

the ordinary Raman process predominates, and where $1/\tau \propto T^\gamma$.

In the latter case, we could intercompare $1/\tau_R$ and $1/\tau_{R0}$ and eliminate the common interaction parameter B from them. In this way, Eq. (24) could be tested. This would not only test the present theory, but also Eq. (18), i.e., the theory of the anharmonic relaxation time of local modes. In other cases, a cruder test is possible by taking $A \simeq B$ and intercomparing τ_{R0} and τ_D .

According to the theory of Montroll and Potts,⁴ one would expect local vibrational modes to occur at paramagnetic ions which are substitutional impurities and are either of lighter mass than the normal atom at that site, or are bound to the neighboring atoms with forces stronger than the normal forces. If a lighter atom was also more weakly bound, such that the effect of the mass was compensated by weaker bonds, a local mode would not occur. In general, we know little about interatomic forces, but it may be presumed that if the paramagnetic ion is substantially lighter than the parent atom (say half), a local mode will occur, and the present considerations will apply. Unfortunately, none of the paramagnetic ions in various environments, whose spin lattice relaxation has been studied to date, fulfills this

condition of local mode occurrence. Examples of cases to which the present theory may apply are paramagnetic ions from Ti through Cu in environments such as cadmium sulfide, silver halides or in a suitable heavy III-V compound (indium antimonide, grey tin).

The present treatment is valid only if the local mode frequency ω_0 is well separated from the continuum of lattice modes. As ω_0 approaches ω_D , the mode becomes progressively less localized, and it is wrong to assume that most of the strain energy lies within the unit cell containing the impurity. Thus e_0^2 will be less than given by (23), and Eq. (24) will likewise overestimate $1/\tau_{R0}$. In the limit as ω_0 becomes ω_D , e_0^2 and thus $1/\tau_{R0}$ vanish, and the spin-lattice relaxation is given by the normal theory. The relationship between ω_0/ω_D and the spatial extent of the local mode is discussed by Montroll and Potts.⁴ It is readily shown that (23) remains a good approximation provided ω_0 is not less than about $1.1\omega_D$, that is, provided the mass difference is not less than about 20%.

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Systematic Analysis of Many-Body Interactions in Molecular Solids*

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An analysis is undertaken of the different possible types of simultaneous interactions between more than two atoms or molecules in so-called molecular solids. The analysis is carried out on the basis of a double series expansion: (1) in terms of linked exchange-clusters of increasing numbers of atoms; (2) as a series in increasing orders of perturbation theory. The use of a multipole series for the electrostatic interactions between different atoms is avoided by retaining this interaction in unexpanded form. Instead, an effective-electron model is used with a Gaussian form for the charge distributions. The method is illustrated by computing the exchange quadrupole moment of two argon atoms as a function of their distance. Calculations by Rosen and by Shostak for first-order interactions between three helium atoms are extended to atoms of the heavy rare gases. It is found that the relative magnitude of this many-body effect may amount to 20% of the first-order interaction energy. Possible implications with respect to stability of the cubic structures of heavy rare-gas crystals are briefly discussed.

INTRODUCTION

THE possible importance of simultaneous interactions between more than two atoms, molecules, or nucleons for the interpretation of properties of compressed gases, liquids, solids, and nuclear matter has from time to time aroused interest in the literature. In molecular physics, this interest arose principally from a possible role of many-body interactions in a solution to the problem concerning the stability of the observed

cubic crystal structures of the heavy rare gases. Calculations based on pair interactions had revealed that a hexagonal structure should be somewhat more favorable, in contradiction with experiment. It seemed, therefore, that the pair assumption (additivity) of interactions between rare-gas atoms could not be reconciled with their crystal structure.

In contrast with nuclear problems, we possess for molecular systems complete knowledge regarding the origin of the forces between the particles, so that, in principle, it should be possible to assess the significance of many-body interactions for the properties of molec-

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ular solids, for example. Yet, the explicit calculations which have so far been carried out were either based on approximations which clearly ceased to be satisfactory at relatively small interatomic distances, or they concerned systems of little interest.

As an example of the first category, we mention the so-called triple-dipole effect for three rare-gas atoms, evaluated by Axilrod and Teller¹ and by Axilrod.² This calculation concerns the induced-dipole interaction in third order of perturbation theory between three non-overlapping distributions of charge. As such, it constitutes simply an extension of van der Waals interactions, as calculated by London, to third order. But many-body interactions occur already in lower orders of perturbation theory (induced by electron exchange); in addition the use of a multipole expansion for the electrostatic interactions becomes increasingly less accurate as the distances between the atoms decrease. In fact, such series usually do not converge at all.³⁻⁵ Tredgold and Ayres⁶ have modified this calculation by using a Gaussian distribution function for the negative charge cloud of each atom, and treating the overlap of charge distributions of neighboring atoms in a classical way. This adds still another source of error, since at small distances the interactions are mainly of exchange type.

