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Pairwise and many-body contributions to interaction potentials in He_n clusters

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High level *ab initio* calculations have been carried out to assess the pairwise additivity of potentials in the attractive or well regions of the potential surfaces of clusters of helium atoms. A large basis set was employed and calculations were done at the Brueckner orbital coupled cluster level. Differences between calculated potentials for several interacting atoms and the corresponding summed pair potentials reveal the three-body and certain higher order contributions to the interaction strengths. Attraction between rare gas atoms develops from dispersion, and so helium clusters provide the most workable systems for analyzing nonadditivity of dispersion. The results indicate that the many-body or nonpairwise contributions tend to be less than a few percent of the attractive interaction across regions around the minima of the potential energy surfaces of small clusters. Dipole-dipole-dipole dispersion and dipole-dipole-quadrupole dispersion are noticeable parts of the small three-body terms.

I. INTRODUCTION

Models of weak interaction potentials are a necessary ingredient for carrying out simulations of weakly bound clusters and ultimately liquids. The most general approaches are for intra- and intermolecular bonding, though rare gas atoms among the interacting species have not been ignored (see, for instance, Refs. 1–3). A number of elements may be thought of as contributing to weak interactions, and they enter into an interaction potential in a variety of ways. Whatever their source, an important issue in developing models for large aggregations is the extent of pairwise additivity. In other words, it is important to know if a sum of pair potentials provides a complete description. If it is not complete, then it is useful to know the relative sizes of nonpairwise contributions from different elements so as to make the most judicious choice of what to include in a model potential. In this report, we focus on pairwise vs nonadditive elements in the vicinity of the potential well and on to long range.

Nonadditivity in the potential well regions of a cluster of rare gas atoms should be mostly associated with dispersion, an attractive contribution that arises through intermolecular quantum effects. An assembly of rare gas atoms lacks the electrical attractions and polarizations that occur among molecules, which may be nonadditive, and so such an assembly provides an ideal system to examine dispersion contributions in as pure a form as possible. We have undertaken to use very high level *ab initio* calculations to determine the extent of pairwise additivity in a series of small helium clusters. Because there are few electrons in these clusters, *ab initio* calculations can be carried out at very reliable levels. The results provide a quantitative assessment of the effect of neglecting three-body and four-body contributions in weak interaction models for helium

atoms. In addition, this serves as a guide for the nonadditivity in weak clusters of other species.

II. THEORETICAL APPROACH

Ab initio calculations were carried out at the coupled clusters level with double substitutions (CCD)^{4–11} with Brueckner orbitals, a calculation level designated B-CCD.^{12,13} The B-CCD calculations (the same as the “BO” treatment of Handy *et al.*¹⁴) used the original Brueckner orbital method of Chiles and Dykstra.¹² This is a pair coefficient operator method where the wave function is represented directly in terms of the atomic orbital basis set, and in place of a conventional full-integrals transform, pair Coulomb and exchange operators are constructed. We have long employed a number of procedures to enhance the computational effectiveness of this approach. These include the selection of optimum external or virtual orbitals, going only to a partially converged double substitution CC wave function when undertaking the first Brueckner iteration, and automatic extrapolations of the energy that accelerate the CCD convergence.¹⁵

In the B-CCD treatment, the molecular orbitals are optimized to annihilate the amplitudes of the single substitutions in the coupled cluster expansion. This is a strictly size-extensive treatment that is exactly equivalent to the full-CI result for separated electron pairs (i.e., noninteracting helium atoms). That is, the full correlation energy is recovered at the separated limit, and so the nature of any lingering correlation error will be an undervaluing of the well depth. Basis set error, which we tried to reduce to an unimportant level will tend to artificially deepen the well.

There have been numerous He₂ *ab initio* calculations (in particular, Refs. 16–30) that serve as a guide to selecting a suitably flexible, nearly complete basis set. In order to

