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The triple-dipole (Axilrod-Teller) and the exchange three-atom potentials are compared for a number of specific arrangements of three argon and xenon atoms. For these configurations, total potentials are constructed, taking a Lennard-Jones (6-12) potential for each pair. It is found that for all arrangements the exchange three-atom potential is by far the more important correction to the two-body interaction. Qualitatively, the changes with respect to the two-body potential are more pronounced for xenon than for argon.

I. INTRODUCTION

The quantitative interpretation of properties of dense atomic or molecular systems necessitates accurate knowledge of interaction potentials over a wide range of interatomic or intermolecular separations. The theoretical determination of such potentials is a problem of long standing which is still being pursued intensively. Excellent recent reviews of this subject can be found in the literature.[1-4]

Out of the very vast spectrum of phenomena covered under the general heading of "interaction potentials" we select the simplest systems, those composed of rare-gas atoms, and we focus our attention to the question whether or not the interactions in such systems can, or cannot, be adequately described by *pair potentials*. To formalize these concepts, we denote by $\langle H_N \rangle$ the expectation value of the total Hamiltonian H_N for a system of N interacting rare-gas atoms, and by $\sum_{i=1}^{N} \langle H_0^{(i)} \rangle$ the sum of one-atom expectation values for a system of *noninteracting* atoms.[5] The static interaction potential is then defined as

$$V(1,2, \ldots, N) \equiv \langle H_N \rangle - \sum_{i=1}^{N} \langle H_0^{(i)} \rangle . \tag{1}$$

Next, we assume validity of a cluster expansion for V

$$V(1,2,\ldots,N) = \sum_{\substack{i,j=1 \\ i<j}}^{N} V(i,j) + \sum_{\substack{i,j,k=1 \\ i<j<k}} V(i,j,k) + \cdots . \tag{2}$$

The meaning of the different terms on the right of (2) is clear from this equation: Suppose Eq. (1) can be solved exactly. Separate from V that part depending on the coordinates of two atoms (i,j) only. Their sum yields the total two-atom interaction $\sum_{i<j} V(i,j)$, etc. However, since (1) cannot be solved exactly, the formal development (2) is *in practice* ambiguous in that *effective* pair potentials can be found which, in dense media, are sufficiently accurate for the interpretation of separate phenomena (cohesive energies of rare-gas solids, viscosity of compressed rare gases, heat conductivity, and the like). An average of such effective potentials for different phenomena can then serve as a first approximation to the "true" interatomic potential.

The interesting question arises whether there are phenomena in dense atomic or molecular systems which cannot be described in terms of *any* acceptable (effective) pair potential. An example is the observed stability of the face-centered cubic crystal structure for solid neon, argon, krypton, and xenon compared to that of the hexagonal close-packed arrangement: pair-potential calculations [e.g., of the Lennard-Jones (6-12) or the Mie (n,m) type] invariably yield an extremely small (order of 0.01 percent) difference between the cohesive energies of the two structures, and invariably of the wrong sign. For a more detailed account of this problem, we refer to the literature.[6]

Axilrod and Teller,[7] and Axilrod[8] were the first to address this problem in terms of three-atom interactions,

i.e., a deviation from an additive pair potential. Another phenomenon necessitating nonadditive potentials concerns low-temperature deviations of elastic coefficients from the so-called Cauchy relations in solids, observed for example with alkali halides. Detailed accounts are found in the literature.[9] However, the Axilrod-Teller three-body potential is not the only low-order contribution to the three-body interactions. It has been shown by one of us and collaborators[9] that exchange interactions may contribute significantly in the short-distance range.

The triple dipole and exchange three-body interactions are discussed in Secs. II and III, respectively. In Sec. IV the strength of the (local) exchange potential is compared to the sum of the two-body interactions and the Axilrod-Teller contribution. In Sec. V some conclusions are drawn regarding the applicability of such potentials to the numerical simulation of properties of matter.

II. TRIPLE DIPOLE POTENTIAL

The Axilrod-Teller (abbreviated AT) three-body potential can be straightforwardly derived by applying third-order Rayleigh-Schrödinger perturbation theory to a triplet i,j,k of rare-gas atoms, i.e., neglecting exchange effects. Let r_{ij}, r_{ik}, and r_{jk} denote the distances between the atomic centers and θ_i, θ_j, and θ_k inner angles of the triangle formed by them. The third-order perturbation energy, V_{AT}, is then

$$V_{AT} = v(1 + 3\cos\theta_i\cos\theta_j\cos\theta_k)/r_{ij}^3 r_{ik}^3 r_{jk}^3 , \qquad (3)$$

where $v = (9/16)\dot{I}\alpha^3$, with $\dot{I}$ the first ionization potential of the atom, and α its polarizability. Just as the Van der Waals second-order induced dipole-dipole (proportional to r^{-6}) interactions, Eq. (3) is the leading term in a multipole expansion; V_{AT} is therefore often called the "triple-dipole potential." The term $(1 + 3\cos\theta_i \times \cos\theta_j\cos\theta_k)$ is positive (repulsive V_{AT}) for all three angles $< 90°$, negative (attractive V_{AT}) if one angle is $> 90°$, reaching a minimum of -2 for three atoms on a straight line.

