PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Quantum Theory of the Equation of State for Solid Hydrogen

J. A. Krumhansl*
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
and
S. Y. Wu*†
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

(Received 24 May 1971)

A variational calculation of the ground-state energy of molecular crystalline hydrogen has been carried out, including the effect of correlation between the motions of the particles. The principal purpose was to obtain the equation of state for solid hydrogen at absolute-zero temperature over a wide range of densities. We are concerned with energies on a scale appropriate to high-pressure phenomena, and therefore approximated the molecular rotational behavior, so that the very low-temperature phase transitions are not describable in the present model. The variational form of the energy was obtained by truncating the cluster expansion of the ground-state energy. The effect of short-range dynamic correlation is taken into consideration through a Jastrow-type pair-correlation function in the trial wave function. To facilitate the fast convergence of the cluster expansion, a model correlation function with an explicit hard-core exclusion effect was employed. With this pair-correlation function, the truncation approximation was extended into the high-density region where previous functional forms for pair correlation had not been satisfactory. Numerical computations were done for a Lennard-Jones potential, a Buckingham exp-6–type potential, and a nonspherical molecular interaction due to Wang Chang. The results compare favorably with experiment, although there is a systematic difference at high density; either all of the assumed potentials are inadequate or the experimental data are in error.

I. INTRODUCTION

This paper reports part of a program of study of the properties of solid hydrogen, and is accompanied by two other reports by Bruce, and Pollack, Bruce, Chester, and Krumhansl. The present paper describes the earliest work in our program, which sets the stage for subsequent studies, and in some sense is more of a historical review with the essential research content being results for the equation of state of solid molecular hydrogen at zero temperature based on the cluster expansion method; selected results were reported in Ref. 1.

We were concerned with the investigation of the behavior of solid molecular hydrogen at 0 °K, particularly in computing the cohesive energy of crystalline hydrogen for a wide range of densities (extending from zero pressure to a pressure of the order of 2×10^4 kg/cm^2), from which an equation of state of cold solid hydrogen (at $T=0$ °K) is obtained. The results obtained are compared with the empirical curve derived from the experimental PV data (for solid hydrogen) obtained by Stewart.[2]

The first extensive attempt to derive the equation of state for solidified gases was carried out by deBoer and Blaisse (1948),[3] who computed the energy of the system at $T=0$ °K in two parts: the static-lattice potential energy and the zero-point energy. In their calculation, a Lennard-Jones intermolecular potential was assumed and the zero-point energy was computed on the harmonic approximation proposed by Herzfeld and Mayer.[4] The computations extend only up to $V^*=V/N\sigma^3\sim1.3$ (where V^* is the reduced volume and $N\sigma^3$ corresponds to the hard-core molar volume); beyond that region, the formula used for determining the zero-point energy breaks down because a nonphysical value for the sound velocity is obtained. It is then clear that this approach does not apply well for elements like hydrogen (with an experimental zero-point reduced volume $V_0^*\sim1.44$) and helium (with $V_0^*\sim2.2$). It is also clear that both elements have small masses and weak interparticle interactions. However, deBoer[5] pointed out that it is the small masses and weak interactions of hydrogen molecules and helium atoms which makes them interesting; the small mass leads to a large de Broglie wavelength and weak interaction augments the quantum effects. The parameter $\lambda^*=h/\sigma(\epsilon m)^{1/2}$ which gives the ratio of the de Broglie wavelength, for relative motion of two particles with relative energy ϵ, to the "diameter" σ of the particle may then serve as an indicator. For $\lambda^*\ll1$, one may expect that the quantum effects are negligible, but for $\lambda^*>1$, the quantum effects should play a dominant role. Hydrogen with $\lambda^*=1.73$, helium four with $\lambda^*=2.68$, and helium three with $\lambda^*=3.08$ certainly belong to the latter category. For substances like these, the zero-point motion is large so that the harmonic approximation can no longer be applied.[6]

It would then seem to be desirable to express the quantum correlations in terms of the parameter λ^*. Bernades[7,8] made a variational calculation, with a trial wave function being a product of nonoverlapping single-particle wave functions each of which is spherically symmetric about a lattice site. The results, although tending in the right direction, were still not in good agreement with experiments for either hydrogen or helium. This approximation to the wave function had not properly included the important effects of the correlation between the motions of the particles. It will be instructive to review his calculation briefly.

An alternate approach to this problem was attempted by Hurst and Levelt.[9] Using the quantum-mechanical cell model previously developed for liquids,[10] they computed the zero-point energy as the lowest eigenvalue of a Schrödinger equation where the potential energy (within the cell) was determined by assuming the neighboring particles uniformly distributed on the spherical shells of radii equal to the nearest-neighbor distance, second-nearest-neighbor distance, etc. This method again had not considered the effects of correlation between the motions of the particles.

Subsequently, Saunders,[11] Nosanow,[12] Mullin,[13] Hansen and Levesque,[14] Brueckner and Frohberg,[15] and also Massey and Woo,[16] employed a trial wave function proposed by Jastrow (1955) which explicitly included the effect of pair correlation in the description of the system. The cluster-expansion method,[12,13] was used to obtain a series expression for the ground-state energy. By truncating the expansion to include two-center correlation, but not three- and higher-center correlations, a variational calculation was carried out to minimize the energy. The computations on solid helium indicated that the cluster-expansion method indeed gave improved results over previous calculations. The cluster approach, however, is not entirely satisfactory in the sense that it does not allow variation in a sufficiently general way, which restricts its effectiveness; indeed, the region of application seemed to be limited to a restricted region in the neighborhood of the experimental equilibrium density at low pressure.

It was the purpose of the present work to carry out a theoretical calculation of the equation of state of solid hydrogen at 0 °K by using the techniques developed for helium. Special attention was given to the two-body correlation function which appears in the trial wave function (Secs. II and III). By modifying the pair correlation to include a "hard core," we found that the cluster method could be used over a much wider density range than had been previously possible. From the calculated results, it appears to be adequate to consider only two-body forces in the basic Hamiltonian (though for hydrogen, not central forces alone; see Secs. IV and V).

Pauling,[17] discussing the wave equation for a diatomic molecule in a crystal, showed that the motion of the molecule in its dependence on the polar angles θ and ϕ may approach either one of two limiting cases, oscillation or rotation, depending on whether the orientation-dependent forces were large or small. We are primarily concerned with the contributions of intermolecular potential energy and translational kinetic energy which determine the main features of the p-V relation over a wide range of pressure. In this instance, orientation-dependent interactions are small, so in the present work we average the effective interaction potential over the free rotational states of each molecule. To account for some of the finer features which we do not deal with, such as the low-temperature phase transitions, an accurate treatment of the directional interaction effects is necessary.

This work may be divided into two parts. The first part deals essentially with the application of the cluster-expansion method, using a specially designed pair-correlation function and a spherical potential. The second part is devoted to an approximate consideration of the nonspherical properties of the hydrogen molecules.

At the time this cluster calculation was first done the results were questioned for various reasons, primarily: (i) We did not use the Nosanow correlation function; (ii) the cluster-expansion method is subject to convergence questions, and (iii) hard-core effects were treated empirically.

By now a variety of independent methods of calculation have closely corroborated our original results on hydrogen; furthermore, the use of the Nosanow correlation function in solid helium is now known to lead to various difficulties, computational and otherwise. Indeed, we believe that calculations of other properties of solid hydrogen,[18] particularly their density derivatives, which have been based on Nosanow-type wave functions are almost certainly in error.

Second, it is agreed that the cluster expansion is subject to convergence questions. For this reason the separate Monte Carlo calculation reported by Bruce was undertaken; his results, which are certainly to be taken as better in principle than the variational-cluster results, do agree closely with ours, but he does obtain a lower ground-state energy by several percent. It has not been possible to establish formal demonstrations of convergence; indeed completely free functional variation of the Jastrow form may lead to a liquid. But from a practical point of view we found good computational stability over a wide density range and, for the few cases tested, third-order cluster corrections were small using the wave function proposed.

Third, it was in the calculation reported here that we first noted that at higher densities crystalline molecular hydrogen seemed to become more "classical." Specifically, the oscillation about the lattice site became relatively more localized; correlation contributions to the cohesive energy became relatively less important; and the ratio of kinetic to potential energy decreased. This led to another study now reported by Pollock, Bruce, Chester, and Krumhansl which shows that whatever formal concerns one may have about "hard-core" and correlation effects at high densities, in fact these become less important.

II. SURVEY OF RELATED WORK

Historically, several efforts have been made to compute the ground-state energy of helium, taking into account the effects of correlation.[7–16]

A. Nonoverlapping Independent-Particle Model (Ref. 7)

For a system of particles interacting with two-body forces, the Hamiltonian is

$$H=-\frac{\hbar^2}{2m}\sum_i \nabla_i^2+\sum_{i<j} v(r_{ij}), \tag{2.1}$$

where $\vec{r}_i$ denotes the position of the ith particle and $r_{ij}=|\vec{r}_i-\vec{r}_j|$ is the distance between particles i and j.

If one is interested only in computing the cohesive energy of the solid, an unsymmetrized wave function provides an adequate description of the system; i.e., the contribution due to exchange is extremely small.[19,20]

Let us denote ψ as the unsymmetrized ground-state wave function of the system where ψ is an N-particle function involving the N nuclear coordinates (the electronic configurations are assumed to follow adiabatically and contribute to the two-body potential). The ground-state energy is then

$$E_0=\left[\psi,\left(\sum_i \frac{-\hbar^2}{2m}\nabla_i^2+\sum_{i<j} v(r_{ij})\right)\psi\right]\Big/(\psi,\psi). \tag{2.2}$$

Because of the strong singularity of typical intermolecular potentials at $r_{ij}=0$, any attempt to describe the system by a product function of single-particle atomic states will lead to the divergencies of terms such as $[\psi, v(r_{ij})\psi]$, on account of the overlapping of the atomic states. Thus, Bernades proposed a trial wave function composed of single-particle wave functions localized about the lattice sites of the crystal, with an important restriction that the single-particle wave functions *do not overlap*. By doing this the singularity at $r_{ij}=0$ is removed. He chose the following trial wave function:

$$\begin{aligned}\Psi&=\Pi_i\phi_i(|\vec{r}_i-\vec{R}|),\\ \phi_i(\xi_i)&=\frac{(\sigma^3\pi/2a^3)^{1/2}\sin(|\pi\sigma\bar{\xi}_i/a|)}{|\pi\sigma\bar{\xi}_i/a|}\quad\text{for } |\xi_i|<a/\sigma\\ &=0\quad\text{for } |\xi_i|\geq a/\sigma,\end{aligned}\tag{2.3}$$

where $\sigma\bar{\xi}_i=|\vec{r}_i-\vec{R}_i|$ is the distance from the center of mass of the ith particle to the ith lattice site at $\vec{R}_i$, and a is a variational parameter.