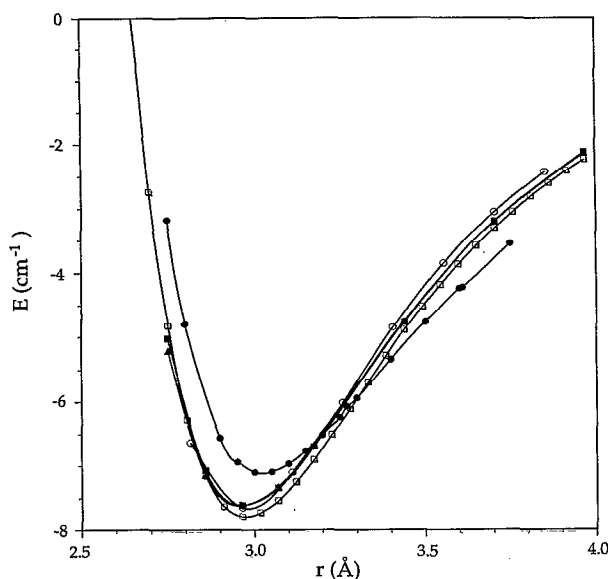


FIG. 1. Helium-helium potential energy curves obtained from the BCCD calculations (filled circle), the HFD-B potential of Aziz *et al.* (Ref. 25) (triangle), the LM2 *ab initio* potential (Ref. 27) (square), the experimental potential ESMVII of Burgmans *et al.* [Ref. 32(a)] (open circle), and the quantum Monte Carlo potential of Lowther and Coldwell (Ref. 31) (open square).

be able to carry out calculations on as many as six interacting helium atoms, we accepted a limit of thirty functions per atom. The basis set we chose was a (10s 4p 2d) set of primitive Gaussian functions contracted to (8s 4p 2d). We may assess the lingering error in this level of treatment by comparison with other results on He₂. The potential of Aziz *et al.*,²⁵ the recent *ab initio* potential of Liu and McLean,²⁷ and the quantum Monte Carlo calculations of Lowther and Coldwell³¹ are the most critical information about the He₂ potential. Relative to these, our potential is 0.5 cm⁻¹ too shallow in the well depth. Along with this small undervaluing of the attractiveness is an error in the separation distance of the minimum of the potential of at least 0.05 Å. A comparison of the calculated He₂ potential with the *ab initio* potential of Liu and McLean,²⁷ the quantum Monte Carlo potential of Lowther and Coldwell,³¹ the scattering potentials of Lee and co-

workers,³² and the potential of Aziz *et al.*²⁵ is shown in Fig. 1. The calculated curve is faithful to these curves, though, again, with the well being 0.4–0.5 cm⁻¹ too shallow.

The selection of the number of polarization functions and their exponents was based, in part, on several basis set tests on the helium dimer potential energy curve. Table I presents basis set information and the calculated values of the equilibrium separation, electronic energy at equilibrium, and the well depth. For most basis sets, we used the 8s basis of Huzinaga,³³ either contracted to 6s functions or uncontracted. Basis A consists of this s set supplemented with two p functions and one d function set. Expanding this basis to three p functions (i.e., basis B) yields a good improvement in the quality of the potential energy curve. The further improvement in the p function and d function sets in basis C yields another significant improvement. The well depth is within 0.54 cm⁻¹ of that of Aziz *et al.*²⁵ A test of the effect of contracting vs not contracting the s set was carried out via basis C', and the results show only a small effect. However, enlarging the primitive s function set to the 10s basis of Huzinaga yielded a slightly more noticeable change as seen for the results with basis D. A final test basis E was constructed from basis D by replacing the primitive s function with the largest exponent (3293.694) with three uncontracted functions with exponents of 8600, 3300, and 1270. This had little effect on the potential curve. Basis D was used for all calculations on larger helium clusters, and it is clear that there still remain basis set deficiencies, of course, in our results. Our treatment represents the compromise needed to explore clusters with up to six helium atoms over the use of an extremely large basis such as the (9s 7p 4d 3f 2g 1h) Slater basis of Liu and McLean.²⁷

Calculations were carried out for the helium dimer at 72 separation distances. The interaction energies (i.e., the total electronic energy less twice the energy of an isolated helium atom) were tabulated for these points. This set of values is the "pair potential" of this study. It was constructed by explicit *ab initio* calculation at many points rather than by curve fitting to fewer points in order to reduce numerical error in extracting three-body effects. In all trimer and larger cluster calculations, the separation

TABLE I. Helium dimer potential curve parameters.