It is of interest, as Axilrod[8] has done, to express the distances r_{ij}, r_{ik}, and r_{jk} in terms of the nearest-neighbor distance, r_0, in the rare-gas solids. This gives rise to a factor $(9/16)\dot{I}\alpha^3/r_0^9$ in Eq. (3). We divide this quantity by the depth, ϵ, of the Lennard-Jones (6-12) potential, to obtain the dimensionless quantity $Z^* \equiv (9/16)(\dot{I}\alpha^3/\epsilon r_0^9)$. The following Table I collects, for later use, values of these parameters for the rare-gas solids Ne, Ar, Kr, and Xe.

The value of Z^* can be taken as a measure of the relative strength of the AT potential. It is very small for neon, increases steeply from Ne to Ar and to Kr, and then flattens off. In principle, the importance of the AT potential lies in providing possibly a key to the stability problem of rare-gas solids; it was in fact devised for this purpose. Axilrod[8] found that, although the AT potential does favor the fcc structure, the difference with the hcp configuration is of the order of 0.01 percent, so that conclusive evidence is not obtained on this basis. Just as the Van der Waals r^{-6} potential represents the long-range tail of the pair interaction, the AT potential constitutes the tail of the three-atom interaction. Higher-multipole contributions have also been investigated;[10-12] however, due to their shorter range, neglecting exchange effects becomes a serious shortcoming. Generally, the AT potential should not be applied for distances smaller than the nearest-neighbor separation in rare-gas solids. Short-range three-atom interactions of *exchange* type will be discussed in the next section.

Primarily because of its simple analytic form, the AT potential has found widespread application in the study of condensed rare-gas (and other) systems (see, for example, Refs. 2 and 4). A recent application by two of us[13,14] concerns the problem of stability and lifetimes of rare-gas (Ar and Xe) microclusters in a molecular dynamics simulation. Such rare-gas clusters are usually produced in the laboratory in expanding supersonic jets. After their formation, the clusters are ionized (photo or electron impact) and detected by time-of-flight mass spectrometry. An interesting feature in these experimental studies was the detection of so-called "magic numbers" in the distribution of their masses: clusters with certain ("magic") numbers of atoms occur much more frequently than their neighbors. The magic-number phenomenon was first observed by Echt, Sattler, and Recknagel[15,16] with clusters of xenon atoms. The concept of magic numbers in connection with atomic clusters of expected high stability was already formulated by Mackay[17] in 1962 on the basis of hard-sphere packing rules, with an icosahedron (thirteen atoms) as building block. The numbers resulting are 13,55,147,309,561, ..., and these numbers (or close to them) are indeed observed with xenon (and other sub-

TABLE I. Values for the different parameters determining the relative strength Z^* of the Axilrod-Teller (triple-dipole) potential between three rare-gas atoms. The values for $\dot{I}$ (first ionization potential), α (polarizability), ϵ [depth of the Lennard-Jones (6-12) potential], and r_0 (nearest-neighbor distance in the solid) are taken from standard literature. The dimensionless parameter Z^* is equal to $(9/16)\dot{I}\alpha^2/\epsilon r_0^9$.

	I (ev)	$\alpha(10^{-24}$ cm^3)	ϵ/k (K)	r_0 (Å)	$\dot{I}\alpha^3/r_0^9(10^{-16}$ erg)	Z^*(average)
Ne	21.56	0.391/0.377	34.9	3.20	0.587/0.526	0.006
Ar	15.76	1.635/1.614	119.8	3.83	6.08/5.85	0.020
Kr	14.00	2.48	171	3.95	14.95	0.037
Xe	12.13	4.03	221	4.34	21.88	0.038

stances). During the past few years, many papers have appeared, on rare gas and other clusters, often reporting exceptional stabilities for certain cluster sizes. A comprehensive list can be found, e.g., in Refs. 14 and 16.