Substituting this trial wave function into the energy expression, one obtains

$$\begin{aligned}E_0=&-\frac{NA^2\hbar^2}{2m}\int\phi_i^*\nabla_i^2\phi_i\,d\vec{r}_i\\ &+A^2\sum_{i<j}\int|\phi_i|^2|\phi_j|^2v(r_{ij})\,d\vec{r}_i\,d\vec{r}_j,\\ 1/A^2=&\int|\phi_i|^2\,d\vec{r}_i,\end{aligned}\tag{2.4}$$

where A is the normalization constant.

If the two-body potential between two helium atoms is assumed to be the Lennard-Jones potential,

$$v(r)=4\epsilon\left[(\sigma/r)^{12}-(\sigma/r)^6\right], \tag{2.5}$$

where ϵ gives the strength of the potential at its minimum and σ may be considered as the "diameter" of the hard core, after some manipulation,[7] one may write

$$\begin{aligned}E_0/N\epsilon&=\lambda^2(\sigma/a)^2+E_{\mathrm{st}}^*+\Delta U^*,\\ \lambda^2&=\hbar^2/2m\sigma^2\epsilon,\end{aligned}\tag{2.6}$$

where the first term represents the kinetic energy, E_{st}^* is the potential energy of a static lattice, and

$$\begin{aligned}\Delta U^*=\frac{1}{2}\sum_{\substack{i=1\\ i\neq j}}^{N}\sum_{j=1}^{N}\sum_{\substack{s=0\\ s+t\neq 0}}^{N}\sum_{t=0}^{N}\frac{\mu_s(a)\,\mu_t(a)}{r_{ij}(2s+1)!\,(2t+1)!}\\ \times W^{[2(s+t)]}(r_{ij}),\end{aligned}$$

with

$$\begin{aligned}&W(x)=xv(x),\qquad W^{[n]}(x)=\frac{d^nW(x)}{dx^n},\\ &\mu_p(a)=\int_0^a\xi^{2p}\,|(\xi)|^2\,d\xi.\end{aligned}\tag{2.7}$$

This last term ΔU^* represents a correction to the static-lattice potential energy due to the zero-point motion.

When the lattice sum is performed, one has, for a close-packed lattice,

$$\begin{aligned}\Delta U^*&=A_1\alpha^2+A_2\alpha^4+A_3\alpha^6+\cdots,\\ A_1&=10^2[5.90(V^*)^{-14/3}-2.84(V^*)^{-8/3}],\\ A_2&=10^3[36.7(V^*)^{-16/3}-5.23(V^*)^{-10/3}],\\ A_3&=10^4[184(V^*)^{-6}-9.8(V^*)^{-4}],\\ \alpha^2&\equiv(a/\pi\sigma)^2.\end{aligned}\tag{2.8}$$

It is then clear that a may be used as the variational parameter in the determination of the ground-state energy.

Bernades found that for small λ(~0.05), the

TABLE I. Energy (erg) per particle calculated by Bernades's method.

$E_0/(N/V^*)$	1.44	1.2	0.88
Expt. data	-1.29×10^{-14}	-1.02×10^{-14}	1.11×10^{-14}
deBoer		-1.86×10^{-14}	1.07×10^{-14}
Bernades	-0.836×10^{-14}	-0.484×10^{-14}	2.11×10^{-14}

correction term ΔU^* may be satisfactorily approximated by the first term in its expansion. However, for both helium three and helium four, λ is of the order of 0.3. Bernades thus used the following approximation:

$$\Delta U^* = A_1\alpha^2 + A_2\alpha^4 + A_3\alpha^6. \tag{2.9}$$

With this expression substituted in Eq. (2.6), the ground-state energy is then approximated by

$$E_0/N\epsilon = \lambda^2(\pi\sigma/a)^2 + E^*_{\rm st}(R) + \Delta U^*(a, R). \tag{2.10}$$

By equating $\partial E_0/\partial a = 0$, one gets, for an fcc crystal,

$$3A_3\alpha^8 + 2A_2\alpha^6 + A_1\alpha^4 - \lambda^2 = 0. \tag{2.11}$$

This equation can be solved numerically to determine α^2, from which the ground-state energy is computed. Bernades's results for helium four, although encouraging in the sense that binding is obtained in the density region appropriate for liquid, are still far from agreeing with experiment.

We used the same approach for exploratory purposes in hydrogen and calculated the ground-state energies at three different densities. As in the case of helium, the results were of quite limited value. However, we were able to compute the energy at an equilibrium density (corresponding to $V_0^* = 1.44$), whereas deBoer's computation failed there. Table I gives the comparison of the theoretically computed energies with the experimental energies derived from Stewart's data. Table II gives values of the parameters α_1, α_2, and α_3 for various reduced volumes. The energy is given in erg per particle.

The large difference between theory and experiment is due to several reasons: (i) The approximation used in the variational calculation

$$\Delta U^* + A_1\alpha^2 + A_2\alpha^4 + A_3\alpha^6$$

may not be accurate enough. Indeed, we found that a series expansion for ΔU^* converged very slowly at low densities. (ii) The Lennard-Jones potential used is not suitable in the region of high density because the repulsive part of the potential is too hard.[21] (iii) The Bernades model usually tends to give a single-particle wave function which is too localized, thus overestimating the kinetic energy. This will contribute an excess positive energy, which is seen to be the direction of error.

It was fruitful to examine Bernades's approach; it demonstrated that neglect of correlation between the motions of particles brings about large errors. At first glance, it seems that Bernades's model has not considered the correlation between particles at all. Actually, it has included the effects of correlation in a simple way by assigning particles to lattice sites and arbitrarily cutting off the single-particle wave function. To take into account the effects of correlation properly, a more careful treatment is needed.

B. Cluster-Expansion Method

To take into account the effect of correlation between the motions of particles, one may first include the two-body correlations. Nosanow[12] used as the ground-state wave function the Jastrow-type wave function

$$\psi = \prod_i \phi_i(|\vec{r}_i - \vec{R}_i|)\prod_{i<j} f(r_{ij}), \qquad r_{ij} = |\vec{r}_i - \vec{r}_j| \tag{2.12}$$

where ϕ_i is a single-particle wave function centered on the ith lattice site and $f(r_{ij})$ is the pair-correlation factor which describe the effects of correlation between the two particles i and j.

The ground-state energy is then obtained by

$$\begin{aligned} E_0 &= \Big(\sum_i (\psi, P_i\psi) + \sum_{i<j} (\psi, V_{ij}\psi)\Big)\Big/ (\psi, \psi), \\ P_i &= -(\hbar^2/4m\phi_i^2)(\phi_i\nabla_i^2\phi_i - \nabla_i\phi_i\cdot\nabla_i\phi_i), \\ V_{ij} &= v_{ij} - (\hbar^2/2mf_{ij}^2)(f_{ij}\nabla_i^2 f_{ij} - \nabla_i f_{ij}\cdot\nabla_i f_{ij}), \end{aligned} \tag{2.13}$$

where $v(r_{ij})$ is the intermolecular potential. The second term in the potential $V(r_{ij})$ is explicitly due to the effect of correlation.

Nosanow used the cluster-expansion method derived by Van Kampen[22] to expand this ground-state energy. Defining

$$\begin{aligned} \omega &\equiv \int d\vec{r}\phi^2(\vec{r}), \\ Y(\gamma) &\equiv (\psi, e^{\gamma\Sigma_i P_i}\psi)/\omega^N, \\ Z(\gamma) &\equiv (\psi, e^{\gamma\Sigma_{i<j} V_{ij}}\psi)/\omega^N, \end{aligned}$$

then

$$E_0 = \frac{\partial}{\partial\gamma}\ln[Y(\gamma)Z(\gamma)]_{\gamma\to 0}. \tag{2.14}$$

TABLE II. Table III in Ref. 7.

β^2/V^*	0.6	0.8	1.0	1.5	2.0	2.5	3.0
$10^2\alpha_1^2$	0.34	0.72	4.5				
$10^2\alpha_2^2$	0.32	0.61	0.96	2.6	6.0		
$10^2\alpha_3^2$	0.31	0.55	0.86	1.7	3.3	5.4	8.2

By denoting

$$\langle g(\vec{r}_1, \ldots, \vec{r}_N)\rangle \equiv \int \frac{d\vec{r}_1}{\omega}\, \phi_1^2 \int \frac{d\vec{r}_2}{\omega}\, \phi_2^2 \cdots \times \int \frac{d\vec{r}_N}{\omega}\, \phi_N^2 \times g(\vec{r}_1, \cdots, \vec{r}_N),$$

Van Kampen's method can be used to show that

$$E_0 = \left(\sum_i \langle P_i + \tfrac{1}{2} \sum_{i,j}{}' \frac{\langle V_{ij} f_{ij}^2\rangle}{\langle f_{ij}^2\rangle} \right) + \left[\sum_{ij} \left(\frac{\langle P_i f_{ij}^2\rangle}{\langle f_{ij}^2\rangle} - \langle P_i\rangle \right) + \tfrac{1}{2} \sum_{i,j,k}{}' \frac{\langle V_{ij} f_{ij}^2 f_{ik}^2 f_{jk}^2\rangle}{\langle f_{ij}^2 f_{ik}^2 f_{jk}^2\rangle} - \frac{\langle V_{ij} f_{ij}^2\rangle}{\langle f_{ij}^2\rangle} \right] . \quad (2.15)$$

If only the first term is kept in the expansion, then

$$E_0 = \sum_i \langle P_i\rangle + \tfrac{1}{2} \sum_{ij}{}' \frac{\langle V_{ij} f_{ij}^2\rangle}{\langle f_{ij}^2\rangle}$$

$$= -\frac{\hbar^2}{2m} \sum_i \int \frac{d\vec{r}_i}{\omega}\, \phi_i \nabla_i^2 \phi_i + \tfrac{1}{2} \sum_{ij}{}' \left(\int \frac{d\vec{r}_i}{\omega} \int \frac{d\vec{r}_j}{\omega}\, \phi_i^2 \phi_i^2 f_{ij}^2 V_{ij} \Big/ \int \frac{d\vec{r}_i}{\omega} \int \frac{d\vec{r}_j}{\omega}\, \phi_i^2 \phi_j^2 f_{ij}^2 \right) . \quad (2.16)$$

To minimize E_0, Nosanow chose a particular analytic form for the pair-correlation function $f(r)$, and then used the variational technique to derive a differential equation for the single-particle wave function $\phi(r)$. From the solution of the differential equation, the ground-state energy E_0 was determined. The procedure was then repeated for different parameters in the correlation function $f(r)$ and the energy was again computed until an absolute minimum of E_0 was obtained, which should be an upper bound to the ground-state energy.