Basis set/number of functions ^a	s set	p-function exponents	d-function exponents	E_{eq}^{BCCD} (a.u.)	R_e (Å)	D_e (cm ⁻¹)
A 18	8s/6s	1.2, 0.3	0.8	-5.795 935 4	3.1318	-4.386
B 21	8s/6s	1.3, 0.51, 0.2	0.8	-5.797 130 8	3.0753	-5.761
C 28	8s/6s	1.4, 0.58, 0.24, 0.1	1.0, 0.2	-5.798 543 0	3.0212	-7.070
C' 30	8s/8s	1.4, 0.58, 0.24, 0.1	1.0, 0.2	-5.798 597 6	3.0224	-7.040
D 30	10s/8s	1.4, 0.58, 0.24, 0.1	1.0, 0.2	-5.798 690 0	3.0217	-7.112
E 33	12s/11s	1.4, 0.58, 0.24, 0.1	1.0, 0.2	-5.798 694 8	3.0217	-7.112
HFD (Ref. 25)					2.963	-7.611
LM-2 (Ref. 27)					2.969	-7.605
QMC (Ref. 31)					2.963	-7.787

^aThe number of functions is per helium atom.

distance between every pair of helium atoms in the cluster was one of these 72 separations.

Calculations on the helium trimer and on clusters with up to six helium atoms were carried out at the same level of calculation as for the dimer. A number of linear and triangular structures were considered for the trimer. The three-body interaction energy, V_3 , was calculated at each point as the difference between the total interaction energy, V , and the sum of the pairwise (dimer) potentials.

$$V_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - V_2(|\mathbf{r}_1 - \mathbf{r}_2|) - V_2(|\mathbf{r}_1 - \mathbf{r}_3|) - V_2(|\mathbf{r}_2 - \mathbf{r}_3|). \quad (1)$$

Likewise, the four-body contributions were isolated in He_{4,5,6} calculations by subtracting two- and three-body potentials.

III. RESULTS AND DISCUSSION

A slice of the potential energy surface of He₃ corresponding to a linear arrangement of the atoms is shown in Fig. 2(a). Subtracting the pair contributions to the energy based upon the *ab initio* data points for He₂ gives the nonpairwise component of the surface in Fig. 2(b). In the very close-in regions, where the helium atoms are much closer than their van der Waals radii, the nonadditivity remains less than 2 cm⁻¹. From long range and through the potential minimum, the nonadditivity is no more than 0.7 cm⁻¹. This is about 5% of the well depth.

Another slice of the He₃ potential energy surface was obtained for triangular arrangements. Two atoms were fixed at a separation distance of 3.0 Å. The lengths of the other two sides of the triangle were varied through a range of values from 2.8–6.0 Å. This slice of interaction potential surface, shown in Fig. 3(a), includes a point very near the He₃ global minimum. The actual minimum energy structure is that of an equilateral triangle with sides 3.0225 Å long and a well depth of -22.1 cm⁻¹. This atom-atom distance is 0.0008 Å less than the equilibrium separation calculated for He₂. There is likely some cancellation of error sources between He₂ and He₃, and so this relative value (the 0.0008 Å atom-atom contraction) is probably more accurate than the absolute value for the He₃ equilibrium separation.

Subtracting the pairwise contributions from the interaction energies at each of the grid points used to generate Fig. 3(a) yields the contours shown in Fig. 3(b). These are the contours of the nonpairwise part of the interaction energy. In the vicinity of the equilibrium, this amounts to no more than 0.4 cm⁻¹ or 2% of the well depth. We have also obtained other slices for triangular arrangements and we find essentially the same degree of nonadditivity and similar features in the contours.

We expect the V_3 surfaces in Figs. 2 and 3 to be mostly a consequence of three-body dispersion interaction; however, the surfaces are total three-body contributions and have not been partitioned into dispersion vs other elements. This is in line with our aim of being able to model, if necessary, the collective three-body effects other than those that arise from charge polarization. The early anal-