A principal difficulty in drawing information on atomic clusters from experiments lies in the complication that the clusters are *ionized* prior to detection, so that the experimentally established exceptional stabilities may refer only to ionized, not to neutral clusters. This issue, at present much debated, has not yet been resolved; the standpoint that ionization often leads to (severe) fragmentation of the atomic clusters has been advanced among others by Haberland and co-workers.[18]

Apart from this issue, the question can be asked regarding validity of Mackay's packing rules for stability of microclusters under a potential more realistic than that pertaining to rigid spheres. It was mentioned earlier that certain of the observed peaks with xenon clusters[15,16] can be "explained" on the basis of Mackay's rules; others, however, are not. For argon no magic numbers for small clusters have been observed. The magic numbers found by Friedman and Beuhler[19] for larger argon microclusters deviate considerably from the Mackay numbers. It is not easy to see why xenon should comply so much better with these rules than argon, also if ionization is important. Molecular-dynamics (MD) simulation of microcluster stability and lifetimes offers an excellent tool for pursuing the magic number phenomenon. In the research quoted above,[13,14] MD computations for argon and xenon in the compressed gas phase were carried out, and the stability and lifetimes of the clusters formed were analyzed as a function of the interaction potential. The potential used was of the Lennard-Jones (6,12) form, supplemented by the AT potential (3). The magic number $n = 13$ was *not* found with a Lennard-Jones potential alone; it *did* appear, however, for xenon clusters upon adding the AT potential. For argon, $n = 13$ was not found to be magic in either case. The question whether $n = 19$ is also magic could not be answered because of limitations in computer time.

The results for $n = 13$ clearly indicate that three-atom potentials may have a decisive influence on the exceptional stability of clusters of certain sizes. In the following section we will discuss the *short-range* counterpart of the AT potential as a step towards MD calculations including the complete three-atom potential.

Another aspect of microclusters stability, but unrelated to magic numbers, concerns the most stable structure for a cluster of a *given* number of rare-gas atoms. On the basis of a Lennard-Jones (6-12) or a Morse potential it is invariably found that $(n > 3)$ small-sized clusters should possess a compact three-dimensional structure.[20-26] It seems realistic to assume that such a result will hold for any acceptable *pair* potential. On the other hand it is tempting to speculate, albeit without *a priori* theoretical foundation, what the most stable configuration would become if the factor Z^* in front of the "reduced" AT potential could be increased by, say, one order of magnitude. Static calculations of this type have been carried through by Hoare *et al.*,[21-23] Halicioglu and White,[24,25] and by Oksuz.[26] At very large values of Z^* a *linear* cluster configuration is found to be energetically favored, in view of

the form of the AT potential. At about $Z^* \sim 0.3$, interesting changes happen, e.g., the close-packed icosahedron for $n = 13$ no longer becomes the structure of lowest potential energy, eventually giving way to two-dimensional structures and, finally, to a one-dimensional arrangement of the atoms. For details, see Refs. 21–26. A look at the Z^* values of Table I, however, reveals that $Z^* \geq 0.3$ is unrealistic on the basis of the AT potential: The values of Z^* for rare-gas solids are smaller by at least one order of magnitude. As such, the question of $(n = 13)$ structures more stable than the icosahedron under the influence of AT-type interactions, can be dismissed as unrealistic. However, the short-range three-atom potential, of exchange type, to which we will now turn, can produce changes in stability and, at the same time, explains the higher stability of the face-centered cubic structure for rare-gas solids.[27]

III. THREE-ATOM EXCHANGE INTERACTIONS

A three-atom exchange potential was proposed by one of us and collaborators,[6] again in connection with the rare-gas crystal stability problem. This potential is obtained from model calculations applying perturbation theory in first and second orders, including exchange. In the model, the electrons on each one of the three atoms are replaced by one ("effective") electron; the spins of the three electrons are taken parallel, to avoid chemical bonding. The orbitals of these electrons are chosen of $1s$-Gaussian form with a parameter β such as to reproduce the r^{-6} part of the Lennard-Jones (6,12) pair potential, or from a fit to the diamagnetic susceptibilities of the atoms.[6,28] A perturbation procedure is followed in which the different orders are defined in terms of powers of a small parameter λ as in the usual Schrödinger perturbation theory without exchange.[29] This necessitates a redefinition of the unperturbed Hamiltonian H_0 and the perturbation H' which for the special case of two hydrogen atoms a and b are defined as follows:

$$H_0 = H_0(1,2)\Lambda_{12} + H_0(2,1)\Lambda_{21} ,$$

$$H' = H'(1,2)\Lambda_{12} + H'(2,1)\Lambda_{21} .$$
(4)

