will be necessary in order to evaluate the validity of the potential models used.

The study of small gas-phase clusters, usually through high-resolution spectroscopy, has become the method of choice in modern investigations of intermolecular forces. Spectroscopic measurements of pure rare gas clusters are extremely difficult due to the relatively small number of experiments that can be applied to the problem. Rare gas homodimers do not possess allowed rotational or vibrational transitions (although recently there have been Fourier transform microwave measurements reported for a number of the heterodimers[142]), therefore high-resolution UV–visible techniques have been used heretofore exclusively to measure the electron spectrum and the associated rotation–vibration fine structure for several of the rare gas dimers.[143] However, these techniques are hindered by limited spectral resolution, such that even with state-of-the-art techniques it would not be possible to resolve rotational structure for clusters larger than the dimer. As was mentioned earlier, many-body effects can induce dipole moments in larger clusters, thus making measurements of pure rotational and vibrational spectra possible, at least in principle. Because of the dominance of large amplitude motions possible in the dynamics of these weakly bound clusters, calculations of rotation–vibration spectra are performed in scattering coordinates using a Hamiltonian that makes no approximations concerning harmonicity or the separability of rotation and vibration. Therefore, to calculate the spectra of rare gas trimers requires an accurate three-dimensional solution to the Schrödinger equation, a start-of-the-art problem. The effects of three-body forces on the rotation–vibration spectra of rare gas trimers have been rigorously investigated by only two groups. In their study of Ar_3, Horn *et al.* found that a pair + ATM potential produced larger shifts in the vibrational frequencies than the *difference* in frequencies calculated for two accurate pair potentials.[144] This result was encouraging since it indicated that the pair potentials were probably sufficiently accurate such that three-body effects could be extracted from experimental spectra (if they could ever be measured). Later, Cooper *et al.* reinvestigated the Ar_3 system with a pair + ATM + three-body exchange repulsion (based on a modified Gaussian effective-electron model) potential.[145] Although their calculations showed inconsistencies in the results of Horn *et al.*, they confirmed that the spectroscopic manifestations of error in the pair potentials were likely to be much smaller than the manifestations of three-body forces, although significant cancellation between the ATM and three-body exchange terms was observed. Cooper *et al.* also estimated intensities for the lowest vibrational transitions from dipole moments calculated from the EQID model discussed by Guillot *et al.*[13] Unfortunately, these calculations indicated extremely low transition dipoles—$\sim 7 \times 10^{-5}$ D—implying intensities that are several orders of magnitude below the detection sensitivity of current far infrared laser techniques.

In an exciting recent development, Xu *et al.* have succeeded in the FTMW observation of the mixed rare gas trimers, Ne_2Kr and Ne_2Xe despite estimated dipole moments as low as 0.01 D.[146] Although their structural analysis tentatively identified a longer Ne—Ne bond length than in neon dimer (indicative of a repulsive three-body interaction), the most direct indication of three-body forces was evidenced in the krypton and xenon nuclear quadrupole hyperfine constants. Assuming pairwise additivity, the out-of-plane projection of the nuclear quadrupole coupling constant for the Ne_2−Kr(Xe) trimer should be twice that of the Ne−Kr(Xe) dimer. Xu *et al.* found that the magnitude and sign of the deviation from the pairwise additive prediction was different for krypton and xenon, perhaps indicating that this experimental observable is a sensitive measure of three-body forces. Definitive conclusions will have to await full three-dimensional dynamics calculations and perhaps more accurate pair potentials.

Because of the extreme sensitivity requirements necessary for the measurement of spectra for the rare gas systems, most spectroscopy has focused on so-called (rare gas)$_n$−chromophore systems that are more amenable to the absorption of radiation, yet still relatively dynamically simple enough to allow comparison with theoretical techniques. Since these chromophores must obviously be molecular, many considerations arise which do not occur in the study of pure atomic systems. Therefore, although these systems may not be perfect analogies to pure atomic systems, they may serve to form a bridge to the pure molecular systems which are of utmost practical concern (i.e. water). Unfortunately, the requirement of accurate pair potentials greatly restricts the number of useful chromophores.

In the late 1980s, Fourier transform microwave spectroscopy (FTMW) techniques ushered in the era of high-resolution spectroscopy of higher-order van der Waals clusters with the measurement of the pure rotational spectra of several Ar_2−chromophore complexes: Ar_2HF,[147−149] Ar_2HCl,[150,151] and Ar_2HCN.[152] Possible three-body effects have also been discussed in connection with more recent FTMW spectra of Ar_2-CO_2[153] and Ar_2OCS.[154] Although harmonic normal mode approximations and assumptions of semirigidity for these complexes should generally be viewed with suspicion, Ar—Ar bond lengths and stretching force constants for these complexes were compared with that of Ar_2 as a first estimate of the influence of three-body forces. The bond lengths were found to be slightly longer in all cases and the force constants slightly smaller for the Ar−Ar interaction in Ar_2HF and Ar_2HCl, perhaps indicating the effects of a destabilizing three-body interaction (as would be expected for the ATM term). However, the manifestations of large amplitude motion in the Ar_2HCN trimer prevented any kind of standard spectroscopic analysis, signaling the dangers in pursuing such simple analyses.

Many-body effects in (rare gas)$_2$−aromatic complexes have been also been studied, despite the increased level of difficulty required to obtain accurate rare gas−aromatic pair potentials. Because of the anisotropy of the rare gas−aromatic potential, the structure with a rare gas atom on each side of the aromatic ring (denoted 1 + 1) can be energetically comparable to that of an isomer with both rare gas atoms on the same side as the aromatic ring (denoted 2 + 0). For these systems, Leutwyler noted that since the 1 + 1 structure is often close in energy to the 2 + 0 structure, the influence of the three-body forces could lead to the relative stability of the 1 + 1 isomer.[31] Using rotational coherence spectroscopy, Ohline *et al.* determined the structure of Ar_2−carbazole to be the 1 + 1 isomer,[155] despite pairwise additive calculations, indicating that the 2 + 0 isomer was more stable by 30 cm^{-1}.[156,157] Spycher *et al.* used FTMW techniques to determine the 1 + 1 structure for Ar_2−furan, again in opposition to the 2 + 0 pairwise additive prediction.[158] Although all of these results must be considered very preliminary due to the quality of the pair potentials, the relevant three-body forces are undoubtedly large enough (i.e. the repulsive ATM term for the 2 + 0 geometries is much larger than an energy difference of only 30 cm^{-1}) to indeed be responsible for such rather dramatic effects.