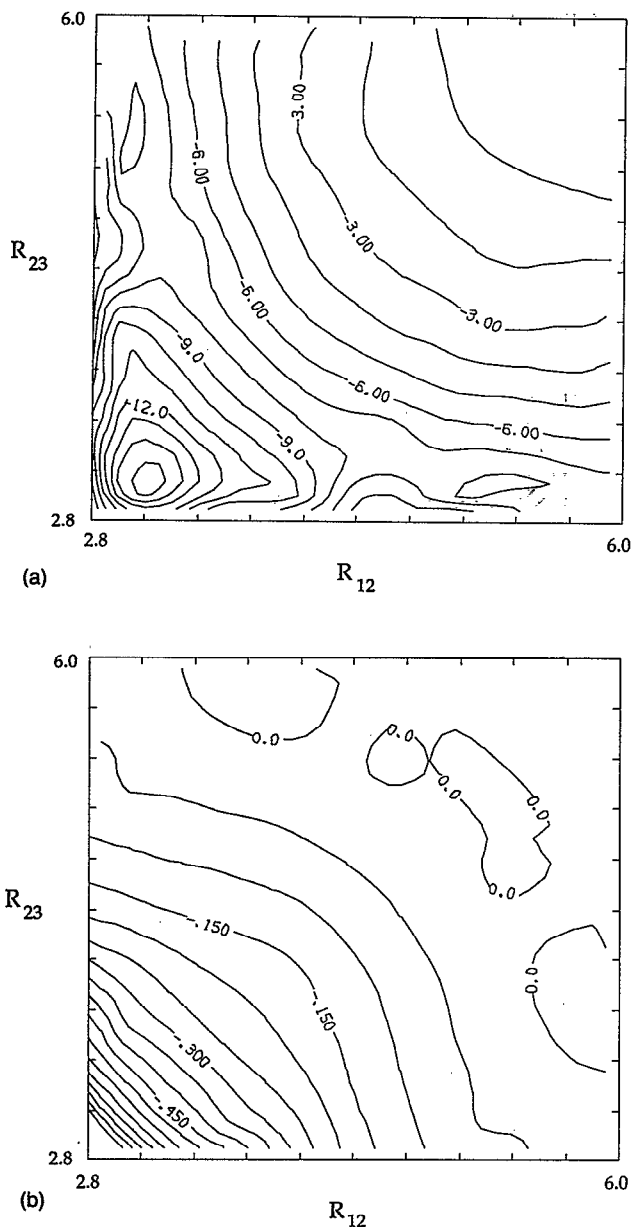


FIG. 2. (a) Potential energy surface contours (in cm⁻¹) for linear He₃. The horizontal axis gives the separation distance in Å between the first and second atoms, and the vertical axis gives the distance between the second and third atoms. (b) Contours (in cm⁻¹) of V_3 , which is the difference between the potential energy surface for linear He₃ and the sum of the dimer potentials given as Eq. (1).

ysis of three-body dispersion by Axilrod and Teller³⁴ indicated a repulsive contribution for an equilateral triangular arrangement of three like atoms and an attractive contribution for a symmetric, linear arrangement. This qualitative conclusion is found to hold in our calculations. On a more quantitative basis, Axilrod and Teller's analysis indicated that the ratio of the three-body interaction for linear to equilateral triangular structure with the same He-He distances (realizing that one of the He-He distances in the linear arrangement is twice the other two) would be -2/11 (or -0.18). At an atom-atom separation distance of 3.0 Å, our results give a value of about -2.4, and even at