Here electron 1 is associated with nucleus a and 2 with b, and Λ_{12} and Λ_{21} are linear operators which project from the permutation-symmetrized wave functions to the associated simple-product functions. In this formalism the first-(E_1) and second-(E_2) order perturbation energies are given by:

$$E_1 = \langle \psi^{(0)} | H' \psi^{(0)} \rangle + C_1 ,$$
(5)

$$E_2 = -\epsilon^{-1}[\langle \psi^{(0)} | H'^2 \psi^{(0)} \rangle - \langle \psi^{(0)} | H' \psi^{(0)} \rangle^2] + C_2 ,$$
(6)

where ϵ is the Unsöld average energy. C_1 and C_2 are correction terms which are neglected with respect to the main terms in the equations. The wave function for a triplet (abc) of atoms is written as

$$\psi^{(0)}(abc) = N \det[\phi_a(1)\phi_b(2)\phi_c(3)] ,$$
(7)

where

$$N = [3!(1 - \Delta_{abc}^2)]^{-1/2} \ ;$$

$$\phi = (\beta/\pi^{1/2})^{3/2} \exp(-\beta^2 r^2/2)$$

and the overlap integral

$$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc} \ .$$

Let E_1, E_2, denote the first- and second-order interaction energies for a given triplet, and $E_1^{(0)}$, $E_2^{(0)}$, the sum of pair interactions in these orders. Then $\Delta E_1 \equiv E_1 - E_1^{(0)}$ and $\Delta E_2 \equiv E_2 - E_2^{(0)}$ are the first- and second-order three-atom interactions, and $\Delta E_1/E_1^{(0)}$, $\Delta E_2/E_2^{(0)}$ their values relative to pair interactions. For isosceles triangles of atoms, opening angle θ, two pairs at nearest-neighbor distance in the solids, from neon to xenon, it is found that (details are given in Ref. 6)

$$\Delta E_1/E_1^{(0)} \simeq \Delta E_2/E_2^{(0)} \ .$$

These relative three-atom energies are negative (10 to 20 percent) at $\theta = 60°$ (equilateral triangle), positive (4 to 7 percent) at $\theta = 180°$ (linear array of atoms) from neon to xenon. For molecular dynamics calculations, we need to know the total three-atom exchange energy ΔE per triplet, with $\Delta E \equiv \Delta E_1 + \Delta E_2$. Denoting the total pair interaction for a triplet by $E^{(0)} \equiv E_1^{(0)} + E_2^{(0)}$ we have, from the equality mentioned above,
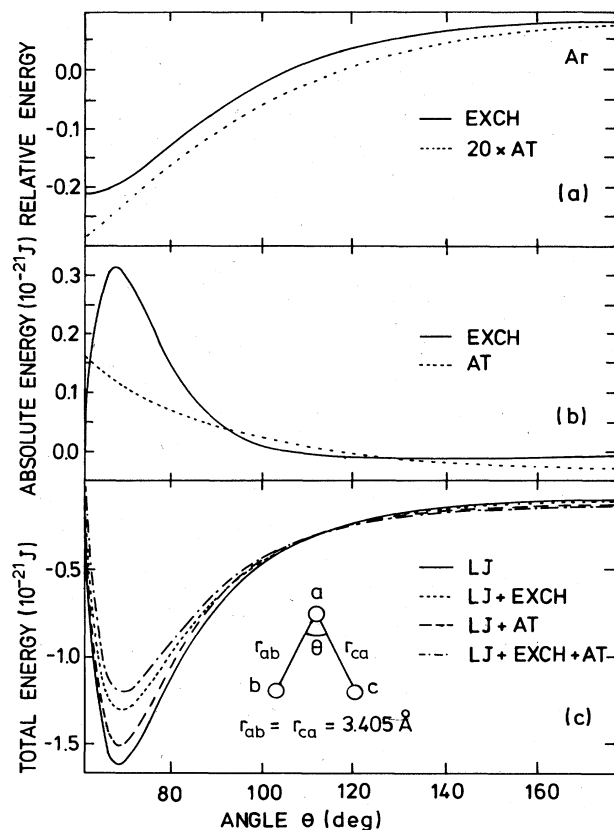

FIG. 1. Relative exchange and relative Axilrod-Teller (multiplied by 20) three-atom interactions [1(a)], absolute three-atom energies [1(b)], and total potentials [1(c)] for isosceles triangles with opening angle θ, for argon. The smallest distance between two atoms is 3.405 Å, corresponding to the Lennard-Jones σ parameter.
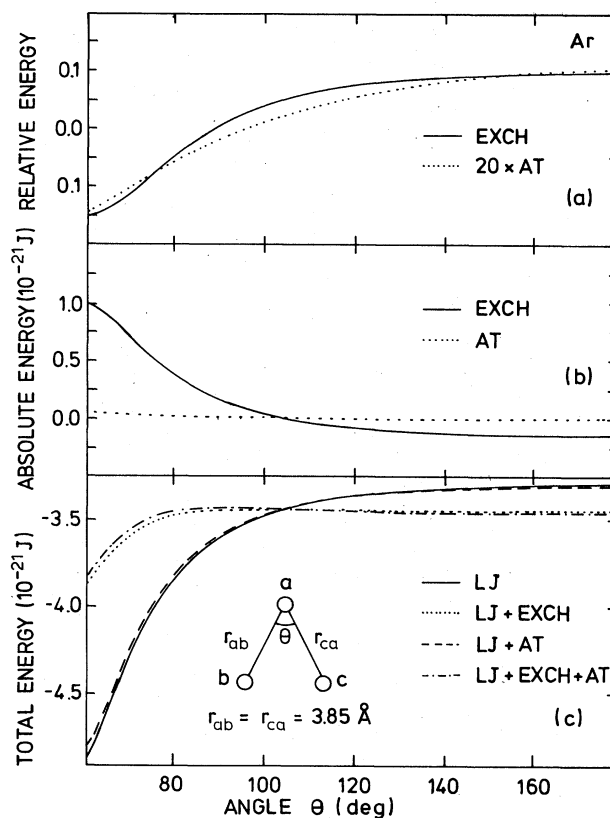