It has turned out that the single-particle wave function can be approximated very well by a simple Gaussian, at least in dealing with the ground-state energy:

$$\phi(\vec{r}) = \text{const} \times e^{-A\vec{r}^2}, \quad (2.17)$$

with the localization factor A treated as a variational parameter.

The trouble with the cluster expansion of E_0 is that there is no apparent physical parameter to characterize the orders of magnitude of successive terms. The validity of the approximation used (i.e., the truncation of the energy expression at the first term) depends entirely on whether all the correction terms in the expansion are negligible. This in turn hinges critically on the choice of the correlation function $f(r)$. Nosanow and others have pointed out that it is not possible to make an arbitrary variation of $f(r)$ within the context of this approximation. The choice

$$f(r) = \exp\{-k[(\sigma/r)^{12} - (\sigma/r)^6]\} \quad (2.18)$$

works only in the restricted sense that, if successful, the correction due to the neglected terms may contribute only a few percent in the computation of the ground-state energy. In actual fact, this particular form of $f(r)$ has been found useful only in a limited range of densities, without including higher-order clusters.

C. Connection between Bernades's Model and Nosanow's Approach

In the cluster expansion, had we chosen

$$\phi(r) = \frac{(\sigma^3 \pi/2a^3)^{1/2} \sin(\pi r/a)}{\pi r/a} \quad \text{for } r \leq a$$

$$= 0 \quad \text{for } r > a$$

and

$$f(r) = 0 \quad \text{for } r \leq R - 2a$$

$$= 1 \quad \text{for } r > R - 2a,$$

all the correction terms in the expansion would vanish and the energy expression would reduce to that of Bernades. This indicates that the nonoverlapping single-particle model can actually be considered as a special case of the cluster-expansion method. It has implicitly taken account of the two-body correlation in a simple way; i.e., $f(r)$ has been taken to be equal to unity outside of the "correlation sphere" of radius $R - 2a$, but zero within.

The truncation of the energy expansion at the first term is then no longer approximate but exact. Hence one may take the energy computed by Bernades's method as an upper bound and try to find better correlation functions to reduce the magnitude of the energy. Conceptually, then, Bernades's and Nosanow's work may be regarded in the same spirit, being different choices of the correlation function.

III. VARIATIONAL CALCULATION OF THE GROUND-STATE ENERGY OF SOLID HYDROGEN

We proceeded to carry out a variational computation of the ground-state energy, using the truncated cluster expansion (Sec. III B). The truncated cluster expansion was attractive for computation because (i) the pair-correlation function $f(r)$ indeed effectively reduces the "contribution" of the repulsive interaction to the potential integral in the region where it is dominant; (ii) both in the formulation and in the variational calculation no assumption of "harmonic approximation" is involved; (iii) it was comparatively easy to set up an appropriate program for machine computation.

Our preliminary calculation for hydrogen showed that the particular choice of the pair-correlation function, Eq. (2.18), was useful only in a limited region of low densities. To compare with available measurements we needed to cover the range from the zero-pressure density of 0.089 to about 0.2 g/cm^3. We therefore developed a more general pair-correlation function for use over a wide range of densities.

In Sec. III A, the formulation of the ground-state energy is discussed; in Sec. III B, we present the model pair-correlation function, which enabled us to extend to high densities.

A. Ground-State Energy

The functional forms and procedures for the variational calculation of the ground-state energy were as follows. Suppose that an appropriate correlation function $f(r)$ has been chosen such that truncation of the cluster expansion at the first term, Eq. (2.16), is a good approximation. With the choice

$$\phi_i = \text{const} \times e^{-A(\vec{r}_i - \vec{R}_i)^2},$$

all the correction terms in the energy expansion involving P_i vanish [see Eq. (2.15)]. Hence the term $\sum_i \langle P_i \rangle$ then gives the exact contribution due to the operators P_i's.

For

$$I_{ij} = \int \frac{d\vec{r}_1}{\omega} \int \frac{d\vec{r}_2}{\omega} \phi_i^2 \phi_j^2 f_{ij}^2 V_{ij} = \left(\frac{2A}{\pi}\right)^3 \int d\vec{r}_1 \int d\vec{r}_2 \, e^{-2A(\vec{r}_i - \vec{R}_i)^2} \times e^{-2A(\vec{r}_2 - \vec{R}_j)^2} f^2(r_{12}) V(r_{12}), \quad (3.1)$$

if one makes the coordinate transformations[12]

$$\vec{r} = \vec{r}_1 - \vec{r}_2, \quad \vec{z} = \vec{r}_2 - \vec{R}_i$$

and carries out the integration over $\vec{z}$, one gets

$$I_{ij} = (A/\pi)^{3/2} \int d\vec{r} f^2(r) V(r) e^{-A(\vec{r} + \vec{R}_{ij})^2}, \quad \vec{R}_{ij} = \vec{R}_j - \vec{R}_i. \quad (3.2)$$

Similarly, one obtains

$$\langle f_{ij}^2 \rangle = (A/\pi)^{3/2} \int d\vec{r} f^2(r) e^{-A(\vec{r} + \vec{R}_{ij})^2}. \quad (3.3)$$

Taking one of the lattice sites as the origin, Eq. (2.16) may now be written as

$$\frac{E_0}{N} = 3 \frac{\hbar^2}{2m} A + \frac{1}{2} \sum_I n_I \frac{I_I}{< f_I^2}, \quad (3.4)$$

where

$$I_I = \left(\frac{A}{\pi}\right)^{1/2} \frac{1}{R_I} \int dr \, r f^2(r) V(r) \times \left[e^{-A(r - R_I)^2} - e^{-A(r + R_I)^2} \right],$$

$$\langle f_I^2 \rangle = \left(\frac{A}{\pi}\right)^{1/2} \frac{1}{R_I} \int dr \, r f^2(r) \times \left[e^{-A(r - R_I)^2} e^{-A(r + R_I)^2} \right], \quad (3.5)$$

where R_I is the length of the Ith lattice shell vector and n_I is the number of equivalent sites in the Ith shell.

For a given nearest-neighbor separation R, one may select a pair-correlation function $f(r)$, and compute E_0/N for different values of A to locate a minimum. The procedure is then repeated for a different $f(r)$ until an absolute minimum of the ground-state energy is obtained.

B. Correlation Function $f(r)$

Using the truncated energy expression, Eq. (2.16), and the correlation function

$$f(r) = e^{-k[(\sigma/r)^{12} - (\sigma/r)^6]},$$

the cohesive energies for helium three and helium four can only be found in a limited region of densities. At high density, in helium no minimum energy could be located.[23] For solid hydrogen with the form of $f(r)$ the calculation fails to locate a minimum for $R \leq 3.57$ Å.

It is obvious that as the interparticle distances decrease, the effects of coupled three- or more body correlations will become more and more pronounced. One can always try formally to include in the computation higher-order terms in the cluster expansion, yet the calculation will certainly become more tedious and there is really no guarantee of fast convergence of the expansion Instead, we took the view that the pair-correlation function could be improved by considering it as representing the average effect of the many-body correlations and thus incorporating physically appropriate modifications, particularly for small interparticle separations.

The truncation approximation (3.5) may be viewed as a Hartree calculation[12,23] in which the bare potential is replaced by an effective potential

$$V_{\text{eff}} = f^2(r) V(r) / \langle f^2(r) \rangle.$$

Thus one may picture the crystal as consisting of "independent" particles vibrating about the lattice sites as determined by this effective potential and the localization factor A. Effectively, there is a potential well whose depth is controlled by the pair-correlation function as well as by the normal lattice (sum) potentials. At low densities where the variational calculation is found to converge to minimum energies, at least one bound state exists in the potential well. If no pair correction is present as the density increases, the bound state moves upward, due to the repulsive component of $V(r)$. The effect of the pair correlation is in fact to shield the repulsive potential. Since $f(r)$ tends to zero at small r, by making $f(r)$ vanish sufficiently rapidly, a bound state can be maintained and the truncated cluster expansion may converge in a consistent manner, and the higher-order cluster terms may be small.

We developed[1] several intuitive arguments regarding the choice of $f(r)$. At the present writing it seems that the main considerations are twofold. First, for computational stability a small genuinely hard, core effect should force $f(r) \equiv 0$, for $r < r_0$. Second, at larger values of r it also is likely that any form of $f(r)$ which does not allow the position of $f_{\max}$ and $f = 1$ to change with density, as is the trouble with $f(r) = e^{-kv_{LJ}(r)}$, is physically incorrect. Brueckner and Frohberg[15] have derived a differential equation for $f(r)$; although too complicated to solve, it exhibits the Hartree-like corrections to $v(r)$ due to the rest of the crystal, and these clearly are density dependent.

As soon as we took the view that $f(r)$ should have (a) a hard core and (b) a surrounding softer region whose shape was density dependent, we found rapid convergence of the cluster method over a wide density range. No claim is made for uniqueness, or for having derived something from first principles; the results obtained are the principal evidence in support of the choice made. Our experience with one form of $f(r)$ in our cluster-variational calculations has been extremely satisfactory. A correlation function which explicitly includes a hard-core effect is

$$\begin{aligned} f(r) &= 0 \quad \text{for } r \leqslant r_0 \\ &= \exp\left\{ -k\left[\left(\frac{\sigma - r_0}{r - r_0}\right)^m - k'\left(\frac{\sigma - r_0}{r - r_0}\right)^n\right]\right\} \\ &\qquad \text{for } r > r_0 , \qquad (3.6) \end{aligned}$$

where (m, n) is a pair of integers, $m > n$, σ is taken arbitrarily as the Lennard-Jones σ, and k' and r_0 are two additional parameters whose significance is next discussed.

The physical significance of r_0 is obvious; it is the "diameter" of the hard core.[24] Other forms of $f(r)$ were tried, but care must be exercised to have $f(r)$ sufficiently smooth at $r = r_0$ to assure convergence of the terms in Eq. (2.13).