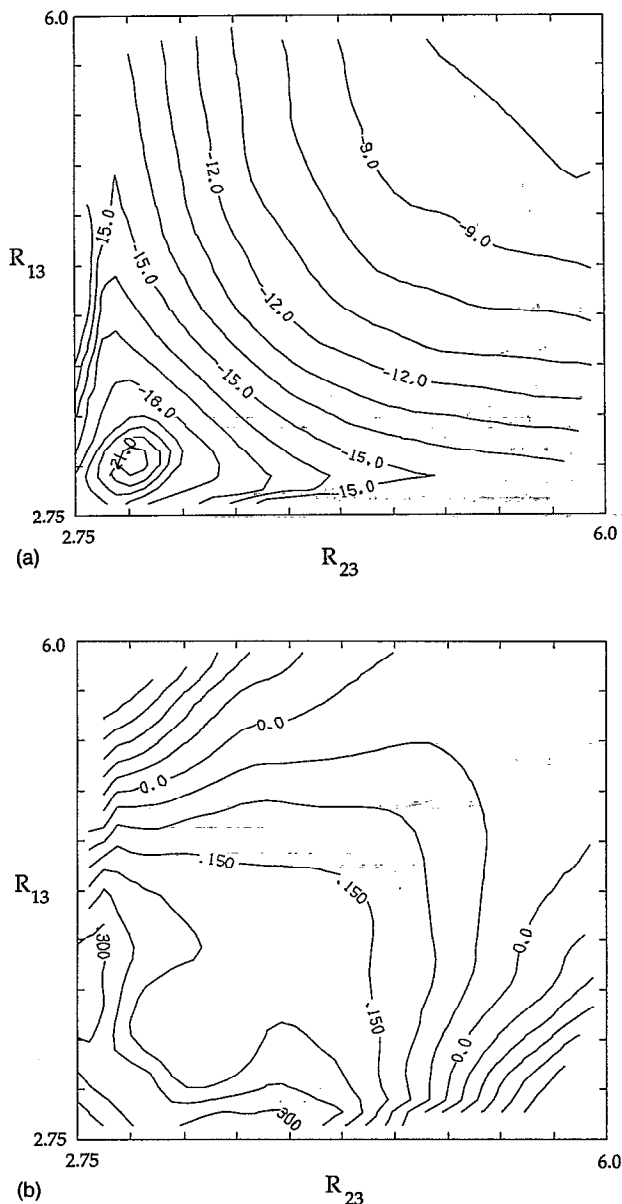


FIG. 3. Three-body interaction energies for nonlinear He₃. (a) Potential energy surface contours (in cm⁻¹) with the separation distance in Å between the first and second atoms on the horizontal axis, and the distance between the second and third atoms on the vertical axis. The third side of the triangle, the separation between the first and third atoms, was fixed at 3.0 Å. (b) Contours (in cm⁻¹) of V_3 for the nonlinear He₃ corresponding to (a).

a distance of 4.5 Å, the ratio is still -0.7 . In this view, the Axilrod and Teller analysis does not entirely describe the nonadditive elements in He₃.

Since the paper by Axilrod and Teller,³⁴ there have been a number of *ab initio* calculations on three helium atoms,³⁵⁻⁴¹ including several addressing the important issue of nonadditivity in the polarizability.⁴²⁻⁴⁴ Also, there have been fundamental efforts at determining nonadditivity in the dispersion contributions to interaction potentials.^{40,45-50} The Axilrod and Teller analysis may be termed a dipole-dipole-dipole (DDD) analysis of the interaction

of the instantaneous atom dipoles, and Spackman has achieved a direct *ab initio* determination of these terms for a number of molecules.⁴⁷ Meath and Koulis⁴⁶ have explained that higher order multipole dispersion contributions (e.g., dipole-dipole-quadrupole or DDQ) should not be overlooked, and that they have a different dependence on the separation distances. The DDD interaction goes as r^{-9} (or more specifically, as $r_{12}^{-3}r_{13}^{-3}r_{23}^{-3}$), whereas the higher order multipole interactions enter as r^{-9-2n} ($n = 1, 2, 3, \dots$).^{46,48} At the same time, as Meath and Aziz concluded,⁴⁵ there may be cancellations between higher multipole many-body terms and other many-body terms. Since our calculations are concerned only with total interaction energies, the results only indirectly address the possibility of different sources.

We have used the data set for the He₃ potential surface to find a representation of the three-body terms. There were 50 unique structures or surface points and the three-body interaction energies were least-squares fitted to several different functional forms. In each case, permutation symmetry [e.g., $V(r_{12}, r_{23}, r_{13}) = V(r_{23}, r_{13}, r_{12})$] was imposed by expanding the data set to include all structures related by permutation to the unique structures and/or by imposing the symmetry in the fitting of the potential.

The first functional fit of the three-body potential data was to a simple function, f_1 , that gives the radial dependence in the Axilrod and Teller³⁴ analysis.

$$f_1 = \frac{1}{r_{12}^3 r_{23}^3 r_{13}^3} \quad (2)$$

The rms error in this single term fit was 0.223 cm⁻¹. The next fit was to the dipole-dipole-dipole dispersion term of Axilrod and Teller, f_2 .

$$f_2 = \frac{1 + 3 \cos \theta_{12} \cos \theta_{23} \cos \theta_{13}}{r_{12}^3 r_{23}^3 r_{13}^3} \quad (3)$$

(The angle designation identifies each angle as being opposite a particular side of the triangle of three atoms.) The rms deviation in this single term fit was 0.202 cm⁻¹, which is slightly better than the fit to f_1 . However, a better improvement in the fit was achieved by a two-term fit to functions f_1 and f_2 , which, of course, is the same as allowing the two terms in f_2 to be independent. The rms deviation was found to be 0.099 cm⁻¹ and the coefficients of f_1 and the cosine part of f_2 are -5225.69 and $79\,034.2$ cm⁻¹ Å⁹, respectively. The difference in these two coefficients indicates that the data have a different sensitivity to the separation distances than that of only dipole-dipole-dipole dispersion.