FIG. 2. Same as Fig. 1 with smallest distance equal to 3.85 Å, corresponding to the nearest-neighbor distance in solid argon.

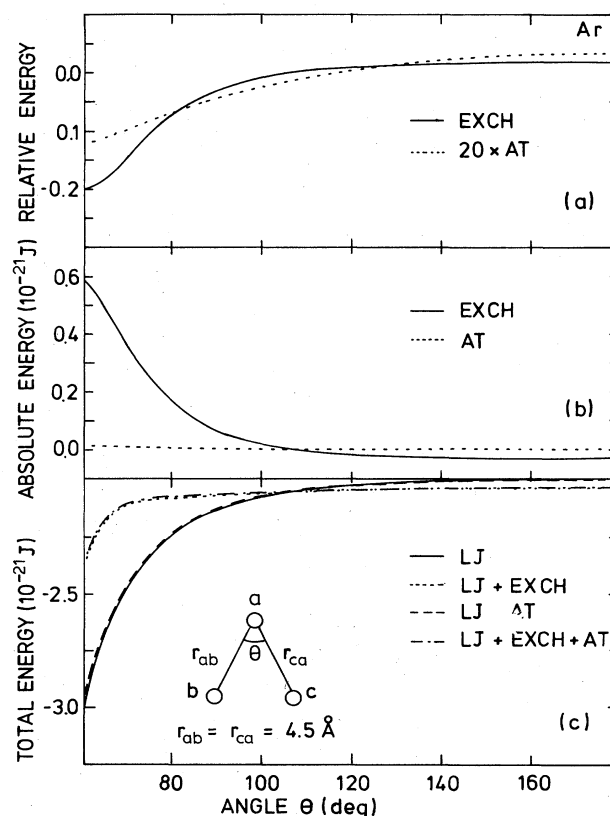FIG. 3. Same as in Fig. 1 with smallest distance equal to 4.5 Å.

$$\frac{\Delta E}{E^{(0)}} = \frac{\Delta E_1 + \Delta E_2}{E_1^{(0)} + E_2^{(0)}} \simeq \frac{\Delta E_1}{E_1^{(0)}} \simeq \frac{\Delta E_2}{E_2^{(0)}} \qquad (8)$$

and thus

$$\Delta E \simeq \frac{\Delta E_1}{E_1^{(0)}} E^{(0)} \simeq \frac{\Delta E_2}{E_2^{(0)}} E^{(0)} \; . \qquad (8')$$