In 1989, Hutson *et al.* performed the first calculations of vibration−rotation spectra for Ar_2HCl, significant in that it was one of the few systems for which both accurate pair potentials were known and experimental data were available, thus making the actual identification of three-body forces more likely.[159] Since Ar_2HCl is isoelectronic to Ar_3, it was hoped that the findings for three-body forces in the rare gases would provide a guide to the three-body forces operative in Ar_2HCl. Although limited computational resources prevented Hutson *et al.* from performing the exact five-dimensional dynamics calculation, they carried out a three-dimensional calculation (the Ar−Ar dynamics were neglected) and compared the results to the FTMW data. They concluded that three-body effects were evident in the experimental data, although there was not enough information in the microwave spectra alone to *determine* the nature of these three-body effects. In particular, they noted

Table 4. Comparison of Theoretical[26] and Experimental[150,160-162] Results for Ar_2HCl

		deviation from pairwise additive calculation					
	pairwise additive	DDD	induced dipole–induced dipole	exchange	exchange-quadrupole	total three-body	experimental
ground state							
binding energy (cm^{-1})	−317.931	6.869	0.709	−0.628	3.447	10.218	
B_x (MHz)	1756.99	−9.55	−1.35	2.00	−16.30	−24.84	−23.13
B_y (MHz)	1688.24	−6.26	−0.16	1.42	2.64	−2.35	−0.32
B_z (MHz)	848.73	−4.01	−0.38	0.84	−3.33	−6.80	−4.28
$\langle P_2(\cos\theta)\rangle$	0.4429	−0.0017	−0.0066	0.0000	−0.0303	−0.0375	−0.0264
$\langle\Delta(\theta,\phi)\rangle$	0.255	0.0006	0.0011	−0.0008	0.0055	0.0085	0.0058
in-plane bend							
ν_0 (cm^{-1})	39.190	−0.331	−0.636	0.047	−3.114	−3.785	−1.994
B_x (MHz)	1744.98	−10.21	−0.27	2.29	−1.58	−9.74	−61.37
B_y (MHz)	1686.04	−5.88	−0.35	0.93	2.83	−3.87	−3.62
B_z (MHz)	849.22	−4.08	−0.14	0.77	0.42	−3.40	−22.52
$\langle P_2(\cos\theta)\rangle$	−0.0031	−0.004	−0.0045	−0.0012	−0.0316	−0.0318	0.002
$\langle\Delta(\theta,\phi)\rangle$	0.3441	0.0028	0.0016	−0.0001	0.0132	0.0135	−0.004
Σ bend							
ν_0 (cm^{-1})	41.325	0.777	−0.504	0.015	−2.660	−2.414	−1.770
B_x (MHz)	1753.72	−11.87	−0.06	2.76	−4.10	−10.65	−23.02
B_y (MHz)	1766.59	−6.85	−4.28	1.04	−60.25	−48.39	−45.70
B_z (MHz)	870.47	−4.77	−1.19	0.95	−17.10	−15.63	12.57
$\langle P_2(\cos\theta)\rangle$	0.2752	−0.0284	0.0056	−0.001	0.0525	0.0167	0.016
$\langle\Delta(\theta,\phi)\rangle$	0.0591	0.0024	−0.0024	−0.0011	−0.0106	−0.0026	0.003
out-of-plane bend							
ν_0 (cm^{-1})	46.542	0.069	−0.418	−0.001	−2.370	−2.574	−1.339
B_x (MHz)	1749.94	−10.10	−0.56	2.32	−5.18	−13.50	24.0
B_y (MHz)	1705.52	−8.09	−0.09	1.45	1.84	−4.98	46.0
B_z (MHz)	856.21	−4.67	−0.17	0.94	−0.85	−4.77	−2.0
$\langle P_2(\cos\theta)\rangle$	−0.0224	−0.0026	−0.0044	−0.0005	−0.0273	−0.0301	−0.003
$\langle\Delta(\theta,\phi)\rangle$	−0.3197	−0.0004	−0.0011	−0.0007	−0.0053	−0.0048	0.025

that the manifestations of three-body effects were predicted to be much larger for the intermolecular bending vibrations, and further conclusions would have to await the experimental measurements of these modes.

In 1991, Elrod *et al.* reported the first far infrared measurement of an intermolecular vibration–rotation spectrum for a van der Waals trimer in a study of Ar_2HCl.[160] The experimental spectroscopic parameters were found to be in significant disagreement with results from the earlier pairwise additive three-dimensional (Ar–Ar fixed) dynamics calculation.[159] Subsequently, Elrod *et al.* measured the two remaining intermolecular vibrations correlating to the j = 1 rotational state of the HCl monomer and found further discrepancies in comparison to the pairwise additive calculation.[161,162] In particular, the intermolecular vibrational frequencies themselves were systematically 2–3 cm^{-1} lower than predictions from the pairwise additive calculations. However, these effects could not be definitively attributed to the influence of three-body forces since the validity of the dynamical approximation was unknown.

In parallel to these experimental efforts, Cooper and Hutson developed an approach to allow the full five-dimensional dynamical calculation to be performed, allowing a more rigorous comparison to the experimental results.[26] This method provides vibrational frequencies, angular expectation values (position of the HCl subunit within the cluster), and estimates for the rotational constants in order to compare with all experimental observables. Calculations were performed using both an older Ar–HCl pair potential [H6(3)][163] and a more recently determined Ar–HCl pair potential [H6(4,3,0)][23] in order to estimate the effect of possible errors in the pair potentials on the calculated spectroscopic properties for Ar_2HCl. The full five-dimensional pairwise additive calculations revealed the poor quantitative accuracy of the approximate three-dimensional approach, as the vibrational frequencies and rotational constants shifted by a few percent (on the order of the expected three-body effects) in the more rigorous calculation. The sensitivity of the results to the Ar–HCl pair potential was seen primarily in the shift of the vibrational frequencies (0.1–0.6 cm^{-1}), which was still relatively small compared to the continued discrepancy between the experimental and pairwise additive values (see Table 4). Additional tests of the accuracy of the H6(4,3,0) Ar–HCl potential were performed by measuring far infrared ArDCl spectra, and it was found that the H6(4,3,0) potential was indeed substantially more accurate than its predecessor.[164] These results led to a conclusion that, at a conservative estimate, the remainder uncertainties in the H6(4,3,0) potential may cause errors up to 0.3 cm^{-1} in the pairwise additive intermolecular vibrational frequencies for Ar_2HCl.[165] This estimated error was still substantially smaller than the observed discrepancies between experiment and pairwise additive calculations, indicating the significant influence of three-body forces in this cluster.

Since the experimental results and the rigorous pairwise additive dynamical calculations indicated the presence of three-body forces, Cooper and Hutson also explored four model three-body terms.[26] The three-body dispersion forces (ATM) are complicated in the case of Ar_2HCl by the anisotropic molecular polarizability of HCl. Although it was possible to treat this effect rigorously, it was found that the anisotropy of the HCl subunit has little effect on the overall three-body dispersion, thus mimicking the simplicity of an atomic system. Considerations in the damping of the ATM term were also discussed, but it was found that damping terms had little effect on the calculated spectroscopic properties. Most importantly, the ATM term was completely incapable of reconciling the disagreement between the experimental results and the pairwise additive calculations. The results contained in Table 4 indicate that the effects of the ATM term on the vibrational frequencies were relatively small and did not even necessarily shift the pairwise additive results in the correct direction. Therefore, these results indicate the inappropriateness of the pair + ATM model even for a simple (isoelectronic to Ar_3) system like Ar_2HCl.