The same type of third-order effect was evaluated independently by Muto⁷ using an oscillator model for the atoms, and later extended by Midzuno and Kihara.⁸ Bade⁹ computed the dipole-dipole part of the London-van der Waals interaction energy in the general order of perturbation theory, without exchange, using a model which represents each molecule as an isotropic harmonic oscillator. His results were applied to a linear chain of atoms by Bade and Kirkwood.¹⁰

On the other hand, first-order forces (exchange, chemical, or valence forces) are predominant when the interatomic distances are small. Margenau¹¹ had already pointed out that they are of a many-body type. Such an effect was evaluated for an equilateral triangle, and a linear symmetric array, of three helium atoms by Rosen.¹² Shostak¹³ repeated the calculations for, the linear array, using molecular orbitals. Unfortunately, helium is of no direct interest as far as its crystal struc-

ture is concerned, since this element crystallizes in a hexagonal lattice, in agreement with the result of calculations based on the assumption of pair interactions.

It is, nonetheless, of interest to note the *sign* of the relative three-body interaction energy; both in the third-order (Axilrod-Teller) and the first-order (Rosen-Shostak) effects this sign is *minus* for an equilateral triangle, and *plus* for a linear array of atoms. This means that for an equilateral triangle the attraction (or repulsion) is weakened, compared to a simple sum over three isolated pairs, whereas the interactions for the linear array are stronger than the pair assumption indicates.

If exchange effects are taken into account, then many-body interactions occur also in second order of perturbation theory, i.e., in the same order as the van der Waals forces.^{14,15} In this case we have to do with a triplet of atoms, two of which overlap, whereas exchange with the third atom is not considered. Calculations were carried out on the basis of a Gaussian model for the electron charge distributions of the atoms, for the dipole-dipole and dipole-quadrupole components of the interactions. Again, the use of a multipole series renders the results unreliable for small interatomic separations, so that quantitative conclusions regarding crystal stability cannot be drawn.

For completeness, we mention many-body interactions between atoms or molecules which are originally in excited electron states. They are of importance at very high temperatures, and have been discussed by Dahler and Hirschfelder.¹⁶ Such effects, together with additional complications arising in case the charge distributions are not spherically symmetric,^{15,16} will not be considered in this paper.

In view of the various shortcomings of the existing calculations, it seems useful to devise a systematic analysis of all possible types of many-body interactions, and to carry out their evaluation in a consistent manner, avoiding assumptions which invalidate their application to, especially, the stability of rare-gas crystal structures. Since the interactions in molecular crystals are very weak compared to those in metals or in ionic crystals, we will use a perturbation expansion starting from free-atom wave functions, but avoid using a multipole series for the perturbation.

LINKED EXCHANGE-CLUSTER EXPANSION

Starting from ground-state free-atom wave functions $\varphi_a, \varphi_b, \varphi_c, \dots$, where a, b, c, \dots denote atoms which are antisymmetric with respect to exchange of electrons of the same atom, we write the zeroth-order wave functions, except for normalization, of the as-

¹ B. M. Axilrod and E. Teller, *J. Chem. Phys.* **11**, 299 (1943).

² B. M. Axilrod, *J. Chem. Phys.* **17**, (1949); **19**, 719, 724 (1951).

³ F. C. Brooks, *Phys. Rev.* **86**, 92 (1952).

⁴ A. Dalgarno and J. T. Lewis, *Proc. Roy. Soc. (London)* **A69**, 57 (1956).

⁵ L. Jansen, *Physica* **23**, 599 (1957); *Phys. Rev.* **110**, 661 (1958).

⁶ R. U. Ayres and R. H. Tredgold, *Phys. Rev.* **100**, 1257 (1955); *Bull. Am. Phys. Soc.* **1**, 292 (1956).

⁷ Y. Muto, *Proc. Phys.-Math. Soc. Japan* **17**, 629 (1943).

⁸ Y. Midzuno and T. Kihara, *J. Phys. Soc. Japan* **11**, 1045 (1956).

⁹ W. L. Bade, *J. Chem. Phys.* **27**, 1280 (1957).

