PHYSICAL REVIEW VOLUME 146, NUMBER 1 3 JUNE 1966

Theory of Quantum Crystals*

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(Received 5 January 1966)

The ground-state properties of quantum crystals (crystals of the isotopes of He and H_2) are studied by means of a variational calculation using cluster-expansion techniques. The cluster expansion for such a crystal is derived in a very general form and applied to a trial wave function that is assumed to be a product of one- and two-particle functions. The energy minimum is calculated by first truncating the expansion to retain only the one-particle and part of the two-particle term. In this form the calculation can be viewed as a Hartree calculation in which the true interaction is replaced by an appropriate effective interaction. The validity of the truncation is assessed by computing all of the leading correction terms. Calculations of the ground-state energy, pressure, and compressibility for the bcc and hcp structures of both ^{3}He and ^{4}He are presented as a function of molar volume. Although the calculated energies are too high, they represent a considerable improvement over previous work and the calculated pressures and compressibilities agree with experiment to about 10%. Tables of the variational parameters which give the minimum energy are presented. A discussion of the accuracy of the approximations used to treat the correlations in the system is given.

I. INTRODUCTION

CRYSTALS of the various isotopes of helium and molecular hydrogen cannot be treated by the classical theory of lattice dynamics.[1] This difficulty is due to the small mass of these substances and the weakness of the attractive part of their van der Waals interaction. Therefore, the quantum-mechanical zero-point kinetic energy in such crystals is comparable to their potential energy, and the root-mean-square deviation of a particle from its lattice site is not small compared to the nearest-neighbor distance. The problem is not simply that the anharmonic terms are large; it is that the harmonic approximation itself breaks down. This result has been demonstrated by de Wette and Nijboer[2] who, in their calculations of the phonon spectrum for solids with potentials and at densities appropriate to crystalline helium and hydrogen, found that the phonon frequencies were imaginary at every point in the first Brillouin zone. Since the classical theory of lattice dynamics cannot be used to treat these crystals, mainly because of their relatively large zero-point motion, we feel that it is appropriate to call them *quantum crystals*.

There were several early attempts to study quantum crystals and, in particular, crystalline helium.[3] In the main, they were variational calculations of the ground-state energy using Hartree trial wave functions, i.e., products of single-particle wave functions. The energies calculated in this work were in fair agreement with experiment. However, many numerical approximations were used, so that it was not clear that an upper bound to the ground-state energy had been obtained. This question was settled by Nosanow and Shaw,[4] who did this variational calculation exactly with the one assumption that the single-particle wave functions were spherically symmetric. They found energies which were of the order of +10 cal/mole for ^{4}He and +30 cal/mole for ^{3}He, results which are to be compared with experimental values of −12 cal/mole and approximately −1 cal/mole, respectively. In addition, the Hartree calculations yielded poor values of the pressure and compressibility.[5] These results showed that a trial wave function which was a product of single-particle functions was inadequate for calculating the properties of crystalline helium.[6,7]

Since it is well known that the Hartree approximation does not include the effect of correlations properly, it is clear that this deficiency is the main reason for the poor results obtained by Nosanow and Shaw. In fact, the importance of correlations had been realized before their work was done. The first attempt to include them was that of Bernardes and Primakoff,[8] who made a partly variational, partly phenomenological calculation of the ground-state energy of crystalline

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* Work partially supported by the U. S. Air Force Office of Scientific Research under grant number AF-AFOSR 840-65.

[1] See e.g., M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1954).

[2] F. W. de Wette and B. R. A. Nijboer, Phys. Letters **18**, 19 (1965).

[3] T. Nagamiya, Proc. Phys. Math. Soc. Japan **22**, 492 (1940); M. Toda, *ibid.* **22**, 503 (1940); D. J. Hooton, Phil. Mag. **46**, 422 (1955); **46**, 433 (1955); **46**, 485 (1955); **46**, 701 (1955); R. P. Hurst and J. M. H. Levelt, J. Chem. Phys. **34**, 54 (1961).

[4] L. H. Nosanow and G. L. Shaw, Phys. Rev. **119**, 968 (1962).

[5] L. H. Nosanow, *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. V. Edwards, F. J. Milford, and M. Yaquab (Plenum Press, Inc., New York, 1965).

[6] The possibility that the assumption of spherical symmetry could be mainly responsible for these high energy values can be ruled out by a simple physical argument. Because the potential has a hard core, the self-consistency of the Hartree calculation requires each particle to be confined to its own Wigner-Seitz unit cell. Since these cells are approximately spherical for the lattices in question, the assumption of a spherically symmetric single-particle wave function should only lead to errors of the order of 10%. In fact, Brueckner and Rosenwald (Ref. 7) have recently calculated the ground-state energy of bcc ^{3}He taking the lattice symmetry into account and found an energy lowering of only 10%.

[7] K. A. Brueckner and D. Rosenwald, (private communication). See also D. Rosenwald, Ph.D. thesis, University of California, San Diego, California, 1965 (unpublished).

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

^{3}He. They introduced the effect of correlations by replacing the true interaction by a one-parameter effective interaction. This parameter was determined for ^{3}He by fitting the ground-state energy of crystalline ^{4}He. Unfortunately, they did not make a sufficiently good guess of the effective interaction, and their phenomenological procedure led to a considerable underestimate of the kinetic energy. Thus they found a rather large root-mean-square deviation and an exchange integral which was three orders of magnitude too large. Nevertheless, their calculation pointed the way for future work.

More recently Saunders[9] has attempted to include the effects of correlations by deriving a differential equation for the correlation function. Unfortunately, it is our opinion that this work has many faults. In particular, the derivation is not systematic, the equation for the single-particle function can be shown to diverge,[10] and the equation for the correlation function is solved incorrectly.[11] Although Saunders obtained quite reasonable results for the thermodynamic properties and the exchange integral, in view of the deficiencies in his work it is our opinion that the agreement with experiment can only be considered fortuitous. Saunder's approach has recently been analyzed thoroughly by Garwin and Landesman,[11] who have made some improvements in it. However, they find that his approach breaks down completely for ^{4}He. In our opinion, this is a most serious difficulty since any theory which describes crystalline ^{3}He should describe crystalline ^{4}He equally as well.

Recently, Bruckner and Frohberg[12] have proposed a new equation for the correlation function. Their derivation is based on a modification of the approach introduced by the author.[13] It is not yet clear whether their approach will be successful.