The presence of permanent multipole moments on the HCl molecule leads to another long-range three-body term arising from the interaction of the induced multipoles that develop on the two Ar atoms in the electrostatic field of the HCl subunit. The induced dipole–induced dipole energy was calculated from the expression

$$E_{\text{idid}} = -[3(\hat{\varrho}\cdot\mu_1)(\hat{\varrho}\cdot\mu_2) - \mu_1\cdot\mu_2]/\varrho^3 \tag{8}$$

where μ_1 and μ_2 are the induced dipole vectors on the two Ar atoms and $\hat{\varrho}$ is a unit vector along the line joining them. This term is particularly interesting because of its obvious anisotropy and the corresponding possibility of large effects on the intermolecular vibrational frequencies. However, Table 4 shows that this term (even when coupled with the ATM term) is not large enough to resolve the discrepancy between the experimental and theoretical results. However, the significant effects of this term on the spectroscopic observables do provide an example of an important three-body force that is *not* present in pure atomic systems.

Cooper and Hutson then considered short-range forces, which also can be decomposed into two classes: those existing for all systems and those which exist only for molecular systems. Although Ar_2HCl was the subject of a perturbation theory *ab initio* calculation,[166] these results cannot be used directly since the actual functional forms for the three-body terms are required for inclusion in the dynamics calculation. Instead, an approach using Jansen's Gaussian effective-electron model was used to model the three-body short-range effects. The three-body exchange repulsion term (extensively discussed above for pure atomic systems) was formulated by treating the HCl charge distribution as equal to that of an argon atom. As discussed for the EQID mechanism, the exchange deformation of a pair of atoms generates a quadrupole moment on the Ar_2 pair. For a pure atomic system, the only effect on the energy is the interaction of this exchange quadrupole with the dipole moment it induces on the third atom. However, for molecular systems such as HCl, the exchange quadrupole moment of the Ar_2 pair can interact directly with the permanent moments of the molecule, a much larger effect than in the atomic case. Therefore, the short-range three-body terms were considered as a sum of the "atomic" three-body exchange and the "molecular" exchange-induced quadrupole interaction terms. In order to model the true short-range energies accurately, the parameters in these models were adjusted to agree with the sum of the perturbation terms from the *ab initio* results of Chałasiński *et al.*[166] at a number of relevant geometries.

The effects of the exchange and exchange-induced quadrupole terms on the spectroscopic parameters are shown in Table 4. The exchange term is relatively small and isotropic and cannot account for the large experimental–theoretical discrepancy. However, the exchange-induced quadrupole term is very anisotropic (destabilizing the equilibrium T-shaped configuration of Ar_2HCl), and its effect on the spectroscopic observables is large and generally shifts the pairwise additive values in the right direction to correct the difference between experiment and theory. In fact, the simple model used in this approach for this term *overcorrects* the vibrational frequencies. The total three-body effect (which is dominated by the exchange-quadrupole term) is also shown in Table 4. Good agreement is obtained for the ground-state spectroscopic parameters, while the excited vibrational states appear to be overcorrected with respect to the pairwise additive potential.

Although these results clearly indicate the importance of a previously unconsidered three body term for Ar_2HCl, there remain important discrepancies between the experimental and calculated properties. In particular, the theoretical approach does not take into account kinetic coupling (Coriolis) between vibrational states because of the increased computational effort required to do so. However, the experimental results indicate substantial perturbations to the rotational constants from these effects, making the comparison of calculated and experimental rotational constants useless for the purposes for the determination of three-body forces. This coupling problem will have to be addressed by even more rigorous, computationally expensive calculations so that this very important information can be utilized. In addition, more careful modeling of the exchange-quadrupole term will be necessary in order to achieve a satisfactory degree of quantitative agreement between experiment and theory.

Similar experiments and calculations have been performed for Ar_2DCl (which possesses a substantially different vibrational energy level structure) in order to address the generality of the findings discussed above.[165] Elrod *et al.* found a situation very similar to that found for Ar_2HCl: significant differences between calculated pairwise additive properties and experimental properties. In addition, it was found that inclusion of all four three-body terms described agove again led to good agreement for the ground-state spectroscopic parameters and *overcorrection* for the excited states experimentally measured. The excited state rotational constants were also in very poor agreement with calculated results, perhaps again indicating the effects of Coriolis coupling and the need to pursue more rigorous calculations of the rotational constants. Because of the definite similarity of the results for the Ar_2HCl and Ar_2DCl systems, it can be concluded that the experimental–theoretical discrepancies are not simply coincidental anomalies, but real manifestations of three-body forces.

Stimulated by the recent work on Ar_2HCl, Szczęśniak *et al.* very recently reinvestigated three-body forces in Ar_2HCl and Ar_2HF with their application of *ab initio* supermolecular Møller–Plesset perturbation theory.[167] A more extensive set of geometries was studied in order to address the anisotropy of the three-body terms and the possible manifestations of these effects on the vibrational frequency of the in-plane mode. Their analysis indicated that the model of Cooper and Hutson was physically reasonable, and that the major anisotropic three-body term does indeed originate from exchange–repulsion interactions. They also found that these three-body effects led to a softening of the in-plane bending coordinate, which would help explain the lowered (relative to pairwise additive) experimental bending frequency. Therefore, the new *ab initio* results generally confirmed the earlier empirical conclusions reached for Ar_2HCl.

In a combined experimental[168]–theoretical[169] approach, McIlroy and co-workers investigated the Ar_nHF ($n = 2-4$) system, for which accurate pair potentials and experimental data also existed. Although they were limited to calculations (using a pairwise additive potential) which neglected the Ar_n dynamics, their most interesting result was that the motion of the HF subunit became increasingly hindered as argon atoms were added to the cluster. This intuitive finding was, however, in opposition to the results obtained from the FTMW measurements, which indicated that the anisotropy of the HF motion stayed constant from $n = 2$ to 4.[148,170] Very recently, near-IR measurements of the in-plane and out-of-plane intermolecular vibrational modes in combination with the HF stretching state have been made,[171] and five-dimensional vibrational calculations similar to those described for Ar_2HCl have been performed for Ar_2HF.[172] Paralleling the previous findings for Ar_2HCl, the pairwise additive calculations overpredicted the Ar_2HF intermolecular modes, and the inclusion of the relevant three-body terms also resulted in improved agreement with experiment. Near-IR measurements of Ar_2DF spectra have also been accomplished.[173] Ernesti and Hutson also calculated red shifts for the HF and HCl stretching fundamentals in the Ar_2HX systems, using pairwise additive and three-body inclusive potential surfaces.[174] Once again, the addition of the exchange-quadrupole term dramatically improved the agreement with experiment, as the measured $v = 0 \rightarrow v = 1$ red shift for Ar_2HF was predicted very accurately.

There exists a substantial body of high-resolution spectroscopic data for rare gas–chromophore systems which has not yet been directly utilized in the study of many-body forces. However, because this information will eventually be useful for this purpose, we list references for the following systems: Ar_3HF,[175,176] Ar_3HCl,[177] Ar_4HF,[178] He_2Cl_2,[179] Ar_2Cl_2, Ar_3Cl_2,[180] Ar_2–glyoxal,[181] $He_2C_5H_5$, $He_2C_5H_4CH_3$,[182] and Ar_nHg.[183]

Therefore, it is clear that the study of van der Waals molecules by high-resolution spectroscopy and rigorous multidimensional quantum dynamics techniques is a very powerful approach to the elucidation of many-body forces. Because of the application of both techniques, the Ar_2HCl system is presently uniquely situated in terms of the detailed knowledge of three-body forces now at hand. The extension of this approach to four-body and higher-order effects, improved theoretical techniques, and the wider availability of accurate pair potentials will undoubtedly lead to further advances in the field. The eventual goal of extending these methods to more chemically important systems, such as water, now seems to be within reach.