For the total pair interaction $E^{(0)}$ of a given triplet it is most accurate to take the sum $\sum^{(LJ)}$ of Lennard-Jones (6,12) potentials for the three pairs of atoms; the relative three-atom exchange interaction is obtained from the model calculations. In the rare-gas solids, nonisosceles triangles as well as those involving atoms from further shells around a central atom play a minor role for stability. On the basis of the above results it is easily established that the face-centered cubic lattice has the higher stability, by a few percent of the cohesive energy, compared with the hexagonal close-packed structure. Details are given in Ref. 6. In the next section we compare ΔE, Eq. (8'), the Axilrod-Teller potential V_{AT}, Eq. (3), and the total Lennard-Jones potential $\sum^{(LJ)}$, for a number of specific arrangements of three argon and three xenon atoms, respectively.
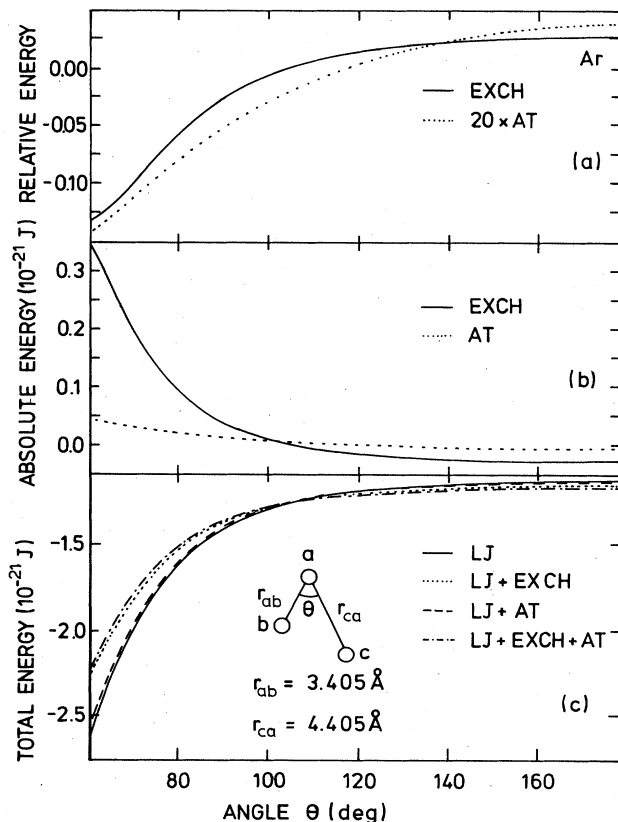
IV. COMPARISON BETWEEN LENNARD-JONES (6-12) POTENTIALS, AXILROD-TELLER (AT) AND THREE-ATOM EXCHANGE POTENTIALS, FOR SPECIFIC ARRANGEMENTS OF ARGON AND XENON ATOMS

As has already been mentioned, three-body contributions to the total potential are expected to play an important role with respect to the stability and structure of matter. It is, therefore, important to know how the potentials described in Secs. II and III contribute to the total energy as a function of the spatial arrangement of the atoms. It is difficult to make this comparison analytically because of the complex mathematical form of the exchange potential.[30] For this reason, a number of different atomic arrangements will be analyzed numerically.

It is instructive first to compare $\Delta E_1/E_1^{(0)}$ (or $\Delta E_2/E_2^{(0)}$) with the Axilrod-Teller potential, relative to the sum $-\sum_{i<j} \frac{3}{4} I \alpha^2/r_{ij}^6$ of the Van der Waals induced-dipole interaction for the three pairs. Abbreviating this sum by $\sum^{(VdW)}$ we obtain, with (3)

$$V_{AT}/\sum^{(VdW)} = - \frac{3\alpha(1 + 3\cos\theta_i\cos\theta_j\cos\theta_k)/r_{ij}^3 r_{ik}^3 r_{jk}^3}{4(1/r_{ij}^6 + 1/r_{ik}^6 + 1/r_{jk}^6)} \; ,$$

(9)

which is negative for angles $< 90°$, and positive for larger angles.

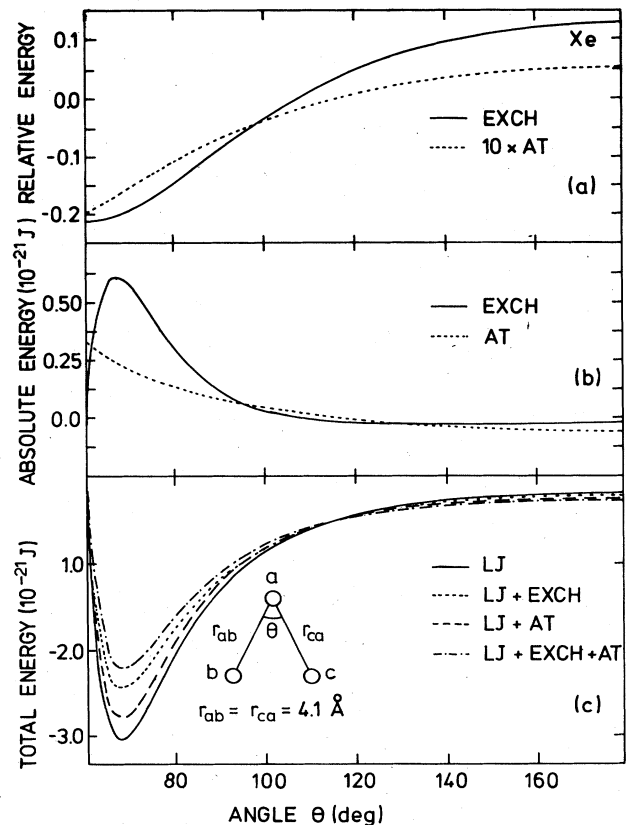FIG. 4. Same as in Fig. 1 but for nonisosceles arrangements of three argon atoms.