The present work is devoted to a study of the ground-state properties of quantum crystals. We give a full exposition of our approach which is a variational calculation utilizing cluster-expansion technqiues.[14] Preliminary accounts of some aspects of this work have already been published.[13,5,15] We begin in Sec. II by formulating the problem. In particular, we give a discussion of the physical reasons for choosing our trial wave function and for the application of the cluster expansion to this problem. In Sec. III, we derive the cluster expansion in a very general form. In Sec. IV this expansion is specialized to treat our particular choice of a trial wave function, and explicit expressions for the terms we need for our calculations are given. In Sec. V, we give our approximation scheme for calculating the ground-state energy and we show how the calculation is done. We point out that our approach corresponds to a Hartree calculation with an appropriate effective interaction. In addition, the leading correction terms are discussed and shown to be small. In Sec. VI, the results of our systematic calculations of the ground-state energy, pressure and compressibility are presented. The calculations are given for both ^{3}He and ^{4}He for both the hcp and bcc structures. In addition, we present tables of the variational parameters, as we feel that they might be useful for future calculations. In Sec. VII, we discuss the validity of the results and possible ways of improving and extending them. In particular, we give a critique of our treatment of the correlation function. The numerical details of our calculation are discussed in the Appendix.

II. FORMULATION

We consider a system of N particles of mass m with the Hamiltonian

$$H=-(\hbar^2/2m)\sum_{i=1}^{N}\nabla_i^2+\sum\sum_{1\leq i<j\leq N} v_{ij}, \qquad (2.1)$$

where $v_{ij}=v(r_{ij})$ is the pair potential, and $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$, where $\mathbf{r}_i$ is the coordinate of the ith particle. In this paper, we shall use the Lennard-Jones form of the potential

$$v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6], \qquad (2.2)$$

which has a minimum at $r_{\min}=2^{1/6}\sigma$, where $v(r_{\min})=-\epsilon$. The two parameters in this potential are usually determined phenomenologically,[16] and for helium, $\epsilon=10.22$°K and $\sigma=2.556$ Å. We believe that this potential is sufficiently accurate for the calculations presented in this paper.

In order to motivate our formulation of this problem, we shall first analyze the assets and deficiencies of the Hartree approximation. In our opinion, the main asset of this approach is that it does yield a self-consistent solution which describes a crystal. Clearly, the existence of a crystalline phase involves correlations in the motion of an arbitrarily large number of particles. Thus, we can say that the Hartree approximation does indeed take into account the effects of what we may call "structural" correlations. On the contrary, the main deficit of the Hartree calculation is that it does not treat properly what we may call "dynamic" correlations. Roughly speaking, there are two kinds of "dynamic" correlations, those of short range which involve the motion of a small number of neighboring particles and those of long range which involve the

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

[10] W. J. Mullin, Ph.D. thesis, Washington University, 1965 (unpublished).

[11] R. L. Garwin and A. Landesman, Physics **2**, 107 (1965).

[12] K. A. Brueckner and J. Frohberg, paper presented at Summer Institute for Chemistry and Physics, University of California, San Diego, 1965 (unpublished).

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

[14] A similar approach has been used for crystalline Ne. See W. J. Mullin, Phys. Rev. **134**, A1249 (1964) and also Ref. 10.

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

[16] See, e.g., J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1110.

motion of a large number of the particles in the crystal. The present work is primarily concerned with the short-range dynamic correlations; the long-range dynamic correlations, which lead to the low-lying excitations in the crystal, have been discussed elsewhere.[17]

The short-range "dynamic" correlations have a large effect on the total energy as they can serve to lower *both* the kinetic and potential energies relative to the Hartree result. They can lower the kinetic energy because they serve to increase the radius of the effective well in which each particle is located. They can lead to a lower potential energy by allowing a pair of particles to have a larger probability of being at a relative separation $\simeq r_{\min}$. It should be emphasized here that in quantum crystals the nearest-neighbor distance R can be as much as 50% larger than $r_{\min}$. Thus, the two-particle probability distribution function is likely to have two "bumps"—a large one at R and a smaller one at $r_{\min}$. Of course, in a "classical" crystal, these "bumps" coalesce.

We also wish to discuss the effect that the proper symmetrization of the wave function would have on the Hartree results. To obtain a finite energy with the Hartree calculation, each iteration of the spherically symmetric single-particle wave function $\phi(r)$ must satisfy the condition

$$\phi(r)=0, \quad \text{for} \quad r\geq R/2. \tag{2.3}$$

Thus, the single-particle wave functions centered on neighboring lattice sites can never overlap and there is no exchange within the Hartree approximation. Therefore, a Hartree-Fock calculation will always yield the same result as a Hartree calculation for a crystal. However, if "dynamic" correlations were included, there would be overlap and it would be necessary to use a properly symmetrized trial wave function.

In this paper we attempt to improve upon the Hartree calculation by using a trial wave function of the form

$$\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N)=\prod_{i=1}^{N}\phi(|\mathbf{r}_i-\mathbf{R}_i|)\prod_{1\leq j<k\leq N}\prod f(r_{jk}). \tag{2.4}$$

Clearly, (2.4) is not properly symmetrized; however, it gives the dominant contribution to the energy since the exchange effects turn out to be small. The modifications to (2.4) that are necessary to include exchange are given in the next section. The functions $\phi(r)$ and $f(r)$ are to be determined to minimize the energy. This type of trial function has been used by many other workers.[18] In particular, it seems to yield excellent results when used in Monte-Carlo calculations.

The function $\prod_i \phi(|\mathbf{r}_i-\mathbf{R}_i|)$ in (2.4) is just a Hartree trial wave function. Thus, it will automatically take the "structural" correlations into account so long as the particles are very nearly localized. The general boundary conditions on $\phi(r)$ are

$$\lim_{r\to 0}\phi(r)=\text{finite}, \tag{2.5a}$$

$$\lim_{r\to\infty}\phi(r)=0. \tag{2.5b}$$

If $\phi(r)\neq 0$ for $r>R/2$, it is possible for neighboring particles to exchange their positions and the effects of symmetrization are nontrivial. It will turn out that useful analytic form for $\phi(r)$ is

$$\phi(r)=\exp(-Ar^2/2); \tag{2.6}$$

and A will turn out to be a convenient variational parameter.