In the conventional cluster expansion,[13,25] if Γ is defined as the volume of the region where the effect of correlation is important [or $f(r)$ is appreciably different from 1] and Ω as the volume per particle, the physical parameter of interest is the ratio Γ/Ω; if this ratio is very small compared to unity, quick convergence of the series expansion can be expected (a formal discussion is given in Appendix A).

Given a set of exponents (m, n) which may be determined from other physical considerations, the parameter k' determines how rapidly $f(r)$ rises from zero to its asymptotic value and thus effectively serves to determine Γ/Ω, along with r_0 and R, the nearest-neighbor distance.

The two parameters k' and r_0 are actually complementary to each other. For a given pair of (m, n), the introduction of the parameter k' into the correlation function extended the region of convergence of the truncated cluster expansion. Indeed, choices of m and n which previously did not lead to convergence were then possible.

The recipe for the variational calculation of the ground-state energy of the system was as follows. The model pair correlation as given by Eq. (3.6) was used in the trial wave function. At a given density corresponding to R, the threshold value of k' which maintained good convergence of the truncated energy expression was chosen. A variational computation was then carried out, which determined the best values of A and k. After checking the validity of the approximation used, an energy minimum was obtained.

C. Physical Interpretation of Pair-Correlation Function

The model pair-correlation function can also be viewed in a more physical way.

Since the truncation approximation employed may be considered as replacing the two-body potential $v(r)$ by an effective potential

$$f^2(r)\, V(r) / \langle f^2(r) \rangle ,$$

where

$$V(r) = v(r) - (\hbar^2/2mf^2)(f\nabla^2 f - \nabla f \nabla f) ,$$

and for $f(r)$, given by Eq. (3.6),

$$V(r) \equiv v(r) + v'(r) ,$$

where

$$\begin{aligned} v'(r) = \epsilon\lambda'^2 k\Bigg[m\left(m - 1 + \frac{2r_0}{r}\right)\left(\frac{\sigma - r_0}{r - r_0}\right)^{(m+2)} \\ - k'n\left(n - 1 + \frac{2r_0}{r}\right)\left(\frac{\sigma - r_0}{r - r_0}\right)^{(n+2)}\Bigg], \end{aligned}$$

$$\lambda^2 = \hbar^2/2m\sigma^2\epsilon , \qquad \lambda'^2 = \sigma\lambda/(\sigma - r_0)^2 , \qquad (3.7)$$

and ϵ is the depth of the potential $[v(r)]$ minimum, we may picture the interacting molecules as having a "hard" core of "diameter" r_0 and a "softer" shell of thickness t determined by $\frac{1}{2}(r' - r_0)$, where r' is defined by $V(r') = 0$. The soft shell is defined to include the region of the effective repulsive potential [the region where $V(r)$ is positive]. The positon of r' which defines the outer boundary of the soft shell is clearly dependent on the zeros of the two potential functions $v(r)$ and $v'(r)$.

The zero of $v(r)$, for a Lennard-Jones-type potential function, is simply σ. The zero of $v'(r)$, r_0' can be determined by

$$r_0' = \sigma + (B - 1)(\sigma - r_0) ,$$

where

$$B = \left(\frac{m(m - 1 - 2r_0/r)}{k'n(n - 1 - 2r_0/r)}\right)^{1/(m-n)} .$$

Since from our preliminary calculations, it was found that at $R = 3.75$ Å, k' was about 0.45 and k' increased with decreasing R, we then concluded that to begin with, B was greater than 1 and r_0' is greater than σ; since k' increases with decreasing R, B will decrease with decreasing R and r_0' will decrease also. It is easy to see that the position of r' will move toward σ and beyond as the density increases (R decreases). Hence, the outer boundary of the soft shell is expected to be "pushed in" as increasing pressure is applied to the system.

IV. INTERMOLECULAR POTENTIALS

In the calculation of the ground-state energy, it became obvious that the majority of the contribution to the potential integrals came from the region of $4a_0 \leq r \leq 15a_0$ (a_0 being the Bohr radius) because of the presence of the two-body correlation function $f(r)$. Thus the detailed structure of the intermolecular potential $v(r)$ in the region $r \leq 4a_0$ is not significant at all in the computation of the ground-state energy. This is fortunate because the potentials to be used are of questionable validity in the region $r \leq 4a_0$.

A. Lennard-Jones Potential

The Lennard-Jones potential is conventionally written

$$v(r) = 4\epsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}], \tag{4.1}$$

where σ gives the distance of closest approach of two molecules which collide with zero initial relative kinetic energy and ϵ is the maximum energy of attraction of the two molecules. The numerical values of the two parameters are determined by the experimental second virial coefficients.

Before 1960, the parameters σ and ϵ used in the literature were given as[21]

$$N\sigma^3 = 15.12\ \mathrm{cm^3/mole}, \quad \epsilon/k = 37.0\ ^\circ\mathrm{K}.$$

In 1960, Michels, deGraaf, and ten Seldam[26] observed that the above-quoted parameters cannot represent the virial coefficients satisfactorily. Using newly measured compressibility data over temperatures ranging from -175 to 150 °C, they redetermined the parameters as

$$N\sigma^3 = 15.6\ \mathrm{cm^3/mole}, \quad \epsilon/k = 36.7\ ^\circ\mathrm{K}.$$

For hydrogen, it is observed by Michels *et al.* that it is impossible to find specific values for $N\sigma^3$ and ϵ/k which meet the experimental results within their accuracy. The values quoted above are only the most probable values of $N\sigma^3$ and ϵ/k. It is probable that the representation of the experimental data by a Lennard-Jones-type potential is not entirely satsifactory for hydrogen molecules.

B. Modified Buckingham (exp-6) Potential

Srivastava and Barua[27] have instead fitted the second virial coefficient data of Michels to the exp-6 potential. The exp-6 potential is defined by

$$\begin{aligned} v(r) &= \frac{\epsilon}{(1-6/\alpha)}\left[\frac{6}{\alpha}\exp\alpha\left(1-\frac{r}{r_m}\right) - \left(\frac{r_m}{r}\right)^6\right] \\ &\quad \text{for } r \geq r_{\max} \\ &= \infty \quad \text{for } r < r_{\max}, \end{aligned} \tag{4.2}$$

where ϵ is the depth of the potential minimum, r_m is the position of the minimum, α is a parameter which is a measure of the steepness of the repulsive potential, and $r_{\max}$ gives the value of r for which $v(r)$ has a maximum.

The parameters for hydrogen as determined by Srivastava *et al.* are $\alpha = 14.0$, $r_m = 3.339$ Å, $\epsilon/k = 38.02$ °K.

Srivastava *et al.* have also computed the second virial coefficients at different temperatures by using the exp-6 potential with the set of parameters given above. The agreement with the experimental data was good over the entire temperature range. They then concluded that the exp-6 potential is an improvement over the Lennard-Jones model; apparently, the relative importance of the nonspherical contributions to the potential may not be extremely critical at the densities considered.

C. Wang Chang's Potential

If one would write down all the known important types of interactions (theoretically derived) between two hydrogen molecules, one would have a very complicated formula including deBoer's valence potential, van der Waal's potential, the quadrupolar interaction, etc. For example, deBoer's potential is written in the form

$$V_{\mathrm{val}} = V\left(e^{-r_{ac}/\zeta} + e^{-r_{bc}/\zeta} + e^{-r_{ad}/\zeta} + e^{-r_{bd}/\zeta}\right),$$

$$V = 2.78\, e^2/a_0, \quad \zeta = a_0/1.87, \quad a_0 \sim \text{Bohr radius},$$

where r_{ac} denotes the distance between the nuclei a and c, and so forth. It is easy to see that an orientation dependence of the potential is given explicitly through the four internuclear distances. This form presents great difficulty in practical computations.

For theoretical calculation, Wang Chang[21] assumed that the intermolecular potential of hydrogen could be represented approximately by the function

$$v(r, \theta_1, \theta_2, \phi) = [b + \beta(\cos^2\theta_1 + \cos^2\theta_2)]\,r^{-12} - ar^{-6}, \tag{4.3}$$

where $\theta_1(\theta_2)$ denote the angle between the molecular axis of the first (second) molecule and the line joining the centers of mass of the two interacting molecules.

Wang Chang adjusted the constants a, b, and β so as to give the best possible agreement with the various quantum-mechanical calculations which have been made for the nonspherical potential field of the hydrogen molecules. She obtained $a = 1.25 \times 10^{-11}$ erg Å^6, $b = 4.438 \times 10^{-9}$ erg Å^{12}, $\beta = 4.784 \times 10^{-9}$ erg Å^{12}.

The region of validity of this potential, of course, is determined by the range of validity of the potentials which it fits. It is estimated that the calculation of deBoer's valence potential is valid in the region from $4a_0$ to $10a_0$ (a_0 is the Bohr radius); hence it is expected that Wang Chang's potential should provide a viable approximation for the intermolecular potential of the hydrogen molecules in the same region.

D. Discussion of Potentials

Although it was known that the Lennard-Jones potential did not give a very satisfactory representation of the empirical second virial coefficient data, we still used it to compute the ground-state energy at a few densities for the purpose of comparing with old computations, thus gaining an understanding of the effects of the zero-point energy and the correlation between the motions of particles.

Our main work using a spherical potential employed the modified Buckingham exp–6 potential. Wang Chang's potential provided at least some approximation to the nonspherical properties of the intermolecular potential of the hydrogen molecules, so we made special computations with it to study effects of noncentral interactions.

V. MODIFICATIONS FOR NONSPHERICAL MOLECULAR INTERACTION POTENTIALS

In the derivation of the energy by the methods discussed in Sec. III, it was implicitly assumed that the particles did not have internal orientation coordinates. Clearly, for interacting hydrogen molecules the interaction potential is orientation dependent. Therefore, we attempted to include the effect of orientation to some extent in our calculation.

We note several points. First, our interest is in the cohesive energy over a wide density range. The order of magnitude of the contributions of kinetic and orientation-independent potential energy to the total energy is 10^{-15}–10^{-14} erg per particle, depending on density. By comparison, over most of the density range the direction-dependent (valence and electric quadrupole) interactions are smaller by about two orders of magnitude. Second, reference to Table 14.4-1 of Hirschfelder, Curtiss, and Bird[21] shows that simple orientation-dependent valence interactions dominate over electric quadrupole forces at almost all densities except near zero pressure, where the intermolecular mean distance is 3.75 Å for solid hydrogen. In this special region several partial cancellations occur and electric quadrupole interactions then dominate orientational effects. The orientation phase transitions which occur at very low temperature and low pressure in solid hydrogen have been studied extensively on that basis,[18] but it is likely that the physical behavior found will quickly change in detail as the density is increased and electric quadrupole forces become secondary.