¹⁰ W. L. Bade and J. G. Kirkwood, *J. Chem. Phys.* **27**, 1084 (1957).

¹¹ H. Margenau, *Revs. Modern Phys.* **11**, 1 (1939).

¹² P. Rosen, *J. Chem. Phys.* **21**, 1007 (1953).

¹³ A. Shostak, *J. Chem. Phys.* **23**, 1808 (1955); see also P. O. Löwdin, *ibid.* **19**, 1570, 1579 (1951) (ionic crystals).

¹⁴ R. T. McGinnies and L. Jansen, *Phys. Rev.* **101**, 1301 (1956).

¹⁵ L. Jansen and R. T. McGinnies, *Phys. Rev.* **104**, 961 (1956); R. T. McGinnies, Ph.D. thesis, University of Maryland, 1957 (unpublished).

¹⁶ J. S. Dahler and J. O. Hirschfelder, *J. Chem. Phys.* **25**, 986 (1956).

TABLE I. Possible types of many-body interactions.

Exchange cluster	Order perturbation theory
monatomic	first
diatomic	second
triatomic	third
⋮	⋮

sembly of atoms as (Slater determinant)

$$\varphi^{(0)} = \sum_{\lambda} (-1)^{\lambda} P_{\lambda} \varphi_a \varphi_b \varphi_c \cdots, \quad (1)$$

an antisymmetric sum of products of atomic wave functions; P_{λ} exchanges electrons between *different* atoms, or it denotes a combination of inter- and intra-atomic exchange.

Relative to a fixed association of electrons with the different atoms, each P_{λ} in (1) can be written as a product of P 's involving exchange clusters of atoms. For example, if P_{λ} denotes exchange of electrons 1 and 2 between atoms a and b , 2 and 3 between atoms b and c , 5 and 6 between m and n , then we call the triplet (abc) a *linked exchange cluster*; the pair (mn) is also such a linked cluster. If we follow a perturbation method for the evaluation of any property of the solid, then we will in principle obtain contributions due to such exchange clusters in every order of approximation. These contributions can be ordered according to the *largest* cluster which they contain: monatomic terms (without exchange), diatomic terms (only pair exchange), triatomic contributions involving triplets of atoms but no larger clusters, etc. With increasing cluster size we describe the solid in terms of units of increasing numbers of atoms: single atoms, pairs, triplets, etc.; this procedure amounts to an increasing delocalization of electrons in the solid.

In this way, a double series expansion is obtained: one, in terms of exchange clusters of increasing size, and one, in increasing orders of perturbation theory. For molecular solids this procedure may be expected to yield convergent series in both directions. In fact, it is convenient to *define* molecular solids by the requirement that both the cluster expansion and the perturbation series *converge rapidly* for any property of interest. Such a solid can be expected to show molecular characteristics to a large extent.

The different possible types of many-body interactions can now be indicated. In Table I, we place to the left the exchange clusters of increasing size, to the right the different orders of perturbation theory. A straight line between left and right columns connects a cluster term with the *lowest* order of perturbation theory in which many-body interactions occur.

If we use two sets of numbers 1, 2, 3, \cdots , to characterize a type of many-body effect, of which the first number denotes the cluster size, the second the order of

perturbation theory, then the Axilrod-Teller^{1,2} effect is of type 1-3, the second-order (van der Waals) many-body term^{14,15} of type 2-2, and the Rosen-Shostak^{8,9} calculation of type 3-1. The common *two-body* interactions may also be indicated in this manner: 1-2, i.e. van der Waals forces, and 2-1, i.e., repulsive interactions between closed shells at small interatomic distances (exchange forces).

A GAUSSIAN EFFECTIVE-ELECTRON MODEL

The task is now to evaluate these different types of many-body interactions. In principle, accurate knowledge of atomic wave functions is required to obtain precise results. However, if we have in mind an application to the stability problem for crystals of the heavy rare gases, then the use of a more approximate model may be justified, since the effect can depend sensitively only on some general characteristics of the wave functions ("size" of the atom, plus eventually symmetry properties).

We will simplify the problem by means of the following assumptions:

- (1) Only single interatomic exchange of electron pairs is taken into account. Effects due to exchange of two or more pairs of electrons between the same two atoms are therefore not considered.
- (2) Contributions due to coupling of inter- and intra-atomic exchange are neglected.
- (3) The electron charge distribution of an atom has spherical symmetry.