The function $\prod_{i<j} f(r_{ij})$ is introduced to include the effects of the short-range "dynamic" correlations. Of course, this particular "ansatz" can only hope to treat two-body correlations with any kind of accuracy. *A priori*, the hope is that this approximation will be sufficient because, having already taken the "structural" correlations into account, the main effect of the "dynamic" correlations will be contained in the two-body terms. The general boundary conditions on $f(r)$ are

$$\lim_{r\to 0} f(r)=0, \tag{2.7a}$$

$$\lim_{r\to\infty} f(r)=\text{constant}. \tag{2.7b}$$

In fact, on physical grounds, we expect that

$$f(r)\simeq\exp(-\text{const}/r^5), \quad \text{for} \quad r\ll\sigma \tag{2.8a}$$

$$\simeq\text{const}, \quad \text{for} \quad r\gtrsim R. \tag{2.8b}$$

Clearly, (2.7a) and (2.8a) express the fact that the large repulsion in $v(r)$ makes it unlikely for two particles to be close together. It is possible to derive (2.8a) by solving the Schrödinger equation for two particles that are so close that only the repulsive term in $v(r)$ is important. Conditions (2.7b) and (2.8b) express the fact that particles on well-separated lattice sites will be uncorrelated. Further, we expect that

$$f(r_{\min})\geq f(\infty), \tag{2.9}$$

i.e., that two particles will not have a larger probability of being far apart than of being at $r_{\min}$. An analytic form which gives this general behavior for $f(r)$ is

$$f(r)=\exp[-K\eta(r)], \tag{2.10}$$

where K is a convenient variational parameter and $\eta(r)=(\sigma/r)^{12}-(\sigma/r)^6$. Clearly (2.10) does not behave like (2.8a) when $r\ll\sigma$; however, the most important region is $r\simeq\sigma$, where (2.8a) certainly does not hold.

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[17] W. Brenig, Z. Physik **171**, 60 (1963); D. R. Fredkin and N. R. Werthamer, Phys. Rev. **138**, A1527 (1965); L. H. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965).

[18] See, e.g., R. Jastrow, Phys. Rev. **98**, 1479 (1955); F. Wu and E. Feenberg, *ibid.* **122**, 739 (1961); W. L. McMillan, *ibid.* **138**, A442 (1965); D. Levesque, D. Schiff, T. Khiet, and L. Verlet (unpublished report).

Since there is no simple analytic form for $f(r)$ that has *all* of the correct properties, we feel that (2.10) is the best compromise.

The general program of this paper is to assume that $f(r)$ is given by (2.10) and then obtain a differential equation for $\phi(r)$ by minimizing the energy. Even with the assumption of an analytic form for $f(r)$, it is not possible to calculate the energy exactly. However, with our choice of $\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N)$, this problem is very much like that of evaluating the partition function of a classical gas in an external field. Thus, it is natural to try to make a cluster expansion[19] of the ground-state energy. In the classical case, this expansion converges when the density is sufficiently small; i.e., when there is a small probability for large numbers of particles to be close together. In our case, one might also expect the cluster expansion to converge because the crystal structure prevents large numbers of particles from being close together. This argument says nothing about the rate of convergence. In fact, this property depends on the precise nature of $f(r)$ and, in practice, can only be tested numerically.

In summary, then, we first choose the form (2.10) for $f(r)$; i.e., we choose a particular value of the parameter K. Then we make the cluster expansion and vary the energy to obtain the equation for $\phi(r)$. This equation is then solved approximately to obtain the ground-state energy E_0 as a function of K. Using that value of K which minimizes E_0, we calculate all of the leading correction terms to E_0. If these turn out to be small and do not significantly alter the position of the minimum, we shall conclude that we have obtained a satisfactory approximation to an upper bound of the ground-state energy.

III. GENERAL CLUSTER EXPANSION

In this section we derive the general cluster expansion of the ground-state energy E_0 by means of a rather straightforward generalization of van Kampen's method.[20] We wish to emphasize that this derivation does *not* depend on the special trial wave function given by (2.4). The special cluster expansion for this wave function is given in the next section.

To make the cluster expansion of

$$E_0=(\Psi,H\Psi)/(\Psi,\Psi)\,, \tag{3.1}$$

it is convenient to introduce

$$M(\gamma)=(\Psi,(\exp\gamma H)\Psi)\,, \tag{3.2}$$

so that

$$E_0=\lim_{\gamma\to 0}\frac{\partial}{\partial\gamma}\ln M(\gamma)\,. \tag{3.3}$$

The idea of van Kampen's approach is to systematically multiply and divide $M(\gamma)$ by many equal factors and group the resultant expression into an identity of the form

$$M(\gamma)=\prod_{n=1}^{N} M_n(\gamma)\,. \tag{3.4}$$

The grouping is done in such a way that the only sizable contribution to $M_n(\gamma)$ comes from those regions of phase space where n particles are close together; i.e., where they form a cluster. Since we are dealing with a crystal, it is important to note that there are many different spatial arrangements which contain n particles. Clearly (3.4) leads to an expression for the energy of the form

$$E_0=\sum_{n=1}^{N} E_{0n}\,. \tag{3.5}$$

We wish to emphasize that such an approach is *a priori* rather arbitrary. It can only be judged *a posteriori* by showing that the resulting series is convergent. In the case of the classical imperfect gas, this result is obtained by isolating a small parameter—the density. In our case, there is really no small parameter; however, for our special trial function the convergence will depend, in part, on the deviation of $f(r)$ from the constant value it has when r is large.

To make the derivation, we introduce the wave function $\Psi_n(\{n\})$ and the Hamiltonian $H_n(\{n\})$, which depend on the coordinates $\{n\}$ of a subset of n particles localized about the lattice sites $\mathbf{R}_1,\ \cdots,\ \mathbf{R}_n$. For the trial function (2.4),

$$\Psi_1(\{n\})=\phi(|\mathbf{r}_1-\mathbf{R}_1|) \tag{3.6a}$$

and

$$\Psi_n(\{n\})=\prod_{i=1}^{n}\phi(|\mathbf{r}_i-\mathbf{R}_i|)\prod\prod_{1\leq j<k\leq N} f(r_{jk})\,, \tag{3.6b}$$

for $n\geqslant 2$. To take the effects of symmetry into account we need a more general trial function. In this case, $\Psi_1(\{n\})$ is given by (3.6a) and the spatial part of $\Psi_2(\{2\})$ is given by

$$[\phi(|\mathbf{r}_1-\mathbf{R}_1|)\phi(|\mathbf{r}_2-\mathbf{R}_2|) \pm\phi(|\mathbf{r}_1-\mathbf{R}_2|)\phi(|\mathbf{r}_2-\mathbf{R}_1|)]f(r_{12})\,. \tag{3.6c}$$