For our purposes, it was decided to choose some orientation-dependent potential which would be a good approximation over most of the density range, so we used the potential developed by Wang Chang as an approximation to the deBoer potential (Sec. IV), recognizing that in the very-low-pressure region it could not be taken literally.

To estimate rotational effects we assumed that since the splitting between rotational levels was very large compared to orientation-dependent terms we could simply average over the free rotational states as a first approximation. By rewriting (4.3) as

$$v = \{b + \tfrac{2}{3}\beta[1 + P_2(\cos\theta_1) + P_2(\cos\theta_2)]\} r^{-12} - ar^{-6} \tag{5.1}$$

it is straightforward, following Nakamura[29] and others, to place v in angular momentum representation of the molecular rotor states and operators. The details are given in Appendix B.

Only the orientation-dependent part $\tilde{v}$ of v depends on whether the molecule is in its ortho or para state. Since we are doing a zero-temperature calculation the molecules are assumed to be in the states $J = 0$ or $J = 1$, respectively. The $J = 0$ states do not contribute to $\tilde{v}$, while for $J = 1$ the contribution depends on the quantity $(3J_{zi}^2 - 2)$, where i indicates site. If for each molecule $J = 1$, we assume that the distribution of J_{zi} is isotropic; then $J_{zi} = 1, 0, -1$ with equal likelihood and $\langle 3J_{zi}^2 - 2\rangle_{\text{av}} = 0$. Then, independent of the orthopara distribution, $\langle\tilde{v}\rangle = 0$, and we simply have an effective potential which is again spherically symmetric:

$$V_{\text{eff}}(r) = (b + \tfrac{2}{3}\beta)\, r^{-12} - ar^{6}. \tag{5.2}$$

We also found the same result on the average when we assumed a state $J_{z'} = 0$ for all ortho molecules, and then summed over lattice sites; the primed subscript refers to an axis fixed in the crystal. This special case is probably not likely.

To a certain extent the above result is dependent on the Wang Chang form of potential, but exploration of other potentials[28] suggested that similar results could be obtained. Having obtained this effective potential, we then proceeded to use it in Eq. (3.5).

VI. NUMERICAL COMPUTATIONS AND RESULTS

The numerical calculation of the ground-state energy of the system was based on Eq. (3.5). In our formulation of the variational computation, only two parameters were taken to be explicit

TABLE III. E' with $n=2$ at $R=3.75$ Å.

s	m	k'	k	A(in 10^{16} Å^{-2})	E'(in 10^{-15} erg)
2	4	0.45	0.2	1.55	−8.68
2.5	5	0.0	0.08	1.8	−8.46
3	6	0.0	0.03	2.1	−8.18

variational parameters: the localization factor A in the single-particle wave function $\phi(|\vec{r}_i - \vec{R}_i|)$, and the strength factor k in the correlation function $f(r_{ij})$.

At a given density and for a certain type of interaction potential, the computation was programmed to vary A and k. After their optimum values were determined by the variational process and the convergence of the truncated energy expression checked, the ground-state energy was then taken as the computed energy corresponding to optimum A and k.

Although the exponents m and n in the correlation function $f(r)$ are not treated as variational parameters *per se*, we did compute the energy at $R=3.75$ Å for different pairs of (m, n). Our purpose was to select a pair of m and n not only to give the best energy under the circumstances, but also to cover a wide range of densities. As for the parameter k', for a given pair of m and n we used the smallest value which still maintained good convergence of the truncated energy expression.

In the actual computation of the ground-state energy, we carried the lattice sum to the thirtieth shell of nearest neighbors. However, during the variational process for the determination of the optimum values of A and k, the lattice sum was only carried to the 3rd shell. The justification is that (i) lattice potential integrals from the fourth nearest neighbor on are comparatively insensitive to the parameters A and k and (ii) the contribution to the energy due to the potential integrals from fourth nearest neighbor on is comparatively insignificant.

The structure of crystalline hydrogen was taken to be fcc in our calculation.[29,30] The results for different potentials are as follows.

A. Lennard-Jones Potential

Using Michels's parameters and $r_0 = 2.0$ Å (we were guided by Cole's high-density quantum hard-sphere calculations[24]), we began computations at $R=3.75$ Å. The procedure was first to vary m, n which was carried out by fixing $s=m/n$, and varying n. The results for the energy E', which is the energy carried to the third shell, are given in Tables III and IV.

TABLE IV. E' with $s=2$ at $R=3.75$ Å.

n	m	k'	k	A(in 10^{16} Å^{-2})	E'(in 10^{-15}erg)
2	4	0.45	0.2	1.55	−8.68
3	6	0.0	0.03	2.1	−8.18
4	8	0.0	0.004	2.4	−7.78

Apparently the value computed (to the third lattice shell) for $m=4$ and $n=2$ seems to give the lowest energy among the different sets of exponents (m, n) considered. It is to be noted that we did not vary k' to negative values and these may be allowable. It was also found that this pair of exponents $(m=4, n=2)$ indeed covers a wide range of densities. Therefore, we used (4, 2) throughout all subsequent computations.

The optimum values for A and k for each density were determined by computing E'; then in the final calculation of the ground-state energy, the lattice sum for the potential integrals in the energy equation was carried to the thirtieth lattice shell. The results are shown in Table V.

Using the Lennard-Jones potential, we also examined the effect of the two parameters k' and r_0 in a slight modification of the choice

$$f(r) = e^{-k[(\sigma/r)^{12}-(\sigma/r)^6]} ,$$

which, in the variational calculation, had previously failed to locate a minimum for the truncated energy at $R=3.18$ Å. However, when we used

$$f(r) = e^{-k[(\sigma/r)^{12}-k'(\sigma/r)^6]} ,$$

a minimum energy was found to be located at the threshold value of $k'=2.3$. The computed E' is 2.14×10^{-14} erg for $A=f.4\times10^{16}$ Å^{-2} and $k=0.05$. The energy thus obtained was far from correct; we tried to vary the two exponents m and n to improve the energy value, but the results were always poor and computationally delicate, so we abandoned this approach in favor of the $f(r)$ which we described in Sec. III.

We examined the convergence of the cluster expansion. The ground-state energy is

$$E_0 = E_{k,1} + E_2 + E_3 + \cdots ,$$

where

$$E_{k,1} = \sum_i \langle P_i \rangle , \quad E_2 = \tfrac{1}{2} \sum_{i,j} \left\langle \frac{V_{ij} f_{ij}^2}{f_{ij}^2} \right\rangle ,$$

TABLE V. Ground-state energy per molecule for Lennard-Jones potential.

R(Å)	V(cm^3/mole)	A(10^{16} Å^{-2})	k'	k	E(10^{-14} erg)
3.75	22.47	1.55	0.45	0.2	−1.07
3.607	20	2.00	0.70	0.17	−0.990
3.483	18	2.75	0.95	0.12	−0.745
3.3	15.31	4.05	1.35	0.075	0.169
3.18	13.7	5.3	1.7	0.05	1.48
3.05	12.09	7.2	2.2	0.028	4.14

TABLE VI. Some third-order cluster terms for $R = 3.75$ Å, with $A = 1.55 \times 10^{16}$ Å^{-2}, $k = 0.2$, and $k' = 0.45$.

R^*_{ij}	R^*_{ik}	R^*_{jk}	$\frac{1}{2}n$	$\Delta_{ijk}(10^{-14}$ erg)	$\frac{1}{2}n\,\Delta_{ijk}(10^{-14}$ erg)
1	1	1	24	-4.69×10^{-3}	-1.13×10^{-1}
1	1	$\sqrt{2}$	24	8.58×10^{-4}	2.06×10^{-2}
1	1	$\sqrt{3}$	48	1.36×10^{-3}	6.53×10^{-2}
1	1	$\sqrt{4}$	12	-1.46×10^{-4}	-1.75×10^{-3}
1	$\sqrt{2}$	$\sqrt{3}$	24	3.58×10^{-5}	8.58×10^{-4}
1	$\sqrt{2}$	$\sqrt{5}$	24	-7.00×10^{-5}	-1.68×10^{-3}
$\sqrt{2}$	1	1	12	3.10×10^{-3}	3.72×10^{-2}
$\sqrt{2}$	1	$\sqrt{3}$	24	-1.50×10^{-4}	-3.60×10^{-3}
$\sqrt{2}$	1	$\sqrt{5}$	24	-1.20×10^{-3}	-2.89×10^{-2}

$$E_3 = \tfrac{1}{2} \sum_{i,j} \left(\frac{\langle V_{ij} f_{ij}{}^2 f_{ik}{}^2 f_{jk}{}^2 \rangle}{\langle f_{ij}{}^2 f_{ik}{}^2 f_{jk}{}^2 \rangle} - \frac{\langle V_{ij} f_{ij}{}^2 \rangle}{\langle f_{ij}{}^2 \rangle} \right) . \quad (6.1)$$

We attempted to estimate formally the higher-order contributions, using certain approximations which are discussed in Appendix A. However, finally we were led to a direct computational approach. Using a program provided by Nosanow, we computed E_3, the first correction term in the series expansion, at two densities corresponding to $R = 3.75$ and $R = 3.3$ Å.

A typical term in E_3 is given by

$$\Delta_{ijk} = \frac{\langle V_{ij} f_{ij}{}^2 f_{ik}{}^2 f_{jk}{}^2 \rangle}{\langle f_{ij}{}^2 f_{ik}{}^2 f_{jk}{}^2 \rangle} - \frac{\langle V_{ij} f_{ij}{}^2 \rangle}{\langle f_{ij}{}^2 \rangle} , \quad (6.2)$$

and E_3 itself is given by the complicated lattice summation over all the indices i, j, k. In the computation, R_{ij} is always used to denote the lattice distance between the ith particle and jth particle which interact with one another through the two-body potential. In the lattice summation, corresponding to each set of combinations of (R_{ij}, R_{ik}, R_{jk}), there are a definite number of equivalent "triangles" (with sides R_{ij}, R_{ik}, R_{jk}). We denote n = number of equivalent triangles, $R_i^* = R_i/R$. The computed results for $R = 3.75$ Å are presented in Table VI.