In conclusion, the investigation of many-body effects in atomic systems (especially the rare gases) have received an enormous amount of experimental and theoretical attention over the last half century. The success of the pair + ATM model to describe the bulk properties of the rare gases is one of the remarkable results from this study. The application of *ab initio* methods to small clusters has led to the conclusion that three-body exchange effects are roughly equal and of opposite sign to the ATM term for all of the rare gas systems. Although these conclusions are seemingly contradictory, LeSar's crystal perturbation theory may provide the connection between the observed condensed-phase properties and the calculated small cluster properties. This remains an important point to reconcile since it has important ramifications for the rate of convergence of the many-body expansion. The results for Ar_2HCl provide a fitting close to the section of this review on many-body effects for atomic systems. Although Ar_2HCl was originally intended to serve as a spectroscopically accessible model for three-body forces in argon, the dominant three-body force was found to originate from the *molecular* subunit. Beyond general interest in many-body forces, these results indicate that the study of the rare gases may provide little direct information that can be applied to the more chemically important (and complex) systems, although the tools developed for such purposes will undoubtedly be useful. Indeed, because these tools (both experimental and theoretical) have become increasingly more powerful, it is the molecular systems which will probably command most of the attention in the future study of many-body forces.

V. Many-Body Effects in Molecular Systems

The investigation of many-body forces in molecular systems has been almost precluded by the general lack of accurate pair potentials. The complicated orientation dependence of the relevant intermolecular forces has made the generation of accurate pair potentials much more difficult than in atomic systems—an atomic pair interaction is a one-dimensional dynamics problem, while a general molecular pair possesses six degrees of freedom. Because of this increased difficulty, the use of experimental data to construct "effective" pair potentials has traditionally been the most common approach to the description of the many-body intermolecular potential. Because of its obvious importance, water has received particularly intense study, such that it is prudent to further subdivide the treatment of many-body forces in molecular systems into those for nonaqueous and for aqueous systems.

A. Nonaqueous Systems

Three-body effects for the hydrogen molecule system were among the first molecular manifestations of many-body forces to be theoretically investigated. Ree and Bender[184] used SCF-CI *ab initio* methods to study $(H_2)_3$ in order to identify three-body forces contained in an experimental effective pair potential obtained from high-pressure measurements.[185] They found that three-body effects influenced the experimental results only at relatively short-range distances ($r < 3.5$ a_0). Les and Radzio used *ab initio* perturbation theory methods to investigate the first-order three-body exchange repulsion effects for $(H_2)_3$ and found that this term was small near the potential minimum and nearly canceled with estimates for the ATM term.[186]

Hydrogen fluoride is known to polymerize into infinite "zigzag" chains with F—F distances of 2.50 Å,[187] which is substantially shorter than the F—F distance (2.75 Å) determined for $(HF)_2$,[188] and thus indicative of the effects of many-body forces. The hydrogen fluoride system has received extensive study by *ab initio* methods. In 1971, Del Bene and Pople performed the first SCF calculations on $(HF)_3$ and found that the cyclic isomer was more stable than the linear one.[189] In addition, the per H-bond stability was found to be greater than in $(HF)_2$, indicating a total "cooperative" three-body effect. Later, higher level SCF calculations contradicted this result, indicating that the linear $(HF)_3$ was actually more stable.[190,191] However, the continued application of larger basis sets in the SCF approach eventually led to a consensus that the ground state of $(HF)_3$ was indeed cyclic, despite the somewhat unfavorable pair interactions imposed by this trimer geometry.[192−195] Indeed, the per H-bond stability for cyclic $(HF)_4$ was found to be substantially greater than in the trimer due to more favorable pair interactions.[194] The total three-body effect in $(HF)_3$ was determined to be 17.2% of the pair interactions, which is substantially greater than the relative three-body effects found in the atomic systems.[195] Using *ab initio* supermolecular Møller−Plesset perturbation theory, Chałasiński *et al.* found that this large three-body effect was completely dominated by the so-called SCF deformation term,[196] which can be classically approximated by polarization effects. At the equilibrium intermolecular separation, three-body exchange−repulsion effects and the ATM term were found to be relatively insignificant, indicating a less complicated total three-body situation than found for the atomic systems. Finally, in 1993 Suhm *et al.* succeeded in measuring high-resolution near-infrared spectra of $(DF)_3$, providing the first definitive experimental evidence for the stability of the cyclic structure.[197] These spectra, in combination with the continued development of an accurate $(HF)_2$ pair potential, may eventually lead to experimental estimates of the three-body effects for the hydrogen fluoride system.

The hydrogen cyanide trimer is particularly interesting because both linear and cyclic forms have been detected by high-resolution spectroscopy methods. In 988, Jucks and Miller reported near infrared spectra of linear and cyclic $(HCN)_3$ formed in a molecular beam, indicating the near equal energies of the two isomers.[198] Subsequently, Ruoff *et al.* measured FTMW pure rotational spectra of several isotopes of the linear form of $(HCN)_3$ and determined accurate intermolecular center of mass separations (4.39 Å) and dipole moments (10.6 D).[199] Previously, the center of mass separation for $(HCN)_2$ had been measured by similar techniques to be 4.45 Å.[200,201] Similar to hydrogen fluoride, HCN is also known to polymerize into infinite chains with an intermolecular separation of 4.34 Å.[202] Thus it appears that three-body forces in $(HCN)_3$ may be responsible for about half of the bond contraction observed in going from the dimer to the bulk chain. In addition, the measured dipole moment is substantially larger than three times the HCN monomer dipole moment (8.83 D), indicating a substantial electrostatic cooperative effect. Although SCF calculations indicate that the linear isomer is substantially more stable than the cyclic form (~2 kcal/mol), the calculated large three-body effect (12% of the pair interactions) and enhanced dipole moment (11.6 D) are in good agreement with the experimental results.[203] More definitive conclusions about three-body forces in this interesting system will also have to await the determination of an accurate pair potential.

Several other molecular systems have been investigated by *ab initio* methods. The hydrogen chloride system was found to be very similar to hydrogen fluoride, although the calculated three-body forces were three times smaller for cyclic $(HCl)_3$ than in cyclic $(HF)_3$.[195,196] Cyclic $(HCl)_3$ has very recently been experimentally observed with high-resolution FTIR methods.[204] Cyclic hydrogen sulfide trimer was studied by SCF-CI methods and found to possess three-body forces that were about 10% of the two-body terms.[205] The ammonia system was studied by both SCF[206] and perturbation theory[207] methods and was found to be somewhat more complicated than $(HF)_3$. Although SCF deformation effects were also found to be dominant in cyclic $(NH_3)_3$ (leading again to a total cooperative three-body effect of about 10%), three-body exchange effects were found to be important in determining the overall anisotropy since NH_3 is not a good proton donor. In contrast to the polar systems but similar to the atomic systems, the total three-body effects for cyclic methane trimer were found to be slightly destabilizing (1.2%).[208,209] The three-body effects were found to be well-described by first- and second-order exchange effects and the ATM term, again paralleling the results for the atomic systems.