In (3.6c), the plus sign is chosen for ^{4}He, whereas for ^{3}He, the plus sign is chosen when the two particles are in a singlet spin state and the minus sign is chosen when they are in a triplet state. In this paper, we shall not consider the effects of symmetry on $\Psi_n(\{n\})$ for $n\geqslant 3$. For the various Hamiltonians, we take

$$H_n(\{n\})=-(\hbar^2/2m)\sum_{i=1}^{n}\nabla_i^2+\sum\sum_{1\leq i<j\leq n} v_{ij}\,. \tag{3.7}$$

It is natural to choose

$$M_1(\gamma)=\prod_{i=1}^{N}(\Psi_1(\mathbf{r}_i),\,\exp[\gamma H_1(\mathbf{r}_i)]\Psi_1(\mathbf{r}_i))\,; \tag{3.8}$$

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[19] See, e.g., J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, (John Wiley & Sons, Inc., New York, 1940), p. 277.

[20] N. G. van Kampen, Physica **27**, 783 (1961).

i.e., $M_1(\gamma)$, the first approximation to $M(\gamma)$, is a Hartree-like product. The next term is

$$M_2(\gamma)=\prod_{1\leq i<j\leq N}\prod\{(\Psi_2(\mathbf{r}_i,\mathbf{r}_j),\exp[\gamma H_2(\mathbf{r}_i,\mathbf{r}_j)]\Psi_2(\mathbf{r}_i,\mathbf{r}_j))$$
$$/(\Psi_1(\mathbf{r}_i),\exp[\gamma H_1(\mathbf{r}_i)]\Psi_1(\mathbf{r}_i))(\Psi_1(\mathbf{r}_j),\exp[\gamma H_1(\mathbf{r}_j)]\Psi_1(\mathbf{r}_j))\};\quad(3.9)$$

i.e., the contribution from all pairs in which the contribution from each pair is divided by the way it was approximated in the previous term. It is to be expected that

$$\lim_{|\mathbf{R}_i-\mathbf{R}_j|\to\infty}(\Psi_2(\mathbf{r}_i,\mathbf{r}_j),\exp[\gamma H_2(\mathbf{r}_i,\mathbf{r}_j)]\Psi_2(\mathbf{r}_i,\mathbf{r}_j))=(\Psi_1(\mathbf{r}_i),\exp[\gamma H_1(\mathbf{r}_i)]\Psi_1(\mathbf{r}_j))(\Psi_1(\mathbf{r}_j),\exp[\gamma H_1(\mathbf{r}_j)]\Psi_1(\mathbf{r}_j)),$$

so that there will be contributions to $M_2(\gamma)$ only from that part of phase space where the two particles are sufficiently close together. The expression for arbitrary n that has this property is

$$M_n(\gamma)=\prod_{1\leq i_1<i_2\cdots<i_n\leq N}\prod\cdots\prod\{(\Psi_n(\{n\}),\exp[\gamma H_n(\{n\})]\Psi_n(\{n\}))/D_n(\{n\})\},\quad(3.10)$$

where

$$D_n(\{n\})=\prod_{m=1}^{n-1}M_m(\gamma;\{n\}).\quad(3.11)$$

In (3.11), $M_m(\gamma;\{n\})$ is defined by (3.10) but for the subset $\{n\}$ of n particles instead of for all N particles; e.g.,

$$D_3(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)=\prod_{\nu=1}^{3}(\Psi_1(\mathbf{r}_\nu),\exp[\gamma H_1(\mathbf{r}_\nu)]\Psi_1(\mathbf{r}_\nu))\prod_{1\leq\mu<\nu\leq 3}\prod\{(\Psi_2(\mathbf{r}_\mu,\mathbf{r}_\nu),\exp[\gamma H_2(\mathbf{r}_\mu,\mathbf{r}_\nu)]\Psi_2(\mathbf{r}_\mu,\mathbf{r}_\nu))$$
$$/(\Psi_1(\mathbf{r}_\mu),\exp[\gamma H_1(\mathbf{r}_\mu)]\Psi_1(\mathbf{r}_\mu))(\Psi_1(\mathbf{r}_\nu),\exp[\gamma H_1(\mathbf{r}_\nu)]\Psi_1(\mathbf{r}_\nu))\}.$$

Each factor $M_n(\gamma)$ is therefore a product of $N!/n!(N-n)!$ factors, the denominator of each of which is constructed from the way the numerator of the factor was approximated in the previous $n-1$ factors of $M(\gamma)$. Therefore,

$$M_N(\gamma)=M(\gamma)/\prod_{n=1}^{N-1}M_n(\gamma_\mu\{N\})\quad(3.12)$$

and, with all of these definitions, (3.4) is an identity.

Using (3.3), we find

$$E_{01}=\sum_{i=1}^{N}C_1(i),\quad(3.13)$$

where

$$C_1(i)=(\Psi_1(\mathbf{r}_i),H_1(\mathbf{r}_i)\Psi_1(\mathbf{r}_i))/(\Psi_1(\mathbf{r}_i),\Psi_1(\mathbf{r}_i)).\quad(3.14)$$

Similarly,

$$E_{02}=\sum_{1\leq i<j\leq N}\sum C_2(i,j),\quad(3.15)$$

where

$$C_2(i,j)=(\Psi_2(\mathbf{r}_i,\mathbf{r}_j),H_2(\mathbf{r}_i,\mathbf{r}_j)\Psi_2(\mathbf{r}_i,\mathbf{r}_j))/(\Psi_2(\mathbf{r}_i,\mathbf{r}_j),\Psi_2(\mathbf{r}_i,\mathbf{r}_j))-C_1(i)-C_1(j).\quad(3.16)$$

In general,

$$E_{0n}=\sum_{\{n\}\subset N}C_n(\{n\}),\quad(3.17)$$

where

$$C_n(\{n\})=(\Psi_n(\{n\}),H_n(\{n\})\Psi_n(\{n\}))/(\Psi_n(\{n\}),\Psi_n(\{n\}))-\sum_{m=1}^{n-1}\sum_{\{m\}\subset\{n\}}C_m(\{m\}).\quad(3.18)$$

In (3.17), the sum runs over all n-particle subsets of N particles; whereas, in (3.18) the last sum runs over all m-particle subsets of the particular n-particle subset of N particles. In contrast to the behavior of the cluster expansion for a gas, $C_n(\{n\})$ depends on the lattice positions of the n particles and therefore has different values for different configurations.