In the preceding calculation, we computed Δ_{ijk} for the first six triangles associated with $R_{ij} = R_{ik} = R$ and the first three triangles associated with $R_{ij} = 2R$ and $R_{ik} = R$. The results show that the contribution to E_3 due to terms associated with $R_{ij} = 2R$ is indeed smaller than that due to terms associated with $R_{ij} = R$. It is also seen from the computations that the internal cancellation between Δ_{ijk} for different triangles is a major factor in yielding a small E_3. Hetherington, Mullin, and Nosanow[23] have given a simple explanation as to why some triangles give a positive or negative contribution.

By summing up separately the terms associated with $R_{ij} = R$ and those associated with $R_{ij} = (2R)^{1/2}$, we obtain for $R_{ij} = R$, $E_{3,1}/N \simeq -2.94 \times 10^{-16}$ erg and for $R_{ij} = (2R)^{1/2}$, $E_{3,2}/N \simeq 4.7 \times 10^{-17}$ erg. The sum of these two terms gives

$$E_3/N \simeq -2.47 \times 10^{-16} \text{ erg}.$$

This, of course, is only an estimate of the value of E_3, but the deviation can be expected to be small. Taking this value as representing the value of E_3/N, we get

$$E_3 = 1.3\%\, E_2$$

when compared to $E_2/N = -1.84 \times 10^{-14}$ erg.

Next we checked our choice of $f(r)$ at $R = 3.3$ Å, where the Nosanow form did not give a converging computation. The results, for $A = 4.05 \times 10^{16}$ Å^{-2}, $k = 0.075$, and $k' = 1.35$, are given in Table VII.

Summing up the terms in the last column of Table VII, we get

$$E_3/N \simeq 1.4 \times 10^{-16} \text{ erg},$$

which is again small compared to $E_2/N = -1.85 \times 10^{-14}$ erg.

We did not attempt either to check the convergence for each density or to include E_3 in the variational scheme simply because of the time of computation involved. However, we may make the following observation. Looking at the cluster expansion, it is seen that if either $f(r)$ or $V(r)$ is constant, all the correction terms in the expansion will be zero. It is also obvious that if there is absolute localization (about the lattice sites), the correction terms again vanish. Therefore, on the one hand, for fixed localization, the correction terms are smaller for smoother varying $f(r)$; on the other hand, for fixed $f(r)$, the correction terms are smaller for larger localization factor A. From the computed results, it is seen that the localization factor A indeed increases with the density while the effective spatial variation of $f(r)$ stays pretty much the same. As for the spatial variation of the potential, in the neighborhood of the potential minimum ($r = 3.3$ Å), the major contribution to the spatial variation is due to $(d^2v/dr^2)_R$; in the remaining region, $(dv/dr)_R$ is most responsible. Thus, taking the computed E_3 at $R = 3.75$ and 3.3 Å, together with the fact that A increases with density while the effective variation of $f(r)$ is essentially unchanged, we propose that the corrections will generally be small.

If E_3 or more terms were included in the variational process, the optimum values of A and k could

TABLE VII. Some third-order terms for $R = 3.3$ Å, with $a = 4.05 \times 10^{16}$ Å^{-2}, $k = 0.075$, and $k' = 1.35$.

R^*_{ij}	R^*_{ik}	R^*_{jk}	$\frac{1}{2}n$	$\Delta_{ijk}(10^{-14}$ erg)	$\frac{1}{2}n\,\Delta_{ijk}(10^{-14}$ erg)
1	1	1	24	-1.45×10^{-2}	-3.48×10^{-1}
1	1	2	24	2.44×10^{-3}	5.85×10^{-2}
1	1	3	48	5.10×10^{-3}	2.45×10^{-1}
1	1	4	12	4.28×10^{-3}	5.14×10^{-2}
1	2	3	24	3.42×10^{-4}	8.21×10^{-3}

TABLE VIII. Ground-state energy per molecule and the pressure for the Buckingham exp-6 potential.

R(Å)	V(cm^3/mole)	A(10^{16} Å^{-2})	k'	k	E(10^{-14} erg)	p(10^3 kg/cm^2)
3.75	22.47	1.7	0.35	0.15	−1.10	0.0
3.607	20.00	2.25	0.65	0.12	−1.02	0.405
3.483	18.00	2.75	0.85	0.11	−0.790	1.03
3.356	16.10	3.60	1.15	0.07	−0.261	2.44
3.285	15.10	3.95	1.30	0.07	0.242	3.93
3.233	14.40	4.45	1.45	0.055	0.741	5.27
3.149	13.30	5.60	1.75	0.030	1.89	8.22
3.084	12.50	6.50	2.05	0.020	3.15	11.6
2.938	10.80	8.70	2.85	0.010	7.81	

be shifted. However, since (i) the magnitude of E_3 is small and (ii) it is insensitive (as compared to E_2) to the changes of A and k, we conclude that the neglect of higher-order terms in the cluster expansion does not influence the result very much. Thus, using a carefully constructed pair-correlation function, one may obtain excellent convergence of the variational method without three-center cluster contributions.

B. Buckingham exp-6 Potential

For the exp−6 potential

$$v(r)=\epsilon[0.75\, e^{\alpha(1-r/r_m)}-1.75\,(r_m/r)^6],$$

where the parameters ϵ, α, and r_m were determined by Srivastava *et al.* to be $\epsilon=52.48\times10^{-16}$ erg, $\alpha=14.0$, $r_m=3.339$ Å, we again used our type of correlation function. The results of the variational calculation are shown in Table VIII.

To compare the calculated results with experimental data, the equation of state in terms $T=0$ °K, the pressure $p=-(dE/dV)$, was computed numerically and is tabulated in Table VIII.

C. Wang Chang's Potential

To carry out the variational calculation for Wang Chang's potential, the modified expression for the energy, Eq. (5.2), was used. It is seen that the formulation is the same as that in the case of pure spherical potential except that the effective two-body potential is given by

$$v_{\text{eff}}=(b+\tfrac{2}{3}\beta)\,r^{-12}-ar^{-6},$$

where the parameters are $a=1.25\times10^{-11}$ erg Å^6, $b=4.48\times10^{-9}$ erg Å^{12}, $\beta=4.78\times10^{-9}$ erg Å^{12}.

In the variational calculation, the same type of 4-2 correlation function was used. The results are shown in Table IX.

VII. SUMMARY AND DISCUSSION

The Lennard-Jones potential was only qualitatively useful. Our experience would lead us to recommend Buckingham's exp-6 potential. The computed results for this potential still differ considerably from the experimental data; from the work of Bruce we now believe that the fault does not lie in our computations. On the one hand, the computation of the ground-state energy by the cluster method now extends well into the low-density region ($R=3.75$ Å), where the semiclassical method had failed; on the other hand, when our form of pair function is used, the truncated cluster approximation extends into the high-density region where previous variational calculations had failed to converge.

For the nonspherical Wang Chang potential, the results, although in general exhibiting the same features as those of the exp−6 potential, give over-

TABLE IX. Ground-state energy per molecule and the pressure for the Wang Chang potential.

R(Å)	V(cm^3/mole)	A(10^{16} Å^{-2})	k'	k	E(10^{-14} erg)	p(10^3 kg/cm^2)
3.75	22.47	1.40	0.25	0.16	−1.06	0.0
3.607	20.00	1.95	0.60	0.12	−1.02	0.295
3.483	18.00	2.50	0.85	0.10	−0.845	0.864
3.356	16.10	3.15	1.10	0.085	−0.446	2.0
3.285	15.10	3.65	1.30	0.071	−0.039	3.16
3.233	14.40	4.20	1.45	0.056	0.364	4.20
3.149	13.30	5.3	1.75	0.036	1.31	6.75
3.084	12.50	6.1	2.00	0.028	2.38	9.71
2.982	11.30	7.75	2.50	0.018	4.92	16.9
2.938	10.80	8.80	2.80	0.013	6.49	

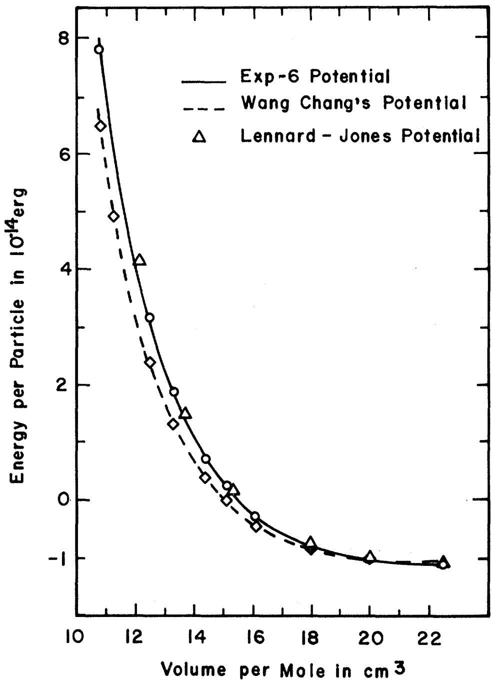

FIG. 1. Energy per particle in 10^{-14} erg vs volume per mole in cm^3.

all better agreement with the experimental p-V data (see Fig. 2), especially in the region from $V=14.4$ cm^3/mole ($R=3.23$ Å) to $V=18.0$ cm^3/mole ($R=3.48$ Å), the computed pressures agreed within a few percent with experimental data. The results begin to show drastic deviation from the experimental results at higher densities, starting from $V=12.0$ cm^3/mole. Since Wang Chang's potential is obtained by fitting deBoer's potential it may be expected to provide a usable approximation for the nonspherical intermolecular potential for hydrogen molecules in the region from $r=4a_0$ to $10a_0$.

From our results, it is seen that the best agreement with experimental pressure measurements is obtained in the region from $R=3.15$ to 3.5 Å. For $R>3.5$ Å, although the near-neighbor integrals fall within the region of validity of the potential, the rest of the potential integrals are all outside of the region. Hence, the results are not expected to be as reliable for $R>3.5$ Å. For $R\leqslant 3.5$ Å (but not less than 2.5 Å), all the important potential integrals are within the region of validity of the potential. The large deviation of the results from the experimental data in this region then seems to suggest that there are other factors, perhaps experimental, contributing to the large errors at high densities. It should be pointed out that the nonspherical character discussed has appeared only in the modified potential Eq. (5.2). Nonspherical corrections to the pair functions or to the single-particle functions were not attempted.