The assumptions (1) and (2) must be applied with care. In many cases the overlap integrals between the atomic orbitals of the constituents are not small, implying that higher order overlap and exchange effects may not be neglected.¹⁷ In the case of rare-gas crystals, effects due to (1) [or (1) and (2)] were found to be negligible, except for very small interatomic distances, for helium and neon.^{14,15} The validity of assumption (3) is somewhat in doubt for atoms of the heavy rare gases, following calculations by Linnett and Poe,¹⁸ but quantitative results are not available.

On the basis of the above three assumptions, the following model can be constructed. We sum over single-exchange effects between all possible pairs of electrons (parallel spins) of two, or three, atoms. The total effect is then replaced by exchange between one "effective" electron on each atom. The problem becomes thus formally the same as that concerning hydrogen atoms with parallel spins. The charge distribution for the effective electron is chosen to be of Gaussian form

$$\rho(r) = (\beta/\pi^{\frac{1}{2}})^3 \exp(-\beta^2 r^2); \quad (2)$$

¹⁷ Cf. P.-O. Löwdin, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 1, for a general discussion of this difficulty.

¹⁸ J. W. Linnett and A. J. Poe, *Trans. Faraday Soc.* 47, 1033 (1951). See also J. Cuthbert and J. W. Linnett, *Trans. Faraday Soc.* 54, 617 (1958).

r is the distance from the effective electron to its nucleus, β is a parameter. Values of β for atoms of the heavy rare gases are determined empirically, by calculating second-order dipole interactions between two Gaussian atoms at large distances and comparing the result with an empirical potential function.¹⁵ In this way we fit the *outer* part of the Gaussian distribution. For short-range interactions the inner part of the charge distribution also plays an important role, so that it becomes necessary to compare such interactions between Gaussian atoms with the repulsive part of an empirical potential function. Such a comparison will be carried out in a following section.

EXAMPLE: THE EXCHANGE QUADRUPOLE MOMENT OF A PAIR OF ARGON ATOMS

To illustrate the use of the Gaussian model, we calculate the electric quadrupole moment of a pair of argon atoms, a distance R apart. The exchange repulsion between closed shells will give rise to a small net positive charge in the region between two argon atoms, and a net negative charge elsewhere. This effect gives rise to exchange multipole moments of even order, of which we determine the first one, an electric quadrupole moment.

Consider two Gaussian atoms at interatomic distance R . The charge distribution of this pair has cylindrical symmetry about an axis z , coinciding with the direction of R . For such cylindrically symmetric distributions of charge we can define scalar multipole moments of arbitrary (positive) order⁶; the first nonvanishing moment is in this case a quadrupole, defined by

$$Q = \langle \sum_i e_i z_i^2 \rangle - \langle \sum_i e_i x_i^2 \rangle, \quad (3)$$

where the x axis is perpendicular to z , but otherwise arbitrary. For two Gaussian atoms a and b , we have two electrons 1 and 2, and the analogy with the case of two hydrogen atoms with parallel spins makes it possible to write the zero-order wave function as

$$\Psi^{(0)} = \{ \varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1) \} / [2(1-\Delta^2)]^{1/2}, \quad (4)$$

where $\varphi^2 = \rho$, the Gaussian charge density of an atom, and Δ is the overlap integral, $\Delta = \int \varphi_a \varphi_b d\tau$. The direct terms in $\Psi^{(0)2}$ give, of course, no contribution to Q or to any other permanent multipole moment, so that we are left with the exchange terms (omitting normalization) $-2\varphi_a(1)\varphi_b(1)\varphi_a(2)\varphi_b(2)$.

We denote the z coordinates of the position vectors of electrons 1 and 2, with respect to the center of the line connecting the two nuclei, by z_1 and z_2 , respectively. Then we obtain

$$\langle \sum_i e_i z_i^2 \rangle = [4eI_3\Delta - 4e(R/2)^2\Delta^2] / 2(1-\Delta^2),$$

where

$$I_3 = \int z^2 \varphi_a \varphi_b d\tau, \quad (5)$$

$$\langle \sum_i e_i x_i^2 \rangle = 4eI_2\Delta / 2(1-\Delta^2),$$

with

$$I_2 = \int x^2 \varphi_a \varphi_b d\tau. \quad (6)$$

The expression for the scalar quadrupole moment of the pair (ab) of argon atoms becomes with (3), (5), and (6),

$$Q = \langle \sum_i e_i z_i^2 \rangle - \langle \sum_i e_i x_i^2 \rangle \\ = [4e\Delta(I_3 - I_2) - 4e\Delta^2(R/2)^2] / 2(1-\Delta^2). \quad (7)$$

For a Gaussian distribution $I_3 = I_2$, so that then

$$Q = -2e[\Delta^2/(1-\Delta^2)](R/2)^2. \quad (8)$$

This quadrupole moment is the same as that caused by an effective negative point charge

$$-(\delta e) = -e[\Delta^2/(1-\Delta^2)]$$

at nucleus a , the same charge at nucleus b , and a positive charge $2(\delta e)$ at the center between the two nuclei.