IV. SPECIAL CLUSTER EXPANSION

In this section we shall apply the results of the previous section to our special trial wave function. The first term in the cluster expansion of E_0 is independent of the statistics. Thus

$$E_{01}=\sum_{i=1}^{N}\omega^{-1}\int d\mathbf{r}_i\ \phi^*(|\mathbf{r}_i-\mathbf{R}_i|)(-\hbar^2/2m)\nabla_i^2\phi(|\mathbf{r}_i-\mathbf{R}_i|), \tag{4.1}$$

where

$$\omega=\int d\mathbf{r}_i\ |\phi(|\mathbf{r}_i-\mathbf{R}_i|)|^2. \tag{4.2}$$

We may also write (4.1) as

$$E_{01}=\sum_{i=1}^{N}\langle T(\mathbf{r}_i)\rangle, \tag{4.3}$$

where

$$T(\mathbf{r}_i)=-(\hbar^2/2m)\nabla_i^2\ln\phi(|\mathbf{r}_i-\mathbf{R}_i|), \tag{4.4}$$

and the average is defined such that for an arbitrary function $g(\mathbf{r}_1,\cdots,\mathbf{r}_n)$,

$$\langle g(\mathbf{r}_1,\cdots,\mathbf{r}_n)\rangle\equiv\omega^{-n}\int d\mathbf{r}_1\cdots\int d\mathbf{r}_n\ |\phi(|\mathbf{r}_1-\mathbf{R}_1|)|^2\cdots|\phi(|\mathbf{r}_n-\mathbf{R}_n|)|^2 g(\mathbf{r}_1,\cdots,\mathbf{r}_n). \tag{4.5}$$

In general, (4.5) depends on $\mathbf{R}_1,\cdots,\mathbf{R}_n$, and this dependence is included in the subscripts on the variables in the argument of g. The quantity $\langle T(\mathbf{r}_i)\rangle$ is independent of $\mathbf{R}_i$ and is a constant equal to $3\hbar^2A/4m$ when ϕ is a Gaussian.

We shall first calculate E_{02} when the wave function is given by (2.4), i.e., when the effects of symmetry are neglected. In this case, the two-body wave function to be substituted into (3.16) is given by (3.6b) for $n=2$. We first need to calculate

$$\begin{aligned}(-\hbar^2/2m)\int d\mathbf{r}_i\int d\mathbf{r}_j\,\Psi_2(\mathbf{r}_i,\mathbf{r}_j)\nabla_i^2\Psi_2(\mathbf{r}_i,\mathbf{r}_j)&=(\hbar^2/2m)\int d\mathbf{r}_i\int d\mathbf{r}_j\,[\nabla_i\Psi_2(\mathbf{r}_i,\mathbf{r}_j)]^2\\&=\int d\mathbf{r}_i\int d\mathbf{r}_j\,|\phi(|\mathbf{r}_i-\mathbf{R}_i|)|^2|\phi(|\mathbf{r}_j-\mathbf{R}_j|)|^2 f^2(r_{ij})[T(\mathbf{r}_i)-(\hbar^2/4m)\nabla_i^2\ln f(r_{ij})],\end{aligned} \tag{4.6}$$

a simplication due to Jackson and Feenberg.[21] We may therefore write E_{02} in the form

$$E_{02}{}^{u}=E_{02V}+E_{02T}, \tag{4.7}$$

where

$$E_{02V}=\frac{1}{2}\sum_{i,j}{}'\frac{\langle V(r_{ij})f^2(r_{ij})\rangle}{\langle f^2(r_{ij})\rangle}, \tag{4.8}$$

$$E_{02T}=\sum_{i,j}{}'\left\{\frac{\langle T(\mathbf{r}_i)f^2(r_{ij})\rangle}{\langle f^2(r_{ij})\rangle}-\langle T(\mathbf{r}_i)\rangle\right\}. \tag{4.9}$$

The superscript u in (4.7) indicates that the effects of symmetry have been neglected. The primes on the sums in (4.8) and (4.9) indicate the omission of those terms for which two indices are equal, and

$$V(r)=v(r)-(\hbar^2/2m)\nabla^2\ln f(r). \tag{4.10}$$

At this stage, it is quite arbitrary to put $E_{02}{}^{u}$ into this form. However, E_{02T} vanishes identically if ϕ is approximated by a Gaussian or if the limit $f(r)=1$ is taken.

The calculation of E_{02} including the effects of symmetry[15] is more complicated. The spatial part of two-body

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[21] H. W. Jackson and E. Feenberg, Ann. Phys. (N. Y.) **15**, 266 (1961).

wave functions is now given by (3.6c). In this case,

$$(-\hbar^2/2m)\int d\mathbf{r}_i\int d\mathbf{r}_j\,\Psi_2(\mathbf{r}_i,\mathbf{r}_j)[\nabla_i^2+\nabla_j^2]\Psi_2(\mathbf{r}_i,\mathbf{r}_j)$$

$$=\int d\mathbf{r}_i\int d\mathbf{r}_j\,|\phi(|\mathbf{r}_i-\mathbf{R}_i|)|^2|\phi(|\mathbf{r}_j-\mathbf{R}_j|)|^2f^2(r_{ij})[T(\mathbf{r}_i)+T(\mathbf{r}_j)-(\hbar^2/2m)\nabla_i^2\ln f(r_{ij})]$$

$$\pm\int d\mathbf{r}_i\int d\mathbf{r}_j\,\phi(|\mathbf{r}_i-\mathbf{R}_i|)\phi(|\mathbf{r}_j-\mathbf{R}_j|)\phi(|\mathbf{r}_i-\mathbf{R}_j|)\phi(|\mathbf{r}_j-\mathbf{R}_i|)f^2(r_{ij})$$

$$\times[T_j(\mathbf{r}_i)+T_i(\mathbf{r}_j)-(\hbar^2/2m)\nabla_i^2\ln f(r_{ij})],\quad (4.11)$$

where

$$T_j(\mathbf{r}_i)\equiv-(\hbar^2/2m)\{[\nabla_i^2\phi(|\mathbf{r}_i-\mathbf{R}_i|)/\phi(|\mathbf{r}_i-\mathbf{R}_j|)]-[\boldsymbol{\nabla}_i\phi(|\mathbf{r}_i-\mathbf{R}_i|)/\phi(|\mathbf{r}_i-\mathbf{R}_i|)]$$

$$\cdot[\boldsymbol{\nabla}_i\phi(|\mathbf{r}_i-\mathbf{R}_j|)/\phi(|\mathbf{r}_i-\mathbf{R}_j|)]\}.\quad (4.12)$$

We note that $T_i(\mathbf{r}_i)=T(\mathbf{r}_i)$.