Table 5 shows the three-body energies as a percentage of the two-body forces for the molecular systems as calculated from *ab initio* theory. Many-body effects in the polar systems were found to be dominated by polarization effects that were substantially larger than the total many-body effects found in atomic systems, while calculations for the nonpolar systems [$(H_2)_3$ and $(CH_4)_3$] indicated that these systems are expected to show many-body effects more similar to the atomic systems. Experimental results from high-resolution spectroscopy methods for $(HF)_3$ and $(HCN)_3$ confirmed the importance of these three-

Table 5. Three-Body Energies for Molecular Systems[a] as a Percentage of Two-Body Terms from *ab Initio* Theory

	total	dispersion	exchange	$\Delta E^{\text{SCF-def}}$	polarization
$(H_2)_3$[186]	+1.1	+2.9	−1.8		
$(CH_4)_3$[209]	+1.2	+1.3	−0.4	−0.03	−0.02
$(NH_3)_2$[207]	−9.6	+0.5	−0.6	−10.0	−6.8
$(H_2O)_3$[255]	−9.2	+0.2	−0.5	−9.2	−5.5
$(HF)_3$[196]	−15.8	+0.1	−1.1	−14.2	−7.8
$(H_2S)_3$[205]	−10.6				
$(HCl)_3$[196]	−5.5	+0.3	−0.1	−6.8	−4.6
$(HCN)_3$[203]	−12.4				

[a] All energies for cyclic geometries (at $R_{\min}$), except for linear $(HCN)_3$.

body effects, although substantial work remains to *determine* these terms.

There has also been a considerable amount of high-resolution spectroscopic data compiled for higher order molecular complexes, although very little of it has been analyzed in terms of the possible effects of many-body forces. For completeness, we list references for the following systems: $(HCCH)_3$,[210] $(HCCH)_4$,[211] $(CO_2)_3$,[212] $(H_2O)_2(CO_2)$,[213] $(H_2O)(CO_2)_2$,[214,215] $(CO_2)_3(HCN)$,[216] $(HCN)_2Ar$,[217] $(HCN)_2(HF)$, $(HCN)_2(HCl)$, $(HCN)_2(HCF_3)$, $(HCN)_2(CO_2)$,[218] $(HCN)_2(NH_3)$, $(HCN)_2(N_2)$, $(HCN)_2(CO)$, $(HCN)_2(H_2O)$,[219] $(HCN)(HF)(CO)$, and $(HCN)(HF)(NH_3)$.[220]

B. Aqueous Systems

The most important aqueous system is, of course, pure water. Although water has received intense study by both theoretical and experimental methods, an accurate "true" pair potential has not yet been determined. Because of the small number of experiments capable of probing the binary complex alone and the six intermolecular degrees of freedom necessary to describe the interaction, the determination of a pair potential for water represents a very formidable problem. Most approaches to the problem of an intermolecular potential for water have used bulk water data to refine "effective" pair potentials which implicitly contain contributions from the full many-body potential. An enormous amount of effort has been directed toward the development and implementation of these potentials and several of them accurately reproduce important properties of bulk water. However, none of them can reproduce all such properties. The nature of this approach does not allow the n-body terms to be extracted, and the physically incorrect modeling of the interaction by two-body terms is probably responsible for the limited success of this approach. For example, some effective pair potentials yield dipole moments for the water monomer as great as 3.0 D, while the experimental value is only 1.85 D. More recently, there have been attempts to refine true [2 + 3]-body potentials for water from mainly bulk water data. Because these methods are more theoretically palatable and explicitly address many-body forces, they hold particular interest for purposes of this review. In addition, the prospects for an accurate determination of a true pair potential for water have improved recently. Although some high-resolution spectroscopic data for the binary complex have existed for almost 20 years, the lack of an adequate computational approach for the calculation of spectra for six-dimensional systems such as water have hindered the determination of a true pair potential. However, recent advances in computational techniques[221] and the first experimental observations of intermolecular vibration–rotation–tunneling transitions for the water dimer[222–224] have dramatically enhanced the prospect for having a rigorous determination of the full six-dimensional potential in the near future. A successful conclusion to these efforts coupled with the recent measurement of high-resolution spectra for the water trimer[225–228] could provide a true quantum leap in the understanding of many-body forces for water.

In 1957, Frank and Wen were the first to discuss the importance of many-body effects in water in their description of the "cooperativity" of hydrogen bonds.[229] They further speculated that liquid water could be characterized by local structure on short time scales referred to as "flickering clusters of hydrogen-bonded molecules". Lesyng and Sanger discussed neutron and X-ray diffraction studies on α-cyclodextrin·$6H_2O$ and noted the manifestations of a hydrophobic effect in the observation of chain and circular arrangements of hydrogen bonds.[230] They also discussed *ab initio* calculations which indicated the existence of stable six-membered rings in a crystal lattice, but also speculated that these structures probably fluctuate in liquid water along the lines of the "flickering" water clusters of Frank and Wen. Many workers have since invoked structural models of liquid water intended to rationalize anomalous properties such as the existence of a density maximum at 4 °C, very high heat capacities and thermodynamic discontinuities in supercooled water.[231] Speedy discussed the importance of obtaining a liquid water structural model which contained the qualities of self-replication and association with cavities (particularly important to explain the observed drop in density from 4 to 0 °C).[232] It was shown that fluctuations in the concentration of pentagonal rings could account for a number of the anomalous properties of water. Benson and Siebert recently discussed a structural model which includes clusters of octamers and tetramers in equilibrium in an effort to find a mechanism that introduced sufficient entropy to contribute to the heat capacity of water.[233] Using this model, they report good agreement with experimental heat capacities and emphasize that a random hydrogen bond breaking model cannot similarly reproduce the experimental results. In a molecular dynamics study, Plummer discussed the critical importance of cooperativity in the reorientation dynamics of liquid water.[234] This results suggests that many-body effects would be expected to significantly influence any dynamic structural model of water. Should any of these structural models of water be verified, knowledge of the individual many-body effects (in contrast to averaged total many-body effects contained in effective pair potentials) would become critical.

The use of effective pair potentials to describe bulk water properties has been the most common way to deal with many-body forces. Although these potentials are not very useful for the purposes of the study of the many-body forces themselves, an understanding of the successes and limitations of this approach provides important information for the development of true many-body models. In 1972, Ben-Naim and Stillinger introduced a model (BNS) which included a four-point-charge model (most point charge models place one unit of positive charge on each of the hydrogen atoms and two units of negative charge on an effective charge center near the oxygen atom) and a Lennard-Jones (LJ) term between oxygen atoms and fit these parameters to second virial coefficients and ice data.[235] Stillinger and Rahman later developed a variant of the BNS potential (ST2) which was adjusted to fit liquid water properties, but no longer accurately yielded second virial coefficients.[236] Berendsen *et al.* described a three-point-charge + LJ term model (SPC) which was fit to liquid data.[237] Jorgensen *et al.* used the same form as the SPC model, but fit their potential (TIP4P) to new neutron diffraction data.[238] Reimers *et al.* continued the evolution of these point-charge models by deriving a three-point-charge + Morse potentials between atoms + dispersion potential (RWK2) which was fit to gas, liquid and solid properties.[239] Reimers *et al.* also presented the best extensive comparison of calculated water properties from various effective potentials and *ab initio* potentials. Although the RWK2 potential was found to be generally the most accurate, there remained significant discrepancies in comparison to some experimental properties. In addition, little gas-phase data were included in the determination, which are the only data for which the *ab initio* potentials can be expected to be reasonably accurate. However, given the simplicity of these models, it should be considered remarkable that they provide even approximately accurate descriptions of bulk water phenomena. Unfortunately, all of these models are undoubtedly too crude to be able to describe the substantially more accurate information now becoming available for small water clusters from high-resolution spectroscopy.