To summarize, in computing the ground-state energy for solid hydrogen, the cluster-expansion method has been found to be quite usable. Our proposed model pair-correlation function, Eq. (3.6), has apparently accomplished what it was meant to do; i.e., (i) it allowed computations to be extended into higher-density regions and (ii) compared to previous computations, it yielded physically reasonable results, for any of several model intermolecular potentials.

Finally, our results are summarized in Fig. 1 (E vs V) and Fig. 2 (p vs V), which were also reported in Ref. 1.

ACKNOWLEDGMENTS

We would like to express our appreciation to many of our colleagues, particularly G. V. Chester, V. Chiu, and K. S. Dy.

APPENDIX A: CONVERGENCE OF CLUSTER EXPANSION

In the energy expression derived from the cluster expansion, if the single-particle wave function is of the Gaussian form

$$\phi(\vec{r}) = \text{const} \times e^{-A\vec{r}^{\,2}} ,$$

then all the correction terms to the operator P_i will vanish identically. The ground-state energy is reduced to

$$E_0 = E_{k,1} + E_2 + E_3 + \ldots ,$$

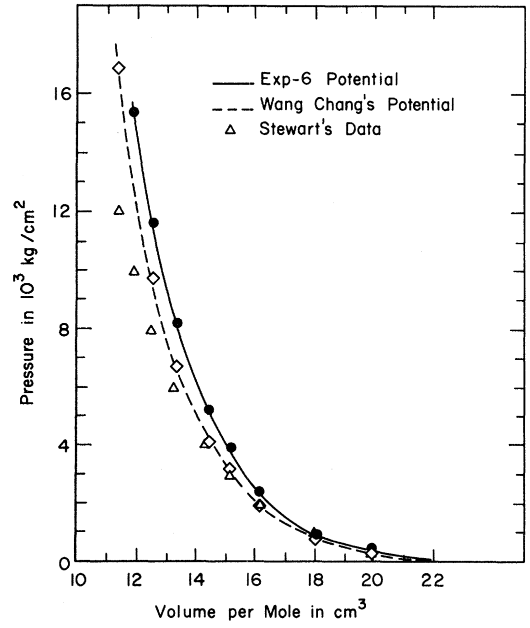

FIG. 2. Pressure in 10^3 kg/cm^2 vs volume per mole in cm^3.

$$E_{k,1}=\sum\nolimits_i\langle P_i\rangle,\quad E_2=\tfrac{1}{2},\sum_{i,j}\frac{\langle V_{ij}f_{ij}^2\rangle}{\langle f_{ij}^2\rangle},$$

$$E_3=\tfrac{1}{2},\sum_{i,j,k}\left(\frac{\langle V_{ij}f_{ij}^2f_{ik}^2f_{jk}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{jk}^2\rangle}-\frac{\langle V_{ij}f_{ij}^2\rangle}{\langle f_{ij}^2\rangle}\right), \tag{A1}$$

where $E_{k,1}$ is the kinetic-energy contribution to the ground-state energy and the expression is exact. The sum of the terms E_2, the lattice sum of all the two-center integrals, E_3, the lattice sum of all the three-center integrals, etc., gives the contribution due to the potential energy.

Regarding the cluster expansion as given by Eq. (A1), it would seem that there is really no physical parameter to indicate the orders of magnitude of the successive terms $E_2, E_3, \cdots$. However, in the appendix, we shall develop a relationship between the orders of magnitude of the terms $E_2, E_3, \cdots$, etc., through a parameter defined by

$$\eta=\langle f^2\rangle-1,$$

which is proportional to the ratio Γ/Ω. The validity of the truncated cluster expansion is then in part dependent on the order of magnitude of η.

Before proceeding to the discussion, we shall write down the sum of all the four-center integrals

$$E_4=\tfrac{1}{2}\sum_{i,j,k}\left(\frac{\langle V_{ij}f_{ij}^2f_{ik}^2f_{il}^2f_{jk}^2f_{jl}^2f_{kl}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{il}^2f_{jk}^2f_{jl}^2f_{kl}^2\rangle}+\frac{\langle V_{ij}f_{ij}^2\rangle}{\langle f_{ij}^2\rangle}-\frac{\langle V_{ij}f_{ij}^2f_{ik}^2f_{jk}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{jk}^2\rangle}-\frac{\langle V_{ij}f_{ij}^2f_{il}^2f_{jl}^2\rangle}{\langle f_{ij}^2f_{il}^2f_{jl}^2\rangle}\right). \tag{A2}$$

Since it is expected that in the variational calculation $f^2(r)\sim 1$ over most of the space characterized by the localization of the particles, we shall thus examine the expansion of the terms E_3, E_4, etc., in terms of δ, where

$$f^2=1+\delta,$$

hence

$$\eta=\langle f^2\rangle-1=\langle\delta\rangle.$$

Let us consider the following term:

$$\langle W_{ij}f_{ik}^2f_{jk}^2\rangle.$$

By substituting

$$f_{ik}^2=1+\delta_{ik},\quad f_{jk}^2=1+\delta_{jk},$$

we have

$$\begin{aligned}W_{ij}f_{ik}^2f_{jk}^2&=W_{ij}(1+\delta_{ik})(1+\delta_{jk})\\&=W_{ij}[1+(\delta_{ik}+\delta_{jk})+\delta_{ik}\delta_{jk}]\end{aligned}$$

and

$$\langle W_{ij}f_{ik}^2f_{jk}^2\rangle=\langle W_{ij}\rangle\left(1+\frac{\langle W_{ij}(\delta_{ik}+\delta_{jk})\rangle}{\langle W_{ij}\rangle}+\frac{\langle W_{ij}\delta_{ik}\delta_{jk}\rangle}{\langle W_{ij}\rangle}\right).$$

Hence,

$$\langle V_{ij}f_{ij}^2f_{ij}^2f_{jk}^2\rangle=\langle V_{ij}f_{ij}^2\rangle\left(1+\frac{\langle V_{ij}f_{ij}^2(\delta_{ij}+\delta_{jk})\rangle}{\langle V_{ij}f_{ij}^2\rangle}+\frac{\langle V_{ij}f_{ij}^2\delta_{ik}\delta_{jk}\rangle}{\langle V_{ij}f_{ij}^2\rangle}\right)$$

and

$$\langle f_{ij}^2f_{ik}^2f_{jk}^2\rangle^{-1}=\langle f_{ij}^2\rangle^{-1}\left[1-\frac{\langle f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle f_{ij}^2\rangle}-\frac{\langle f_{ij}^2\delta_{ik}\delta_{jk}\rangle}{\langle f_{ij}^2\rangle}+\left(\frac{\langle f_{ij}^2(\delta_{ik}+\delta_{ik}+\delta_{jk})\rangle}{\langle f_{ij}^2\rangle}\right)^2+\cdots\right]$$

to the second order in δ.

Thus

$$\frac{\langle V_{ij}f_{ij}^2f_{ik}^2f_{ik}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{jk}^2\rangle}=\langle V_{ij}f_{ij}^2\rangle\Big/\langle f_{ij}^2\rangle\left[1+\left(\frac{\langle V_{ij}f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle V_{ij}f_{ij}^2\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle f_{ij}^2\rangle}\right)+\left(\frac{\langle V_{ij}f_{ij}^2\delta_{ik}\delta_{jk}\rangle}{\langle V_{ij}f_{ij}^2\rangle}-\frac{\langle f_{ij}^2\delta_{ik}\delta_{jk}\rangle}{\langle V_{ij}f_{ij}^2\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle f_{ij}^2\rangle}\right)+\cdots\right] \tag{A3}$$

to the second order in δ.

A typical term in E_3 is then expressed as

$$\begin{aligned}\frac{\langle V_{ij}f_{ij}^2f_{ik}^2f_{jk}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{jk}^2\rangle}-\frac{\langle V_{ij}f_{ij}^2\rangle}{\langle f_{ij}^2\rangle}=\langle V_{ij}f_{ij}^2\rangle\Big/\langle f_{ij}^2\rangle\Bigg[&\left(\frac{\langle V_{ij}f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle V_{ij}f_{ij}^2\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle f_{ij}^2\rangle}\right)\\&+\left(\frac{\langle V_{ij}f_{ij}^2\delta_{ik}\delta_{jk}\rangle}{\langle V_{ij}f_{ij}^2\rangle}-\frac{\langle f_{ij}^2\delta_{ik}\delta_{jk}\rangle}{\langle f_{ij}^2\rangle}\right)-\langle f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle\Big/\langle f_{ij}^2\rangle\left(\frac{\langle V_{ij}f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle f_{ij}^2V_{ij}\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}+\delta_{jk})\rangle}{\langle f_{ij}^2\rangle}\right)+\cdots\Bigg].\end{aligned} \tag{A4}$$

Similarly, we have

$$\begin{aligned}W_{ij}f_{ik}^2f_{il}^2f_{jk}^2f_{jl}^2f_{kl}^2=W_{ij}[1&+(\delta_{ik}+\delta_{jk}+\delta_{il}+\delta_{kl}+\delta_{kl})+(\delta_{ik}\delta_{jk}+\delta_{ik}\delta_{il}+\delta_{ik}\delta_{jl}+\delta_{ik}\delta_{kl}+\delta_{jk}\delta_{il}+\delta_{jk}\delta_{jl}\\&+\delta_{jk}\delta_{k}+\delta_{il}\delta_{jl}+\delta_{il}\delta_{kl}+\delta_{jl}\delta_{kl})+\cdots]\end{aligned}$$

and

$$\frac{\langle W_{ij}f_{ik}^2f_{il}^2f_{jk}^2f_{jl}^2f_{kl}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{il}^2f_{jk}^2f_{jl}^2f_{k}^2\rangle}=\langle W_{ij}\rangle\Big/\langle f_{ij}^2\rangle\left[1+\left(\frac{\langle W_{ij}(\delta_{ik}+\cdots)\rangle}{\langle W_{ij}\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}+\cdots)\rangle}{\langle f_{ij}^2\rangle}\right)\right.$$
$$\left.+\left(\frac{\langle W_{ij}(\delta_{ik}\delta_{jk}+\cdots)\rangle}{\langle W_{ij}\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}\delta_{jk}+\cdots)\rangle}{\langle f_{ij}^2\rangle}\right)-\frac{\langle f_{ij}^2(\delta_{ik}+\cdots)\rangle}{\langle f_{ij}^2\rangle}\left(\frac{\langle W_{ij}(\delta_{ik}+\cdots)\rangle}{\langle W_{ij}\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}+\cdots)\rangle}{\langle f_{ik}^2\rangle}\right)+\cdots\right]$$

to the second order in δ.