We may therefore write

$$(\Psi_2(\mathbf{r}_i,\mathbf{r}_j),H_2(\mathbf{r}_i,\mathbf{r}_j)\Psi_2(\mathbf{r}_i,\mathbf{r}_j))/(\Psi_2(\mathbf{r}_i,\mathbf{r}_j),\Psi_2(\mathbf{r}_i,\mathbf{r}_j))=[\langle f^2(r_{ij})\rangle\pm\langle f^2(r_{ij})\rangle_x]^{-1}$$

$$\times[\langle f^2(r_{ij})\{T(\mathbf{r}_i)+T(\mathbf{r}_j)+V(r_{ij})\}\rangle\pm\langle f^2(r_{ij})\{T_j(\mathbf{r}_i)+T_i(\mathbf{r}_j)+V(r_{ij})\}\rangle_x],\quad (4.13)$$

where, if $g(\mathbf{r}_i,\mathbf{r}_j)$ is an arbitrary function,

$$\langle g(\mathbf{r}_i,\mathbf{r}_j)\rangle_x\equiv\omega^{-2}\int d\mathbf{r}_i\int d\mathbf{r}_j\,\phi(|\mathbf{r}_i-\mathbf{R}_i|)\phi(|\mathbf{r}_i-\mathbf{R}_j|)\phi(|\mathbf{r}_j-\mathbf{R}_j|)\phi(|\mathbf{r}_j-\mathbf{R}_i|)g(\mathbf{r}_i,\mathbf{r}_j).\quad (4.14)$$

If we multiply and divide (4.13) by $\langle f^2(r_{ij})\rangle\mp\langle f^2(r_{ij})\rangle_x$, we may write E_{02} in the form

$$E_{02}{}^s=\tfrac{1}{2}\sum_{i,j}{}'\,\{[\langle f^2(r_{ij})\rangle^2-\langle f^2(r_{ij})\rangle_x{}^2]^{-1}[\langle f^2(r_{ij})\rangle\langle f^2(r_{ij})\{T(\mathbf{r}_i)+T(\mathbf{r}_j)+V(r_{ij})\}\rangle-\langle f^2(r_{ij})\rangle_x$$

$$\times\langle f^2(r_{ij})\{T_j(\mathbf{r}_i)+T_i(\mathbf{r}_j)+V(r_{ij})\}\rangle_x]-\langle T(\mathbf{r}_i)\rangle-\langle T(\mathbf{r}_j)\rangle\pm[\langle f^2(r_{ij})\rangle^2-\langle f^2(r_{ij})\rangle_x{}^2]^{-1}$$

$$\times[\langle f^2(r_{ij})\rangle\langle f^2(r_{ij})\{T_j(\mathbf{r}_i)+T_i(\mathbf{r}_j)+V(r_{ij})\}\rangle_x-\langle f^2(r_{ij})\rangle_x\langle f^2(r_{ij})\{T(\mathbf{r}_i)+T(\mathbf{r}_j)+V(r_{ij})\}\rangle\}].\quad (4.15)$$

It turns out that

$$\langle f^2(r_{ij})\rangle\gg\langle f^2(r_{ij})\rangle_x,\quad (4.16)$$

$$\langle f^2(r_{ij})\{T(\mathbf{r}_i)+T(\mathbf{r}_j)+V(r_{ij})\}\rangle\gg\langle f^2(r_{ij})\{T_j(\mathbf{r}_i)+T_i(\mathbf{r}_j)+V(r_{ij})\}\rangle_x,\quad (4.17)$$

so that we have

$$E_{02}{}^s=E_{02}{}^u+E_{02J},\quad (4.18)$$

where

$$E_{02J}=\pm\tfrac{1}{8}\sum_{i,j}{}'\,J_{ij},\quad (4.19)$$

$$J_i=4\langle f^2(r_{ij})\rangle^{-2}[\langle f^2(r_{ij})\rangle\langle f^2(r_{ij})\{T_j(\mathbf{r}_i)+T_i(\mathbf{r}_j)+V(r_{ij})\}\rangle_x-\langle f^2(r_{ij})\rangle_x\langle f^2(r_{ij})\{T(\mathbf{r}_i)+T(\mathbf{r}_j)+V(r_{ij})\}\rangle].\quad (4.20)$$

In the ^{4}He case, only the plus sign in (4.19) occurs. For the ^{3}He case, both signs occur and we have defined J_{ij} so that $\frac{1}{2}J_{ij}$ is the difference in energy between a parallel and an antiparallel alignment of spins on sites i and j. In the limit $f(r)=1$, (4.19) reduces to the results previously obtained by Carr[22] and Mullin.[23]

We shall only calculate E_{03} for the unsymmetrized case. The derivation is essentially the same as that leading to (4.7). We find

$$E_{03}{}^u=E_{03V}+E_{03T},\quad (4.21)$$

where

$$E_{03V}=\frac{1}{2}\sum_{i,j,k}{}'\left\{\frac{\langle f^2(r_{ij})f^2(r_{ik})f^2(r_{jk})V(r_{ij})\rangle}{\langle f^2(r_{ij})f^2(r_{ik})f^2(r_{jk})\rangle}-\frac{\langle f^2(r_{ij})V(r_{ij})\rangle}{\langle f^2(r_{ij})\rangle}\right\},\quad (4.22)$$

$$E_{02T}=\frac{1}{2}\sum_{i,j,k}{}'\left\{\frac{\langle f^2(r_{ij})f^2(r_{ik})f^2(r_{jk})T(\mathbf{r}_i)\rangle}{\langle f^2(r_{ij})f^2(r_{ik})f^2(r_{jk})\rangle}-2\frac{\langle f^2(r_{ij})T(\mathbf{r}_i)\rangle}{\langle f^2(r_{ij})\rangle}+\langle T(\mathbf{r}_i)\rangle\right\}.\quad (4.23)$$

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[22] W. J. Carr, Phys. Rev. **92**, 28 (1953).
[23] W. J. Mullin, Phys. Rev. **136**, A1126 (1964).