The study of many-body effects in small water clusters began with *ab initio* SCF investigations in the early 1970s. Del Bene and Pople performed SCF calculations on small water clusters and found that cyclic asymmetric rings were the most stable geometries for $(H_2O)_3$.[240,241] Due to three-body effects, the per hydrogen bond stability was found to be higher than in $(H_2O)_2$, despite somewhat unfavorable pair interaction geometries. For the larger clusters where the pair interactions are more favorable, the per hydrogen bond stability was found to be very large, again indicating the effects of substantial nonadditivities. Hankins *et al.* also used SCF methods to study the linear water trimer and found very large nonadditivities, suggesting the possibility of three-body effects stabilizing linear over cyclic geometries.[242,243] Lentz and Scheraga performed higher level SCF calculations on the dimer, trimer, and tetramer of water in an effort to address this question.[244] In order to specifically address the effects of many-body forces, they separately calculated all pair interaction energies at their geometries within each of the higher-order clusters. They found that linear $(H_2O)_3$ was more stable than cyclic water trimer, although cooperative three-body effects were found to be 15% of the total pair interaction for the cyclic form. For the cyclic water tetramer, they found three-body effects were 12% and four-body effects were about 1% of the pair energies. Del Bene and Pople questioned the finding of a lower energy water trimer chain in a systematic study of basis set effects on low energy structures and nonadditivities.[245] They found the water trimer to be cyclic for all basis sets and the nonadditivities to be relatively insensitive to basis set effects.

In 1974, Clementi and co-workers introduced a different approach to the problem by using an analytical fit to points obtained by Hartree–Fock calculations on $(H_2O)_2$ to search for (pairwise additive) low-energy structures of small water clusters.[246] Once these structures were found, Hartree–Fock calculations were performed on the whole cluster to determine nonadditive effects. They found that the cyclic trimer was the most stable isomer using this pairwise additive approach and that the calculated three-body nonadditivity was about 10% of the pair interaction. Their results for the cyclic water tetramer were similar to those of Lentz and Scheraga: 10% three-body and 1% four-body contribution. Lie *et al.* later extended this approach to the HF/CI level and used Monte Carlo simulations to determine radial distribution functions and thermodynamic properties.[247] These pairwise additive calculations indicated that the nonadditive forces were more likely to affect properties such as the internal energy more noticeably than the structure of liquid water. In 1980, Clementi *et al.* performed SCF calculations (with corrections for basis set superposition error) on $(H_2O)_3$ and found that relatively small basis sets worked well for the attractive regions, but failed for the repulsive regions.[248] At the potential energy minimum, three-body effects were found to be 11% of the pair interaction, of which half could be attributed to classical polarization effects (arising from the electron density redistribution resulting from the intermolecular interaction). Habitz *et al.* later extended the previous calculations to include configuration interaction, but found that these corrections (which include dispersion terms such as the ATM) contribute little to the total three-body effect in water trimer.[249] Clementi *et al.* later directly fit these three-body effects to the classical polarization analytical form[250] and extended this formalism to four-body terms.[251] The polarization energy (for a model based on bond polarizabilities) is written as

$$E_{\mathrm{pol}} = -\frac{1}{2}\sum_{i}^{N_{\mathrm{m}}}\sum_{\lambda}^{N_{\mathrm{d}}}\bar{\mu}_{i_\lambda}\cdot\bar{E}_{i_\lambda} \qquad \bar{\mu}_{i_\lambda} = \tilde{\alpha}_{i_\lambda}\bar{E}_{i_\lambda} \tag{9}$$

where N_{m} is the total number of molecules in the system, N_{d} is the number of induced dipole moments per molecule, $\bar{\mu}_{i_\lambda}$ is the induced dipole moment at the λth bond of the ith molecule, and $\bar{E}_{i_\lambda}$ is the electric field at the i_λ bond. Kim *et al.* later used this [2 + 3 + 4]-body analytical potential in a Monte Carlo simulation to find minimum energy structures for $(H_2O)_n$ ($n = 4-8$).[252] The three- and four-body terms were found important in the determination of relative energies for structures with $n > 5$. On the basis of results from molecular dynamics calculations, Niesar *et al.* concluded that many-body effects in the analytical potential may be underestimated.[253] In an effort to find a source for this error, Corongiu and Clementi described a more rigorous handling of the many-body polarization term.[254] The efforts described in this paragraph to provide theoretically accurate *analytical* many-body potentials (particularly the success of classical polarization terms in mimicking the many-body effects) will be shown to be very important for statistical mechanics simulations and could find eventual utility in the calculation of spectra for small water clusters.

As has been the case for all systems, atomic or molecular, discussed thus far, the *ab initio* perturbation theory approach is the most useful for a rigorous understanding of the various many-body terms in water. Although the SCF deformation term was found to be the most important three-body term for the $(H_2O)_3$ cyclic minimum, the relative ratio of this term to three-body exchange repulsion effects was quite anisotropic.[255] Chałasiński *et al.* also concluded that a classical polarization model would not be a very accurate approximation for three-body effects in $(H_2O)_3$ since it accounted for only about 60% of the total three-body effect at the minimum, indicating that current approaches utilizing only the classical polarization model may be insufficiently accurate.

There have been a number of recent calculations which have specifically addressed higher-order many-body terms for water. Koehler *et al.* performed SCF/CI calculations on cyclic water tetramer with geometry optimization and found a "total" cooperativity that was 29% of the pair interactions.[256] This total cooperativity included 18% arising from three-body effects, 11% from two-body nonneighbor interactions, and 1% from four-body effects. Gil-Adalid and Ortega-Blake carried out SCF calculations on Monte Carlo-generated liquid water tetramer structures and found that the four-body forces were larger than in similar calculations for gas- and solid-phase structures, perhaps indicating slower convergence of the many-body expansion for liquid water.[257] Hermansson performed SCF calculations on tetrahedral $(H_2O)_5$ and found that the total nonadditivity was small due to a fortuitous cancellation of the individual many-body effects.[258] Newton performed *ab initio* calculations on relevant dimer and trimer geometries for Ice I and found that three-body effect accounted for more than half of the O—O bond contraction observed from $(H_2O)_2$ to ice.[259] Yoon *et al.* fit *ab initio* points to an analytical [2 + 3]-body potential and also found that the O—O bond contraction was primarily due to three-body effects, indicating that the many-body expansion may converge relatively quickly for solid water.[260] Pastor and Ortega-Blake investigated "distorted" water clusters via *ab initio* methods, rather than the usual practice of investigating the higher symmetry structures which tend to be the lowest energy conformations.[261] These "distorted" geometries are postulated to exist in the local structure of liquid water. Interestingly, the distorted geometries were characterized by much larger many-body effects than the high symmetry structures, indicating that the many-body forces in liquid water may be more important than in the more symmetrical gas and solid phases. Mhin *et al.* also used *ab initio* methods in a study of the water hexamer in order to investigate probable global minimum energy structures.[262] They found that the various semiempirical water potentials did not predict similar ground-state structures nor did any of them predict a cyclic confirmation, while *ab initio* calculations revealed that the cyclic geometry is roughly isoenergetic with other structures due to the influence of many-body forces. Dykstra applied a classical electrostatic model (which implicitly contained the effects of the many-body polarization term) to the calculation of small water cluster structures (up to $n = 10$) and found substantial many-body effects.[263] However, the per hydrogen bond stability for the trimer was calculated to be less than for the dimer, in disagreement with high level *ab initio* calculations.