Values of $\Delta^2/(1-\Delta^2)$ can be determined with the help of those of the parameter β in the Gaussian distribution function, for the heavy rare gases.¹⁵ For nearest neighbors in solid argon $\Delta^2/(1-\Delta^2) = 0.06$ and $R/2 = 1.92$ Å. The resulting value for the scalar quadrupole moment of a pair of nearest-neighbor argon atoms is then

$$Q = 2.14 \times 10^{-26} \text{ esu} = 0.45 \times 10^{-16} e \text{ cm}^2,$$

i.e., a value of the *same* order of magnitude as for a nitrogen molecule. This large value is not due to a large displacement of charge, but in the first place to the large value of the distance between two argon atoms, which enters as the square in the expression for the quadrupole moment (compare a nitrogen molecule: $R/2 = 0.55$ Å).

In view of the approximations which are inherent in this type of model, quantitative conclusions do not seem to be justified. The result indicates, however, that effects due to diatomic exchange clusters of heavy rare-gas atoms may be significant for the determination of some solid-state properties.¹⁹

THE TRIATOMIC FIRST-ORDER (3-1) MANY-BODY EFFECT

The task is now to evaluate the different possible types of many-body interactions in first, second, and third orders of perturbation theory. The remainder of this paper is devoted to a calculation of the 3-1 effect, involving a cluster of three atoms, in first order of perturbation theory. It was mentioned earlier that Rosen and Shostak computed such interactions for three helium atoms. Helium is, however, of no direct interest as far as its crystal structure is concerned, and a direct extension of the methods used by these authors to the heavy rare gases would be very complicated, since

¹⁹ This quadrupole effect may possibly be observed by means of spectra emitted by trapped radicals in rare-gas matrices, e.g., from excited nitrogen atoms or excited alkali atoms in solid argon.

detailed knowledge of the wave functions is required. We will, therefore, make use of the Gaussian model: one effective electron per atom, with a charge density given by (2), and variable β .

Consider such a triangle (abc) of atoms. The zero-order wave function is (Slater determinant)

$$\Psi^{(0)} = [3!(1 - \Delta_{abc}^2)]^{-1/2} \det\{\varphi_a(1)\varphi_b(2)\varphi_c(3)\}, \quad (9)$$

with

$$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc}. \quad (10)$$

The perturbation Hamiltonian H_{abc}' can be written as

$$H_{abc}' = H_{ab}' + H_{ac}' + H_{bc}'.$$

For the first-order energy we have to evaluate

$$E_1 = \langle H_{abc}' \rangle = \langle H_{ab}' \rangle + \langle H_{ac}' \rangle + \langle H_{bc}' \rangle.$$

After substituting the expressions for H_{ab}' and $\Psi^{(0)}$ into E_1 , the following result is obtained:

$$\begin{aligned} \langle H_{ab}' \rangle / e^2 &= \frac{1}{R_{ab}} - 2 \frac{1 - \frac{1}{2}(\Delta_{ac}^2 + \Delta_{bc}^2)}{1 - \Delta_{abc}^2} G_{aa(b)} \\ &+ 2 \frac{\Delta_{ab} - \Delta_{ac}\Delta_{bc}}{1 - \Delta_{abc}^2} G_{ab(a)} + \frac{\Delta_{ac} - \Delta_{ab}\Delta_{bc}}{1 - \Delta_{abc}^2} G_{ac(b)} \\ &+ \frac{\Delta_{bc} - \Delta_{ab}\Delta_{ac}}{1 - \Delta_{abc}^2} G_{bc(a)} + \frac{1}{1 - \Delta_{abc}^2} (A_{abab} - A_{aabb}) \\ &+ \left(\frac{\Delta_{ac}}{1 - \Delta_{abc}^2} \right) (A_{abbc} - A_{abcb}) \\ &+ \left(\frac{\Delta_{bc}}{1 - \Delta_{abc}^2} \right) (A_{abac} - A_{abca}), \quad (11) \end{aligned}$$

where the symbols G and A are abbreviations for the following integrals:

$$G_{ab(c)} = \int \frac{\varphi_a \varphi_b}{r_c} d\tau, \quad G_{aa(b)} = \int \frac{\varphi_a \varphi_a}{r_b} d\tau,$$

etc., with r_c = distance between an electron and nucleus of atom c , r_b = distance between an electron and nucleus of atom b , and

$$\begin{aligned} A_{abac} &= \iint \frac{\varphi_a(1)\varphi_b(2)\varphi_a(1)\varphi_c(2)}{r_{12}} d\tau_1 d\tau_2, \\ A_{aabc} &= \iint \frac{\varphi_a(1)\varphi_a(2)\varphi_b(1)\varphi_c(2)}{r_{12}} d\tau_1 d\tau_2, \end{aligned}$$

etc., with r_{12} = distance between electrons 1 and 2.

The first-order energy between a and b , without c present, is

TABLE II. List of integrals for E_1 .

Integral	Value for Gaussian distribution
Δ_{ab}^2	$\exp(-\beta^2 R_{ab}^2/2)$
Δ_{ac}^2	$\exp(-\beta^2 R_{ac}^2/2)$
Δ_{bc}^2	$\exp(-\beta^2 R_{bc}^2/2)$
$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc}$	
$G_{aa(b)} = G_{bb(a)}$	$(2\beta/\sqrt{\pi})F(\beta^2 R_{ab}^2)$
$G_{ab(a)} = G_{ab(b)}$	$(2\beta/\sqrt{\pi})\Delta_{ab}F(\beta^2 R_{ab}^2/4)$
$G_{bc(a)}$	$(2\beta/\sqrt{\pi})\Delta_{bc}F(\beta^2 R_{a(bc)}^2)$
$G_{ac(b)}$	$(2\beta/\sqrt{\pi})\Delta_{ac}F(\beta^2 R_{b(ac)}^2)$
A_{abab}	$\beta(2/\pi)^{1/2}F(\beta^2 R_{ab}^2/2)$
A_{aabb}	$\beta(2/\pi)^{1/2}\Delta_{ab}^2$
A_{abac}	$\beta(2/\pi)^{1/2}\Delta_{bc}F(\beta^2 R_{a(bc)}^2/2)$
A_{abcb}	$\beta(2/\pi)^{1/2}\Delta_{ac}F(\beta^2 R_{b(ac)}^2/2)$
A_{aabc}	$\beta(2/\pi)^{1/2}\Delta_{ab}\Delta_{ac}F(\beta^2 R_{bc}^2/8)$
A_{abbc}	$\beta(2/\pi)^{1/2}\Delta_{ab}\Delta_{bc}F(\beta^2 R_{ac}^2/8)$

$$\begin{aligned} \langle H_{ab}' \rangle^{(0)} / e^2 &= \frac{1}{R_{ab}} - \frac{1}{1 - \Delta_{ab}^2} \\ &\times [2G_{aa(b)} - 2\Delta_{ab}G_{ab(a)} - (A_{abab} - A_{aabb})], \quad (12) \end{aligned}$$

The three-body component of $\langle H_{ab}' \rangle / e^2$, namely

$$\{\langle H_{ab}' \rangle - \langle H_{ab}' \rangle^{(0)}\} / e^2,$$

is obtained by subtracting (12) from (11). We do not need any further equations, since $\langle H_{ac}' \rangle$, for example, is obtained from (11) by replacing b by c .

The integrals G and A have, for Gaussian distributions of charge, been evaluated by Boys.²⁰ For the atomic wave functions we take

$$\varphi = \rho^{1/2} = (\beta/\pi)^{1/2} \exp(-\beta^2 r^2/2).$$

It is convenient to use the following abbreviation:

$$F(x) = \frac{1}{\sqrt{x}} \int_0^{\sqrt{x}} \exp(-y^2) dy;$$

also, we denote by $R_{a(bc)}$ the length of the line connecting the nucleus of atom a with the center of the line R_{bc} , etc. Table II contains a list of the integrals occurring in the equation for E_1 .

MACHINE CALCULATIONS

The computations were carried out on the digital computer Bull Gamma AET (word length: 12 digits; memory access: 172 μ sec; type of storage: magnetic drum of 8192 memories). After calculating the arguments of the F and Δ functions for various triangular configurations, these functions were evaluated by interpolation, using *Tables of the Error Function and its Derivative* (Natl. Bureau of Standards, Washington, 1953). The interpolation was carried to the fifth term of a Taylor expansion; this appeared sufficient for the

²⁰ S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950).

accuracy desired. The intermediate results were transmitted by punchcards to the main program, i.e., the computation of $\langle H_{abc}' \rangle$, $\langle H_{abc}' \rangle^{(0)}$, their difference, and the relative 3-body component of the first-order interactions, for values of βR from 1.5 to 3.5, in intervals of 0.1, for each triangular configuration.