Both E_{03V} and E_{03T} vanish in the limit $f(r)=1$. In fact, all the higher terms of the cluster expansion vanish in this limit, in which case the expansion reduces to the Hartree result. Of course, all of the integrals which involve overlap vanish because the overlap also vanishes in the limit $f(r)=1$.

V. CALCULATION OF E_0

In this section we shall present the details of the method we use to calculate E_0. The basis of our approach is to truncate the cluster expansion so that

$$E_0 \simeq E_{01}+E_{02V}. \tag{5.1}$$

There are then three types of corrections to (5.1), the leading terms of which are E_{02T}, E_{03V}, and E_{02J}. Our procedure is to minimize (5.1) and then evaluate these corrections at and near the minimum. If the corrections are all small and do not seriously affect the position of the minimum, we feel that it is reasonable to suppose that we have a good approximation to an upper bound for E_0.

To minimize (5.1), it is convenient to introduce

$$u(r)=(4\pi)^{1/2}r\phi(r), \tag{5.2}$$

where $u(r)$ can be chosen to be real and

$$\omega=\int_0^\infty dr\, u^2(r). \tag{5.3}$$

We may now write

$$E_0/N=-(\hbar^2/2m\omega)\int_0^\infty dr\, u(r)u''(r) +\tfrac{1}{2}\sum_{\beta=1}^{\infty} n_\beta P_\beta Q_\beta^{-1}, \tag{5.4}$$

where

$$P_\beta=\omega^{-2}\int_0^\infty dr\int_0^\infty d\rho\, u^2(r)u^2(\rho)F_1(r,\rho,R_\beta), \tag{5.5}$$

$$Q_\beta=\omega^{-2}\int_0^\infty dr\int_0^\infty d\rho\, u^2(r)u^2(\rho)F_2(r,\rho,R_\beta), \tag{5.6}$$

and

$$F_1(r,\rho,R_\beta)=(16\pi^2)^{-1}\int d\Omega_r\int d\Omega_\rho\, f^2(|\mathbf{r}-\boldsymbol{\rho}+\mathbf{R}_\beta|) \times V(|\mathbf{r}-\boldsymbol{\rho}+\mathbf{R}_\beta|), \tag{5.7}$$

$$F_2(r,\rho,R_\beta)=(16\pi^2)^{-1}\int d\Omega_r\int d\Omega_\rho\, f^2(|\mathbf{r}-\boldsymbol{\rho}+\mathbf{R}_\beta|). \tag{5.8}$$

Here Ω_r represents the solid angle of r and n_β is the number of lattice sites at a distance R_β from a given lattice site.[24] In writing (5.4) in this way, we have assumed that all sites are equivalent and have therefore neglected surface effects.

We first minimize (5.4) with respect to $u(r)$. We find that $u(r)$ must be a solution of

$$-(\hbar^2/2m)u''(r)+[w(r)-e]u(r)=0, \tag{5.9}$$

with the boundary conditions

$$\lim_{r\to 0} u(r)/r=\text{finite}, \tag{5.10}$$

$$\lim_{r\to\infty} u(r)=0. \tag{5.11}$$

and

$$w(r)=\sum_{\beta=1}^{\infty} n_\beta\left\{(\omega Q_\beta)^{-1}\int_0^\infty d\rho\, u^2(\rho)F_1(r,\rho,R_\beta) -(\omega Q_\beta^2)^{-1}P_\beta\int_0^\infty d\rho\, u^2(\rho)F_2(r,\rho,R_\beta)\right\}. \tag{5.12}$$

The ground-state energy per particle is

$$E_0/N=e_0+\tfrac{1}{2}\sum_{\beta=1}^{\infty} n_\beta Q_\beta^{-1}P_\beta, \tag{5.13}$$

where e_0 is the lowest eigenvalue of (5.9).

We wish to point out that (5.9), (5.12), and (5.13) are essentially the same as the Hartree equations of Nosanow and Shaw,[4] with the exception that the true interaction $v(r)$ is replaced by an effective interaction which is approximately given by

$$v_{\text{eff}}(r)\simeq f^2(r)[v(r)-(\hbar^2/2m)\nabla^2\ln f(r)]. \tag{5.14}$$

This result is only approximate as we have neglected

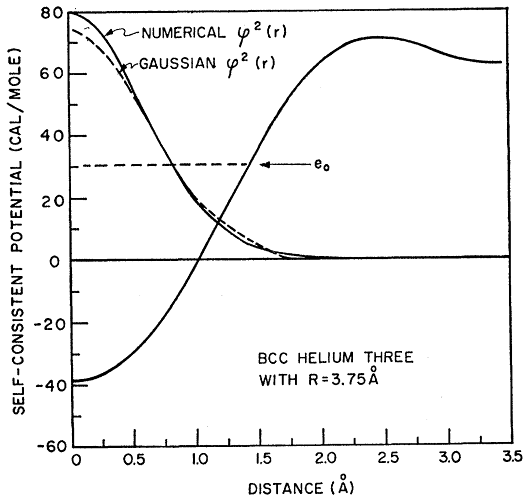

FIG. 1. Plot of $w(r)$ (in units of cal/mole) and $\phi^2(r)$ (in arbitrary units) for bcc ^{3}He with $R=3.75$ Å; the numerical and Gaussian $\phi^2(r)$ are normalized to the same value. Here $\log_{10}K=-0.75$ and $A=1.30$ (Å^{-2}). The difference between the numerical and Gaussian $\phi^2(r)$ near $r=0$ is not significant since they are always weighted by r^2.

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[24] The best tabulation of these values is in *International Tables for X-ray Crystallography*, (The Kynoch Press, Birmingham, England, 1959) Vol. II, p. 350.

the small effect due to the Q_β denominators. In any case, we may view (5.14) as a local approximation to the appropriate t matrix for this problem.

We are able to solve (5.9) and obtain E_0/N to within 1%; the details of the computation are given in the Appendix. Typical results for given values of R and K are displayed in Figs. 1 and 2. The self-consistent potential is very much like a parabola for small r but levels out for $r\simeq 2$ Å. The single-particle wave function $\phi(r)$ is remarkably well approximated by a Gaussian. If $w_{\max}$ and $w_{\min}$ are, respectively, the maximum and minimum values of $w(r)$, we note that in Fig. 1

$$(e_0-w_{\min})/(w_{\max}-w_{\min})=0.634\,,$$

whereas in Fig. 2

$$(e_0-w_{\min})/(w_{\max}-w_{\min})=0.716\,.$$

Thus as the density increases, the bound state moves up in the well. In fact, for sufficiently high densities, there is *no* bound state in the well. We feel that this behavior is due to the inadequacy of the analytic form used for $f(r)$ and we shall discuss this point in detail in Sec. VII.