Much of the work described above was motivated by the desire to perform statistical mechanical simulations to allow comparison to the bulk experimental properties of water. In order to stay within the stated bounds of this review, only simulations which specifically include many-body effects (i.e. no effective pair potentials) will be discussed. Since one of the motivations for the effective pair potential approach is the limits imposed by available computer power, it should be no surprise that explicit many-body calculations have been performed only relatively recently. Barnes *et al.* introduced a two-body + classical polarization model and using Monte Carlo techniques showed that pair properties such as the second virial coefficient could be reproduced and improvement in liquid water properties could be achieved.[264] In addition, they showed that the dynamics at aqueous interfaces (such as protein—water) are significantly affected by many-body forces. Clementi and co-workers reported improved agreement with experimental radial distribution functions using increasing more rigorous forms for the many-body potential (classical polarization).[250,251,265] In a study of ion solvation properties, Lybrand and Kollman generated an empirical [2 + 3]-body potential by refitting the RWK2 potential and using the classical many-body polarization model for the three-body water interactions and an exchange repulsion term for water—water ion interactions.[266] They found good agreement with pure water properties (gas and solid) and ion solvation energies, as well as evidence for a changes in coordination number due to many-body forces. Cieplak *et al.* later reported an improved potential and simulations for liquid water properties and found good agreement with all experimental properties except ice lattice densities and the O—O radial distribution function.[267] Caldwell *et al.* described a model similar to that described above, except that it was based on the SPC potential and the polarization terms were calculated from atom-centered induceable point dipoles (vs the bond polarizability approach of Clementi and co-workers).[268] This model was later successfully reparameterized to more accurately yield the O—O radial distribution function.[269] Corongiu and Clementi reported the results of molecular dynamics simulations (including vibrational corrections) from analytical [2 + 3]-body *ab initio* potentials and claimed that all calculated radial distribution functions were within the experimental estimates.[270] Saint-Martin *et al.* used a similar approach with Monte Carlo simulations and also found radial distribution functions in good agreement with experiment.[271] Guillot used the SPC potential + a three-body dipole-induced-dipole (DID) mechanism in his molecular dynamics simulation of the far infrared spectrum of liquid water and found better agreement with experiment than with two-body dipoles only.[272] From the work described above, it is clear that many-body effects can have important manifestations in a number of bulk water properties. Since the many-body forces operative in water have such a substantial effect on its equilibrium properties, it seems even more unlikely that the effective pair potential approach will ultimately be capable of adequately describing the water interaction.

The reliance on statistical mechanics simulations and bulk water properties is due to the dearth of experiments which directly probe three- and higher-order interactions in the gas phase. In 1972, Dyke and Muenter reported molecular beam deflection experiments on water polymers and found that only the dimer was polar, suggesting that the higher-order clusters were cyclic with very small dipole moments.[273] This result was eventually reproduced by high level *ab initio* calculations. In 1982, Vernon *et al.* used infrared vibrational dissociation spectroscopy and found that the trimer spectrum was much more consistent with a cyclic structure.[274] However, neither of these techniques provided high-resolution data on the energy levels of a higher-order complex. To aid in this effort, Mó *et al.* performed SCF/MP2 calculations on $(H_2O)_3$, confirmed the asymmetric cyclic ring structure (two hydrogen atoms above the plane and one below), and determined harmonic intra- and intermolecular vibrational frequencies.[275] Finally, in 1992, using far infrared laser spectroscopy, Pugliano and Saykally succeeded in measuring vibration–rotation–tunneling transition for $(D_2O)_3$.[225] This work provided the first definitive evidence that the water trimer was indeed cyclic and indicated the existence of complicated intermolecular dynamics. These findings stimulated a number of other theoretical investigations into the spectroscopic properties of the water trimer. Xantheas and Dunning also performed SCF/MP2 calculations on the water trimer and determined harmonic vibrational frequencies.[276] In addition, they found that the O—O bond distance contracts to 2.80 Å, which should be compared to experimental estimates of 2.98 Å for the water dimer[277] and 2.76 Å for Ice I.[278,279] Similar calculations were carried out by van Duijneveldt-van de Rijdt *et al.* which yielded a total contraction of 0.12 Å, of which 0.05 Å occurs for a pairwise additive potential and a further 0.07 Å is due to three-body effects.[280] Spectral shifts of the free O–H vibrational modes were also reported. Fowler and Schaefer also reported high-level *ab initio* calculations on the water trimer (including vibrational frequencies) and determined possible transition-state structures that were postulated to be important in explaining the observed intermolecular dynamics.[281] Schütz *et al.*[282] and Wales[283] also used SCF/MP2 *ab initio* calculations in an effort to specifically explain the spectral splittings observed by Pugliano and Saykally in terms of low-barrier intermolecular rearrangement processes. Liu *et al.* succeeded in measuring two additional vibration–rotation–tunneling bands (two for $(H_2O)_3$ and one for $(D_2O)_3$) and found rotational structure consistent with that of an exact oblate symmetric top, which is consistent with fast vibrational averaging of the out-of-plane hydrogen atoms.[226] The small spectral splittings were attributed to tunneling of protons between equivalent configurations. Subsequent measurements of more $(D_2O)_3$ vibration–rotation–tunneling spectra by Suzuki[227] and Cruzan[228] also appear to support these conclusions. Although this data is highly accurate, the number of degrees of freedom and the effects of dynamical averaging on the rotational constants have thus far prevented a structural determination which might reveal the effects of three-body forces in contracted O—O bond lengths.

Table 6. Comparison of the Lowest *ab Initio* $(H_2O)_3$ Harmonic Intermolecular Vibrational Frequencies (cm^{-1}) with Experimental Results

Xantheas *et al.* with CI[276]	Fowler *et al.*[281]	Honnegger *et al.*[a]	Mó *et al.*[275]	exp	exp $(D_2O)_3$
158	132	134	134	87[226]	41[227]
173	142	146	146		82[228]
185	145	149	149		90[224]
193	165	167	166		98[226]
218	176	182	182		

[a] Honegger, E.; Leutwyler, S. *J. Chem. Phys.* **1988**, *88*, 2582.