FIG. 5. Same as in Fig. 1 for three xenon atoms in which the smallest distance is 4.1 Å, corresponding to the Lennard-Jones σ parameter.
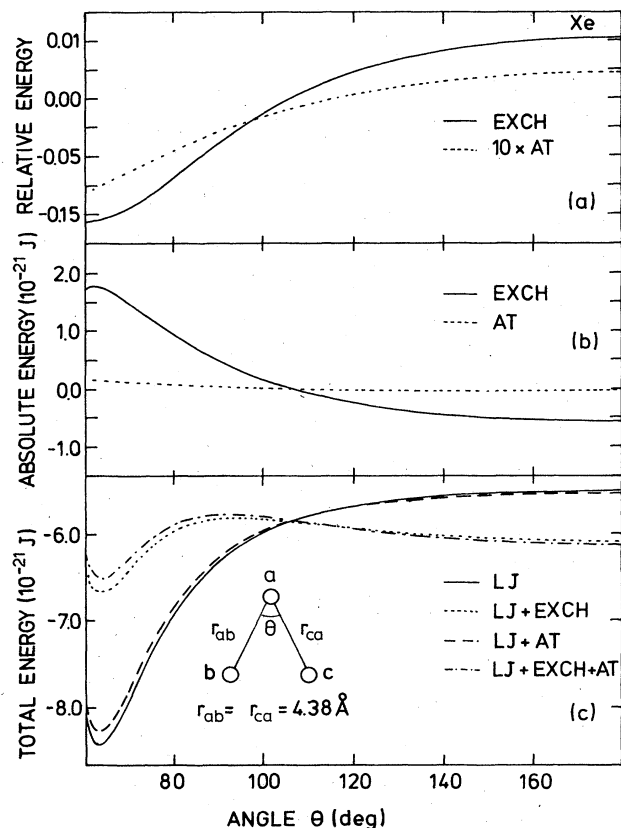
FIG. 6. Same as in Fig. 1 with smallest distance equal to 4.38 Å, corresponding approximately to the nearest-neighbor distance in solid xenon.

In the following figures, 1(a), 2(a), and 3(a) for argon, and 5(a), 6(a), and 7(a) for xenon, we compare the two relative potentials for a triplet of argon or xenon atoms in isosceles arrangements in which the opening angle is θ, the Gaussian β parameters are 0.623 and 0.454 Å^{-1}, the nearest-neighbor distances 3.85 and 4.38 Å, ϵ/k is 119.8 and 221 K, and σ is 3.405 and 4.1 Å for argon and xenon, respectively.

From these figures we conclude:

(i) the strength of the relative first- or second-order exchange interaction is for argon about *twenty times* that of the relative Axilrod-Teller potential [Eq. (9)] for all isosceles triangles. This factor is found to be about *ten* for xenon atoms;

(ii) the dependence of the relative exchange interaction on the opening angle θ of the isosceles triangle resembles that of the relative AT potential [Eq. (9)]: it is negative for small θ, positive for larger θ. The relative exchange interaction first increases more steeply with increasing θ and then flattens off more markedly.