For values of βR larger than about 3 the results are somewhat irregular, since the different terms in Eqs. (11) and (12) are then very small, and the sums and differences of a large number of such terms have to be determined. The program was devised in such a way that different triangles require only slight modifications.

RESULTS FOR SOME SPECIAL TRIANGLES

The three-body, first-order interaction energies were evaluated for a number of special triangles, among others, an equilateral triangle, a 120° -symmetric array, and a linear symmetric array. These three types of triangles occur among those formed by a central atom and two of its twelve nearest neighbors in the cubic, and hexagonal, close-packed lattices. The relative three-body contribution is

$$\frac{\langle H_{abc}' \rangle - \langle H_{abc}' \rangle^{(0)}}{\langle H_{abc}' \rangle^{(0)}}, \quad (13)$$

where $\langle H_{abc}' \rangle^{(0)} = \langle H_{ab}' \rangle^{(0)} + \langle H_{ac}' \rangle^{(0)} + \langle H_{bc}' \rangle^{(0)}$, a sum of first-order energies over three *isolated* pairs of atoms. The relative three-body component (13) is a function only of the dimensionless parameter βR , where R is the smallest distance between neighbors on the triangle. Calculations were performed for the three types of triangles with $\beta R = 1.5; 1.6; \dots; 3.5$, in intervals of 0.1. This range covers the βR values for neon, argon, krypton, and xenon, which are 3.44, 2.40, 2.10, and 1.99, respectively.¹⁵ The results are collected in Fig. 1.

The main characteristics of the 3-body interactions are:

(1) *Equilateral triangle.* The relative 3-body interaction is practically *independent* of βR , i.e., of the size of the triangle (at constant β). It amounts to about 20% and its sign is *minus*, meaning that the total first-order interaction is weaker (less repulsive) than obtained on the basis of an additive sum-over-pairs. The sign agrees with the result obtained by Rosen for three helium atoms;

(2) *120° -symmetric array.* For this configuration the relative 3-body component is only at most 5% of the additive first-order interactions and its sign is *plus*, signifying slightly enhanced repulsion compared with the sum over three isolated pairs;

(3) *Linear symmetric array.* The relative 3-body interaction is very nearly decreasing *linearly* with increasing βR , from 20% at $\beta R = 1.5$ to a few percent at $\beta R = 3$. Its sign is *plus*, which means that the effect enhances the repulsion between the three atoms, compared with an additive sum-over-pairs. The sign agrees with that obtained by Rosen and by Shostak for three helium atoms.

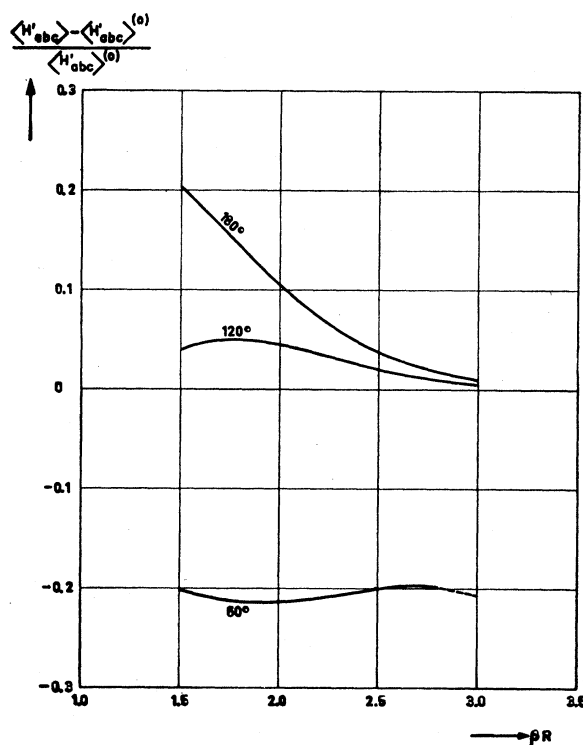


FIG. 1. Relative 3-body, first-order interactions for an equilateral triangle, a 120° symmetric, and a linear symmetric array, as a function of βR .