Because of the predicted large anisotropy of the three-body forces in $(H_2O)_3$, the position of the intermolecular vibrational modes should be sensitive manifestations of these effects. Table 6 lists the lowest harmonic intermolecular vibrational frequencies determined from various *ab initio* calculations for $(H_2O)_3$. Although only one experimental frequency [for $(H_2O)_3$] may be directly compared to the theoretical results, it is obvious that there are very serious discrepancies. In particular, it may be noted that the results from the only calculation carried out at a correlated level of theory (Xantheas *et al.*[276]) are in the worst agreement with experiment. There are two possible explanations for this very marked disagreement. The far infrared spectra have already indicated the existence of very large amplitude vibrational motion which can completely invalidate harmonic normal mode calculations such as those employed in the *ab initio* work. The other possibility is, of course, that the *ab initio* theory applied thus far is not at a sufficient level of theory to correctly yield the lowest intermolecular frequencies. From past experience with similar systems, both of these problems probably contribute to the observed discrepancies. Once rigorous dynamical methods are capable of calculating the vibrational spectrum of $(H_2O)_3$ and an accurate water pair potential is known, these spectra will undoubtedly yield exciting and important information on three-body effects in water.

In summary of the results for pure water systems, an extensive theoretical effort (both quantum and statistical mechanical) has been mounted to elucidate many-body forces and to identify possible many-body effects in the existing bulk water experimental data.

Three-body forces have been found to be substantially larger than in atomic systems and a single three-body term (orbital deformation as modeled by classical polarization) was identified as the leading many-body effect. However, *ab initio* perturbation theory calculations have indicated the limitations of this approach and discrepancies with respect to bulk experimental properties still exist. Investigations of higher order effects were found to be in conflict with regard to the convergence properties of the many-body expansion for the different phases of water. The measurement of high-resolution spectra for small water clusters was identified as an important new approach capable of addressing each term in the many-body series in the goal of building up a rigorous many-body model of bulk water.

The investigation of many-body effects in ion solvation has received much attention, as the subject is vitally important for a rigorous understanding of aqueous chemistry. As in the approach for pure water, *ab initio* methods were used to study the many-body effects and statistical mechanical simulations were used to predict experimental properties. In 1972, Kollman and Kuntz used *ab initio* methods to calculate $Li^+(H_2O)_n$ ($n = 1-3$) clusters in order to address the important many-body effects.[284] They found that $Li^+(H_2O)_2$ three-body forces were important and repulsive (unlike pure water), but the $(H_2O)_3$ three-body and the four-body forces were relatively less significant. The coordination sphere for Li^+ was found to be tetrahedral, in agreement with experiment.[285] Clementi *et al.* also addressed this system, finding, as was the case for pure water, that the many-body effects could be approximated by the classical polarization model.[286] They also found the need to use a three-body exponential repulsion term at short-range to model the *ab initio* data. Ortega-Blake *et al.* investigated magnesium and calcium ions solvated with one or two water molecules using SCF methods.[287] They found that three-body forces destabilized the hydration of the cation, and that these effects could lead to a smaller coordination number of the ion. Mathers and Kestner investigated hydrating a point charge rather than an actual ion in SCF calculations in order to better elucidate the nature of the many-body forces.[288] The findings were very similar to those for actual ions, indicating that the polarization model provides a good approximation to the many-body forces in ion−water systems. Cordeiro *et al.* performed SCF calculations on $Cu^{2+}(H_2O)_n$ ($n = 1-3$) in order to elucidate three- and four-body effects and then used these results to predict the coordination number of Cu^{2+}.[289] They found that many-body effects caused the coordination number to drop from eight for the pairwise additive potential to six for the many-body potential, with the three-body ion−water−water term being the most important. Curtiss and Jurgens used *ab initio* methods to study the hydration of Cu^+ and Cu^{2+} and found that many-body effects were much larger for Cu^{2+} and that the many-body expansion did not seem to converge using only two- and three-body terms.[290] Rode and co-workers used a combined *ab initio* Monte Carlo approach to predict the effects of many-body forces on the coordination number for the hydration[291] and ammoniation[292] of Zn^{2+}. They found that three-body effects were very important in the ammonia system as these forces dropped the coordination number from nine for a pairwise additive potential to six and into agreement with experiment.

Statistical mechanical simulations have also been used to predict a number of properties for ion solvation from *ab initio* or empirical potentials. Perez *et al.* used the polarizable water model of Barnes *et al.*[264] to perform a molecular dynamics simulation on $Na^+(H_2O)_n$ and found that the calculated solvation energies were in good agreement with experiment.[293] Curtiss *et al.* used results from *ab initio* calculations for Fe^{2+} and Fe^{3+} with one and two waters in a molecular dynamics simulation intended to predict the coordination number of each cation.[294] They found that the addition of the three-body ion−water−water term was critical to yield a coordination number of six (in agreement with experiment). Perera and Berkowitz also used molecular dynamics techniques on $Na^+(H_2O)_n$ and $Cl^-(H_2O)_n$ using the TIP4P effective pair potential[238] and the empirical [2 + 3]-body potential of Caldwell *et al.*[268] and found that only the latter potential was capable of reproducing the experimental solvation energies.[295] Cieplak and Kollman used Monte Carlo simulations on aqueous Li^+ and Cl^- using a [2 + 3]-body empirical potential, but found that many-body effects did not lead to a smaller coordination number for these ions.[296] Further investigations of these systems by Dang and co-workers indicated that three-body effects were, in fact, important to achieve agreement with experimental coordination numbers and solvation energies.[297,298]

In summary, all evidence seems to indicate that many-body effects in ion solvation are more important than in any other system considered in this review. Unlike most of the atomic and molecular systems, many-body effects in hydrated ion systems can result in substantial structural changes. Rigorous treatments of ion solvation will require detailed treatments of these effects.

VI. Conclusion

The foregoing pages have hopefully provided a broad overview of the field of many-body effects in intermolecular forces while still adequately relating the details of how such effects may be manifested in a number of important systems. The most important conclusion resulting from this survey is that a consideration of the relevant many-body forces depends greatly on the nature of the constituent units. For the small rare gas clusters, *ab initio* theory indicated that the ATM and first-order three-body exchange interactions were both very important at typical intermolecular separations, while the success of the pair + ATM potentials for the condensed phases remained somewhat of a mystery. For Ar_2-HCl, a representative rare gas−chromophore system, the dominant many-body force was found to originate from the molecular subunit and to be of short-range origin, although several other terms were also found to be significant. In the molecular systems, including water, many-body effects were found to be dominated (although not completely described) by interactions well-described by a classical polarization model. Application of the polarization model to the problem of ion solvation revealed extremely large many-body effects, leading to pronounced structural changes in the coordination shell of the ion and presumably, quite different aqueous chemistry. Although most of the experimental insight provided in the pursuit of the many-body problem has thus far come from studies of the condensed phases, the prospect of employing high-resolution spectroscopy of van der Waals molecules in conjunction with rigorous dynamics methods for calculating the spectra will clearly be an important direction in the future. Since the ongoing effort to understand many-body forces will undoubtedly continue to concentrate on more complex systems such as liquid water, the impact of this endeavor will continue to gain in importance.

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