In Figs. 1(b), 2(b), and 3(b) for argon, and 5(b), 6(b), and 7(b) for xenon, we plot the absolute three-body energies corresponding to the Axilrod-Teller and exchange potentials for the same isosceles arrangements. As can be seen from Figs. 1(b) and 5(b), the Axilrod-Teller potential be-
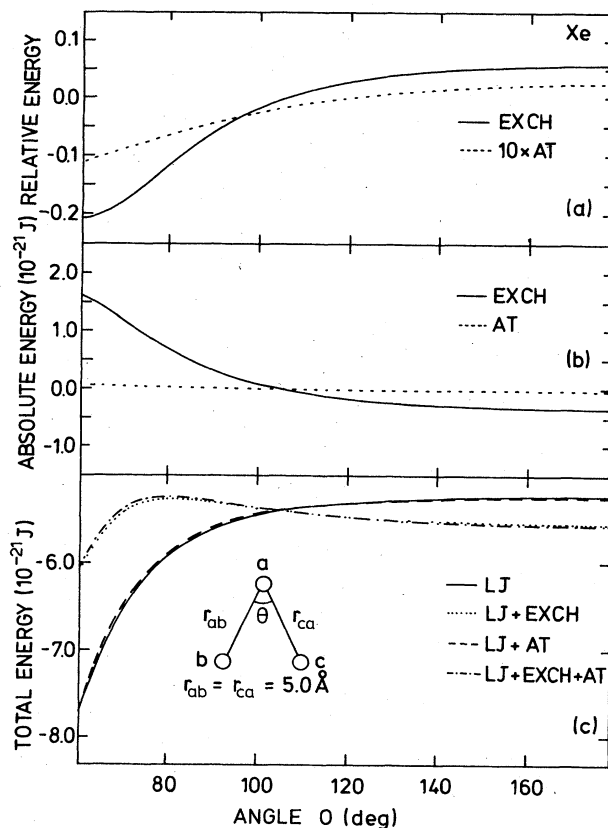
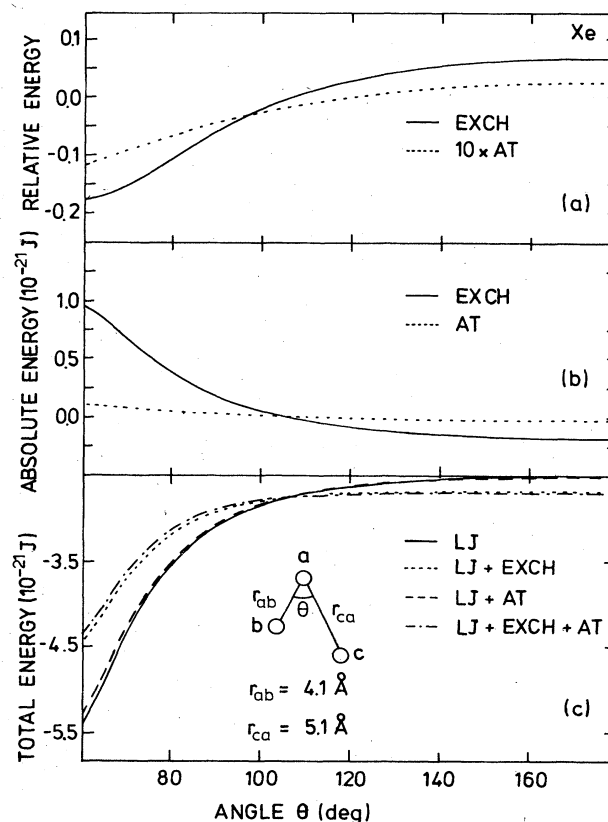FIG. 7. Same as in Fig. 1 with smallest distance equal to 5.0 Å.

FIG. 8. Same as in Fig. 1 but for nonisosceles arrangements of three xenon atoms.

comes relatively important for angle less than 100°. We note that at 60° the exchange potential becomes zero in Figs. 1(b) and 5(b), because the sum of Lennard-Jones potentials vanishes.

The potential for the isosceles arrangements given above are presented in Figs. 1(c), 2(c), 3(c) for argon and 5(c), 6(c), and 7(c) for xenon. For distances smaller than the nearest-neighbor separation in the solid the *qualitative* behavior of the total energy as a function of the angle is not affected by three-body contributions. *Quantitatively* the exchange potential contributes significantly more than the AT-potential. With increasing distances also qualitative changes occur in the angle dependence of the potential. The change in the pair potential because of the three-atom exchange interactions is of the magnitude expected if the factor Z^* in the AT potential increases by an order of magnitude.[24−26]

Finally, in Figs. 4(a)—4(c) and 8(a)—8(c) we compare the relative, the total three-body interactions and the total potentials for nonisosceles configurations for argon and xenon, respectively. The same trends as those found for isosceles arrangements are also observed for these triangles under the assumption that $\Delta E_1/E_1^{(0)} \simeq \Delta E_2/E_2^{(0)}$ also for nonisosceles triangles. Therefore, the relative impor-

tance of the three-body exchange potential is not restricted to particular arrangements of the atoms.

V. SUMMARY

By applying first- (and second-) order exchange perturbation theory, supplemented by third-order nonexchange (Axilrod-Teller) three-atom interactions, we have constructed potential-energy functions for three rare-gas atoms (argon and xenon) for specific spatial configurations. The exchange three-atom interactions affect only the immediate neighborhood of an atom selected, whereas the Axilrod-Teller potential is of longer range. The total interaction for a three-atom configuration, taking a Lennard-Jones (6-12) potential for each pair, differs considerably from a two-body description if the distance between closest neighbors is larger than the Lennard-Jones σ parameter. These differences are qualitatively more pronounced for xenon than for argon. It is expected that these differences will play an important role with respect to the stability and lifetime of rare-gas clusters. Consequently, these effects should be taken into account in numerical analyses of the properties of condensed matter. Molecular-dynamics calculations on the above basis are in progress.

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[27]Differences in pair interactions between the two structures appear only starting from the third shell of atoms around a central atom. Apart from ionic solids, such differences carry no weight for crystal stability. Concerning three-atom interactions, there are 66 ($=12\times11/2$) contributions involving a central atom and two atoms of the first shell around it. It is found that 57 of these 66 triplets are common to the two configurations, whereas 9 are different.

[28]Since solid neon, argon, krypton, and xenon have the same (face-centered cubic) structure, only the *range* of β values is of primary importance for relative stability. In addition, *ratios* of the three-atom interactions, relative to the respective pair interactions in first and second orders, are calculated in the model.

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