VALIDITY OF GAUSSIAN MODEL AT SMALL DISTANCES

At small interatomic distances the inner part of the charge distribution plays an important role in the determination of the repulsive interactions between closed shells of electrons. Since the values for the parameter β in the Gaussian distribution were determined empirically from a comparison with *long-range* interactions, it is of interest to check whether or not β changes appreciably with decreasing distance between the atoms. To this end we use the repulsive part of a modified Buckingham potential,

$$E(r) = [\epsilon / (1 - 6/a)] (6/a) \exp[a(1 - R/R_0)],$$

with values of ϵ , a , and R_0 for neon, argon, krypton, and xenon as given by Hirschfelder, Curtiss, and Bird²¹ as an empirical basis, and compare the results with $\langle H_{ab}' \rangle^{(0)}$, Eq. (12), taking for β the values for the heavy rare gases, and varying R . The results of this comparison are given in Fig. 2.

It is seen from Fig. 2 that the Gaussian model yields excellent values for the repulsive potential between two neon atoms, but that with increasing atomic weight the two curves deviate more and more. This implies that β

²¹ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 12.

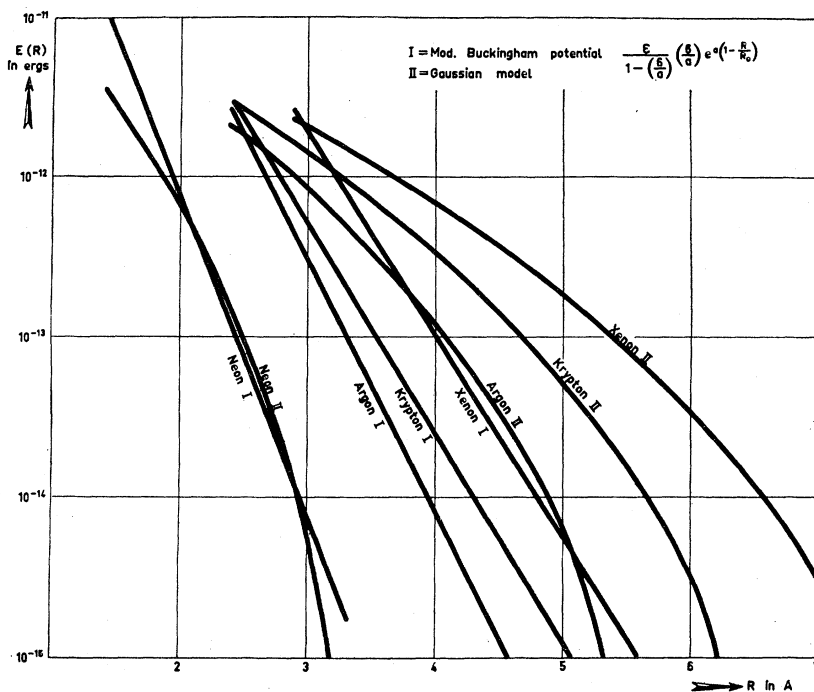


FIG. 2. Comparison between repulsive part of modified Buckingham potential and $\langle H_{ab} \rangle^{(0)}$ for a Gaussian distribution, for the heavy rare gases, as a function of interatomic distance R .

for argon, krypton, and xenon *increases* somewhat as R decreases, indicating a certain "quenching" of the three-body effect. It should be remembered, however, that with decreasing R multiple-exchange effects become more and more important, rendering the single-exchange model less and less valid. For neon, argon, krypton, and xenon, the nearest-neighbor distances in the crystals are 3.20, 3.84, 3.94, and 4.37 Å, respectively.

CONCLUSIONS

(1) It is possible to classify the various many-body interactions between atoms in "molecular solids" on the basis of a double series expansion; one in terms of linked exchange clusters of increasing size, and one in increasing orders of perturbation theory. Molecular solids may then be defined by the requirement that both expansions converge rapidly.

(2) With the help of a Gaussian effective-electron model, the triatomic first-order 3-body interactions given by Rosen and Shostak for helium atoms may be extended to the heavy rare gases. Both for an equilateral triangle and a linear symmetric array the sign of the

relative 3-body interaction agrees with previous results for helium.

(3) For a single triangular configuration the relative 3-body interaction may amount to 20% of the additive first-order energy.

(4) Values for the parameter β of the Gaussian distribution, obtained from a comparison with long-range interactions, give excellent values for short-range forces between two neon atoms. For argon, krypton, and xenon β appears to increase somewhat with decreasing interatomic distances.

In a following paper the foregoing results will be applied to the stability problem of crystals of the heavy rare gases, and in which the diatomic second-order (2-2) many-body interactions will be evaluated.

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