The size of the dipole-dipole-dipole dispersion interaction may be expressed as an integral over frequency of the product of the frequency-dependent dipole polarizabilities of the three interacting atoms.⁴⁷⁻⁴⁹ As a point of comparison for future investigations, we note that α , the frequency independent dipole polarizability (i.e., the $\omega=0$ value), for helium from our *ab initio* calculations is 1.395 a.u. The correlation treatment is full configuration interaction, as this is the separated helium atom limit of the

Brueckner orbital CCD approach, and so any error in α must be entirely attributed to basis set deficiency. Tests of the effect on α of enlarging the p and d sets and varying exponent values, yielded changes in the dipole polarizability of less than 0.001 a.u. This indicates that the basis is

near the complete limit with respect to the dipole polarizability, and that provides further assurance that the basis is suited to analyzing the multibody dispersion effects.

The dipole-dipole-quadrupole dispersion term is⁴⁸

$$f_3 = (1 + \hat{P}_{12,13} + \hat{P}_{12,23}) \frac{9 \cos \theta_{12} - 25 \cos(3\theta_{12}) + 6 \cos(\theta_{23} - \theta_{13}) [3 + 5 \cos(2\theta_{12})]}{r_{12}^3 r_{23}^4 r_{13}^4}, \quad (4)$$

where the \hat{P} operators interchange variable subscripts so that the symmetry of the potential is preserved. This is sometimes assumed to be the next most important dispersion term. A least-squares fit of our data to the functions f_1 , f_2 , and f_3 improves the rms deviation to a value of 0.062 cm⁻¹. However, a somewhat better fit was obtained from the set of functions f_1 , f_2 , and f_4 , where the last of these is

$$f_4 = \frac{\cos \theta_{12} \cos \theta_{23} \cos \theta_{13}}{r_{12}^4 r_{23}^4 r_{13}^4}. \quad (5)$$

The rms deviation of this fit was 0.053 cm⁻¹. The radial dependence in f_4 was determined by testing other powers of the separation distances; $r_{12}^4 r_{13}^4 r_{23}^4$ gave the smallest rms deviation of all. Tests were also carried out with higher powers of the cosine functions, but none proved important in the fit. f_4 does not correspond to a higher multipole dispersion term, and we attribute its importance to the need for a different radial dependence for the triple cosine product of f_2 .

The four term fit of the data to f_1 , f_2 , f_3 , and f_4 gave an rms deviation of 0.044 cm⁻¹, and this was the best four-term fit we found. This fit could be improved to an rms deviation of about 0.03 cm⁻¹ by including an additional term that could be either a pure radial term or the triple cosine product of f_2 with a different radial dependence in the denominator. The best of these choices was the following function.

$$f_5 = \frac{\cos \theta_{12} \cos \theta_{23} \cos \theta_{13}}{r_{12}^5 r_{23}^5 r_{13}^5}. \quad (6)$$

A fit of the data to f_1 , f_2 , f_3 , f_4 , and f_5 gave an rms deviation of 0.027 cm⁻¹ and the fitting coefficients are in Table II. Further tests gave rather small improvements.

TABLE II. Coefficients of function terms in least-squares fit^a of three-body energies of He₃.

Function	Coefficient (cm ⁻¹ Å ⁿ)
f_1	$3.099\ 93 \times 10^4$
f_2	$3.311\ 76 \times 10^5$
f_3	$-3.894\ 35 \times 10^3$
f_4	$-1.581\ 77 \times 10^7$
f_5	$2.707\ 80 \times 10^8$

^a $V_3 = \sum_{i=1}^5 c_i f_i$.

The optimum fitting function differs from the multipole dispersion elements in a way that can be regarded as a few additional terms in a series expansion over radial coordinates. That is, it has the form

$$V_3 = \frac{1}{r_{12}^3 r_{13}^3 r_{23}^3} \left[C_0 + \cos \theta_{12} \cos \theta_{13} \cos \theta_{23} \sum_{n=0}^2 \frac{B_n}{r_{12}^n r_{13}^n r_{23}^n} \right] + C_3 f_3. \quad (7)$$

The difference between the simple Axilrod and Teller formula and Eq. (7) is the dipole-dipole-quadrupole dispersion term (i.e., f_3) and the more complicated radial dependence. The exponents of the separation distances that we have used in the additional terms in Eq. (7), $n=1$ and $n=2$, are not definite forms because the numerical precision of the data (about 0.002 cm⁻¹) and the geometrical range covered by the data preclude such a determination.