A typical term in E_4 is then given by

$$\frac{\langle V_{ij}f_{ij}^2\rangle}{\langle f_{ij}^2\rangle}+\frac{\langle V_{ij}f_{ij}^2f_{ik}^2f_{il}^2f_{jk}^2f_{jl}^2f_{kl}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{il}^2f_{jk}^2f_{jl}^2f_{k}^2\rangle}-\frac{\langle V_{ij}f_{ij}^2f_{ik}^2f_{jk}^2\rangle}{\langle f_{ij}^2f_{ik}^2f_{jk}^2\rangle}-\frac{\langle V_{ij}f_{ij}^2f_{il}^2f_{jl}^2\rangle}{\langle f_{ij}^2f_{il}^2f_{jl}^2\rangle}$$
$$=\langle V_{ij}f_{ij}^2\rangle\Big/\langle f_{ij}^2\rangle\left[\left(\frac{\langle W_{ij}(\delta_{ik}\delta_{jk}+\cdots)\rangle}{\langle W_{ij}\rangle}-\frac{\langle f_{ij}^2(\delta_{ik}\delta_{jk}+\cdots)\rangle}{\langle f_{ij}^2\rangle}\right)+\cdots\right]. \qquad \text{(A5)}$$

Now it is clear that as far as δ is concerned, E_2 is of zeroth order in δ, E_3 of the first order, E_4 of the second order, and so on. If one writes

$$E_2=\textstyle\sum_J n_J\epsilon_J^2\,,\quad \epsilon_J^2=\langle V_{IJ}f_{IJ}^2\rangle/\langle f_{IJ}^2\rangle\,, \qquad \text{(A6)}$$

where J denotes the positions of the lattice sites with respect to a definite site chosen as origin, then one may also write

$$E_3=\textstyle\sum_J n_J\epsilon_J^3\,,$$
$$E_4=\textstyle\sum_J n_J\epsilon_J^4\,,\quad \text{etc.}, \qquad \text{(A7)}$$

where

$$\epsilon_J^3=\epsilon_J^2\sum_k n_k\left[\left(\frac{\langle V_{IJ}f_{IJ}^2(\delta_{Ik}+\delta_{Jk})\rangle}{\langle V_{IJ}f_{IJ}^2\rangle}-\frac{\langle f_{IJ}^2(\delta_{Ik}+\delta_{Jk})\rangle}{\langle f_{IJ}^2\rangle}\right)+\cdots\right], \qquad \text{(A8)}$$

$$\epsilon_J^4=\epsilon_J^2\sum_{k,1}\left[\left(\frac{\langle V_{IJ}f_{IJ}^2(\delta_{Ik}\delta_{Jk}+\cdots)\rangle}{\langle V_{IJ}f_{IJ}^2\rangle}-\frac{\langle f_{IJ}^2(\delta_{Ik}\delta_{Jk}+\cdots)\rangle}{\langle f_{IJ}^2\rangle}\right)+\cdots\right]. \qquad \text{(A9)}$$

Thus a relationship is obtained for each pair of (E_2, E_3), (E_2, E_4), etc.

It is important to notice that the lattice sums appearing in Eq. (A7) need not be carried too far since the correlation function $f(r)$ [hence $\delta(r)$] tends to 1 (to zero) for r beyond a few nearest-neighbor distances (not more than the fourth in most cases).

Therefore the leading term in the ratio $\epsilon_J^3/\epsilon_J^2$ is of the order $\langle\delta\rangle$, and that in the ratio $\epsilon_J^4/\epsilon_J^2$ is of the order $\langle\delta^2\rangle$, and so on. If $\langle\delta\rangle$ is sufficiently small in the region characterized by the localization factor A, we may use it to determine the orders of magnitude of the successive terms in the expansion. We did not explore the application of this formal method to our computations to any great extent, because of the availability of a program to compute E_3 numerically.

APPENDIX B

Within the subspace of a single J, the rotational quantum operator, we have the following operator equivalence[28]:

$$P_2(\cos\theta)\simeq p_J[\tfrac{3}{2}J_z^2-\tfrac{1}{2}J(J+1)]\,,$$
$$\cos\theta\,\sin\theta\, e^{\pm i\phi}\simeq\tfrac{1}{2}\,p_J(J_\pm+J_\pm J_z)\,,$$
$$\sin^2\theta\; e^{\pm 2i\phi}\simeq p_J J_\pm J_\pm\,,\quad J_\pm=J_x\pm iJ_y\,.$$

It is easy to show that, for $J=0$,

$$p_J=0$$

and, for $J=1$,

$$p_J=-\tfrac{2}{5}\,.$$

The orientation-dependent part of Wang Chang's potential is then written as

$$\tilde{v}=\tfrac{2}{3}\beta\{p_{J1}[\tfrac{3}{2}J_{z1}^2-\tfrac{1}{2}J_1(J_1+1)]$$
$$+p_{J2}[\tfrac{3}{2}J_{z2}^2-\tfrac{1}{2}J_2(J_2+1)]\}\,.$$

Hence, for a para-para pair

$$\tilde{v}=0;$$

for an ortho-para pair

$$\tilde{v}=-\tfrac{2}{15}\beta(3J_{z1}^2-2);$$

and for an ortho-ortho pair

$$\tilde{v}=-\tfrac{2}{15}\beta[(3J_{z1}^2-2)+(3J_{z2}^2-2)]\,.$$

The results of averaging are discussed in Sec. IV.

---

*Supported by the Advanced Research Projects Agency, Materials Science Center, Cornell.

†In partial fulfillment of the Ph. D. requirement, Cornel University, 1967. Article issued as Cornell MSC Report No. 1057 (1967).

[1] J. A. Krumhansl and S. Y. Wu, Phys. Letters 28A,

263 (1968).

[2]J. W. Stewart, J. Phys. Chem. Solids 1, 146 (1956).

[3]J. deBoer and B. S. Blaisse, Physica 14, 149 (1948).

[4]K. F. Herzfeld and M. Goeppert-Mayer, Phys. Rev. 46, 995 (1934).

[5]J. deBoer, in *Progress in Low Temperature Physics II* (North-Holland, Amsterdam, 1957).

[6]F. W. DeWette and B. R. A. Nijboer, Phys. Letters 18, 19 (1965).

[7]N. Bernades, Phys. Rev. 112, 1534 (1958).

[8]N. Bernades and H. Primakoff, Phys. Rev. 119, 968 (1960).

[9]R. P. Hurst and J. M. H. Levelt, J. Chem. Phys. 34, 54 (1961).

[10]J. M. H. Levelt and R. P. Hurst, J. Chem. Phys. 32, 96 (1960).

[11]E. M. Saunders, Phys. Rev. 126, 1724 (1962).

[12]L. H. Nosanow, Phys. Rev. Letters 13, 270 (1964).

[13]W. J. Mullin, Phys. Rev. 134, A1249 (1964).

[14]J. P. Hansen and D. Levesque, Phys. Rev. 165, 293 (1968).

[15]K. A. Brueckner and T. Frohberg, Progr. Theoret. Phys. (Kyoto), Extra Suppl., 383 (1965).

[16]W. E. Massey and C. W. Woo, Phys. Rev. 169, 241 (1968).

[17]L. Pauling, Phys. Rev. 36, 430 (1930).

[18]A. Brooks Harris, Phys. Rev. B 1, 1881 (1970).

[19]D. J. Thouless, *The Quantum Mechanics of Many Body Systems* (Academic, New York, 1961).

[20]L. H. Nosanow and W. J. Mullin, Phys. Rev. Letters 14, 133 (1965).

[21]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), pp. 1083–1092.

[22]N. G. Van Kampen, Physica 27, 783 (1961).

[23]J. H. Hetherington, W. J. Mullin, and L. H. Nosanow, Phys. Rev. 154, 175 (1967).

[24]Hard-core models have been used for high-density quantum gas calculations [see R. K. Cole, Jr., Phys. Rev. 155, 114 (1967)].

[25]F. Iwamoto and M. Yamada, Progr. Theoret. Phys. (Kyoto) 17, 543 (1957).

[26]A. M. Michels, W. deGraaf, and C. A. ten Seldam, Physica 26, 393 (1960).

[27]I. B. Srivastava and A. K. Barua, Indian J. Phys. 35, 320 (1961).

[28]K. Tomita, Proc. Phys. Soc. (London) A68, 214 (1955)

[29]T. Nakamura, Progr. Theoret. Phys. (Kyoto) 14, 135 (1955).

[30]R. L. Mills and A. F. Schuch, Phys. Rev. Letters 15, 722 (1965).

PHYSICAL REVIEW B VOLUME 5, NUMBER 10 15 MAY 1972

Equation of State for Solid Hydrogen*

Thomas Alexander Bruce

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 24 May 1971)

An equation of state for solid hydrogen is obtained from variational calculations for pressures up to 112 kbar. The Lennard-Jones potential is assumed and a brief investigation of the Buckingham exp-6 potential is also made. It is suggested that for high densities, quantum crystals may become harmonic and that Monte Carlo variational calculations for these high-density regions may not be necessary.

I. INTRODUCTION

During the last several years there has been a growing interest in the properties of solid hydrogen.[1,2]

The properties of the predicted high-density metallic phase have been discussed in detail by Ashcroft.[2] To predict the existence of this phase requires an accurate equation of state for both the molecular and metallic phases. This paper will be concerned with the first of these phases; we attempt a first refinement of the equation of state for the molecular phase which should ultimately enable a more precise prediction of the transition pressure. We must at once point out that there is considerable uncertainty in the intermolecular potential and thus any highly refined calculations are not very valuable at this time. Indeed the only useful purpose such calculations can serve at the present time is to remove some of the uncertainty in the potential. It is for this reason that we have limited our Monte Carlo calculations to fairly small numbers of particles and intermediate-length runs.

Krumhansl and Wu[3] have used the cluster-expansion method to do a variational calculation of the equation of state of molecular hydrogen in the 0–20-kbar range. However, Monte Carlo calculations are more reliable because the trial wave functions that may be used are not as limited as those which can be used in the cluster method, and the convergence of the cluster expansion is sometimes uncertain.

In the present study, a trial wave function is chosen, and the integrals necessary to calculate the ground-state energy are evaluated by a Monte