The practical consequence of this work is that the first realistic representation of three-body effects in helium clusters is one in which the two terms of the Axilrod and Teller formula³⁴ are allowed to be independent. With that still-simple functional form, the error in V_3 should be less than 1% of the He₃ well depth. If greater accuracy is required, then a power series expansion of these two terms in r_{12} , r_{23} , and r_{13} may be used plus the next higher multipole dispersion term. For clusters with heavier rare gas atoms, or other heavier atoms, it is possible that higher order multipole dispersion terms will be of greater relative importance partly as a consequence of the higher multipole polarizabilities being larger in heavier elements. For instance, in a study of the vibrational states of Ar₃, Horn *et al.*⁵⁰ concluded that the dipole-dipole-quadrupole term was the most important higher-multipole three-body dispersion term and that its effects on vibrational transition frequencies were smaller by only a factor of 2 than the effects of the Axilrod-Teller dipole-dipole-dipole dispersion term.

The final aspect of this study was to examine larger helium clusters. The nonadditivity of the interaction energy was evaluated for a number of geometries of He₄. The results of these calculations are given in Table III. Again, they show that the nonadditivity of the interaction potential amounts to tenths of wave numbers or just a few percent of the net attractiveness.

Additional calculations were performed for linear He₅ and He₆ clusters. The separation distance between adjacent atoms was 3.0 Å. The energies are decomposed by first

TABLE III. Calculated energies of He₄.

Geometry of He ₄ ^a <i>r</i> (Å) <i>θ</i>	<i>E</i> (B-CCD) a.u.	ΔE^b cm ⁻¹	Interaction energy less pair terms	
2.8	180	-11.597 394	-17.328	-2.313
	120	-11.597 391	-16.724	-1.103
	90	-11.597 399	-18.343	-0.771
	60	-11.597 412	-21.271	-0.909
3.0	180	-11.597 420	-23.131	-1.459
	120	-11.597 419	-22.771	-0.724
	90	-11.597 424	-23.942	-0.440
	60	-11.597 449	-29.465	-0.361
3.2	180	-11.597 409	-20.705	-0.904
	120	-11.597 409	-20.524	-0.501
	90	-11.597 412	-21.365	-0.282
	60	-11.597 437	-26.745	-0.236
4.0	180	-11.597 353	-8.292	-0.320
	120	-11.597 352	-8.208	-0.212
	90	-11.597 353	-8.354	-0.126
	60	-11.597 364	-10.723	-0.104

^aThe geometries of the clusters were with three atoms (1, 2, and 3) collinear with $r_{12}=r_{23}=r$. The fourth was at an angle θ with respect to the line of the first three and at a distance r from atom 3.

^b ΔE is the interaction energy, which is E (B-CCD) less four times the helium atom energy of $-2.899\,328\,8$ a.u.

removing the pair contributions. As shown in Table IV, the total nonpairwise attractiveness grows as a percent of the interaction energy to nearly 10% in He₆. This is mostly a consequence of the fact that there are $N(N-1)(N-2)/3! \approx N^3$ three-body interactions in an N -atom cluster, whereas the interaction energy is dominated by the nearest neighbor pair interactions (for the linear arrangements studied) and they grow as N .

The four-body interaction terms in the linear helium clusters are seen to be small in the results in Table IV. In He₆, where there are 15 four-body interactions and 6 five-body interactions, the *ab initio* results show that these total only 0.61 cm^{-1} . For small and intermediate sized clusters, accuracy in representing three-body terms is probably more important than inclusion of more-than-three body terms.

TABLE IV. Decomposition of the energies (in cm⁻¹) of linear^a He_n clusters.

Cluster size <i>n</i>	Interaction energy	Interaction energy less pair terms	Interaction energy less two- and three-body terms	Interaction energy less two-, three-, and four-body terms
2	-7.101			
3	-15.000	-0.628		
4	-23.131	-1.459	-0.184	
5	-31.313	-2.340	-0.449	-0.081
6	-39.388	-3.112	-0.606	-0.021

^aThe separation distance between adjacent atoms was 3.0 \AA .

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