To complete the calculation it is necessary to minimize E_0 with respect to K. A typical result is shown in Fig. 3. The energy has a broad minimum with respect to K so that sufficient accuracy is obtained by determining $\log_{10}K$ to ± 0.05. It turns out that, to the accuracy we use, the calculation yields $\log_{10}K=-0.75$ for ^{3}He and $\log_{10}K=-0.65$ for ^{4}He independently of the density. Again we feel that this result is due to the inadequacy of the analytic form used for $f(r)$ and we shall discuss this point in Sec. VII.

It should be pointed out that the above calculation is not really complete for helium since this substance crystallizes only under pressure. In this case, it is E_0+PV and not E_0 itself that is a minimum. However, if one wishes to obtain E_0 as a function of molar volume V_m, the two calculations will give the same result. Further, one obtains the ground-state pressure and compressibility by use of the well-known formulas $P=-dE_0/dV$ and $\kappa^{-1}=-V(dP/dV)$. We obtained P and κ simply by numerical differentiation of E_0 so that they have been less accurately determined than E_0.

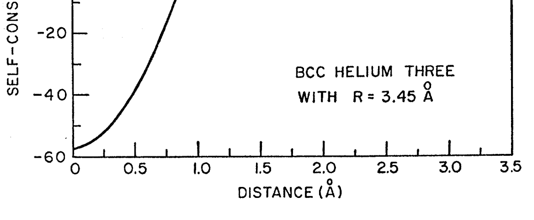

FIG. 2. Plot of $w(r)$ (in units of cal/mole) and $\phi^2(r)$ (in arbitrary units) for bcc ^{3}He with $R=3.45$ Å; the numerical and Gaussian $\phi^2(r)$ are normalized to the same value. Here $\log_{10}K=-0.75$ and $A=1.65$ (Å^{-2}). Again $\phi^2(r)$ is weighted by r^2 so that the discrepancy near $r=0$ is not significant.

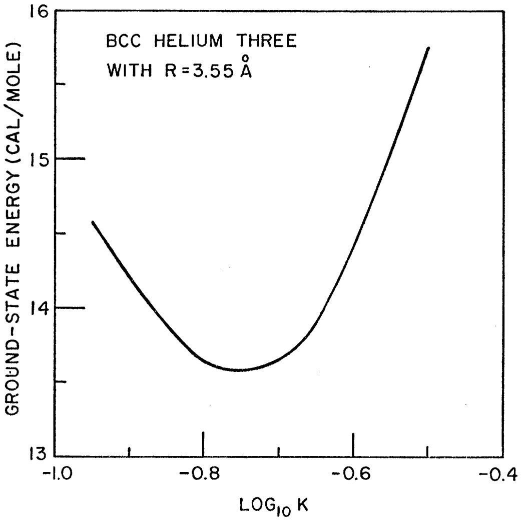

FIG. 3. Plot of E_0 (in units of cal/mole) versus $\log_{10}K$ for bcc ^{3}He with $R=3.55$ Å. The Hartree approximation corresponds to $\log_{10}K=-\infty$.

It remains only to evaluate the various correction terms to (5.1). The term E_{02T} vanishes when $\phi(r)$ is a Gaussian because $T(r)$ is a constant. Since $\phi(r)$ is so closely approximated by a Gaussian, it is clear that E_{02T} is negligible compared to $E_{01}+E_{02V}$. Further, E_{02J} has been evaluated by Mullin and Nosanow[15] and it turns out to be four orders of magnitude smaller than $E_{01}+E_{02V}$. The calculation of E_{03V} is very difficult and will be the subject of a forthcoming paper.[25] It is possible to see that, at the minimum of E_0, $f(r)$ satisfies the necessary condition for E_{03V} to be small; i.e., that $f(r)\simeq 1$ where ϕ^2 is large. This behavior is pictured in Fig. 4. However, there are so many terms in E_{03V} and the cancellations turn out to be so delicate that an exact numerical calculation is absolutely necessary. In this paper, we shall give the results for one density and refer to the future paper[25] for more details. For bcc ^{3}He with $R=3.65$ Å, $E_{01}+E_{02V}=11.8$ cal/mole when calculated using the Gaussian ϕ, whereas $E_{03V}=0.3$ cal/mole. Further, although the position of the minimum is shifted a bit by E_{03V}, the value of $E_{01}+E_{02V}+E_{03V}$ is still accurate to within 1%.

In view of the small effect of the leading correction terms, we feel that our procedure yields an approxi-

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[25] J. H. Hetherington, W. J. Mullin, and L. H. Nosanow (to be published).

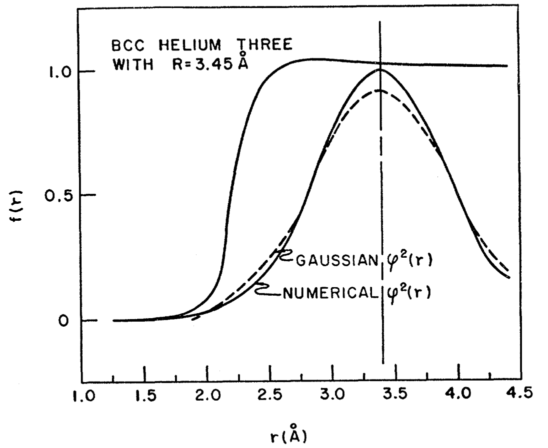

FIG. 4. Plot of $f(r)$ [normalized so that $f(\infty)=1$] and $\phi^2(r)$ (in arbitrary units) for bcc ^{3}He with $R=3.45$ Å. Here $\phi^2(r)$ is centered about 3.45 to show that $f(r)\simeq 1$ in the region where $\phi^2(r)$ is large.

mation to an upper bound for E_0 that is reasonably accurate.

VI. PRESENTATION OF RESULTS

In this section we shall give the results of our calculations of the ground-state energy, pressure, and compressibility for the bcc and hcp structures of both ^{3}He and ^{4}He. In each case we present two results, one for a $\phi(r)$ determined numerically by solving (5.9) and one for a Gaussian $\phi(r)$. In the latter case, we also give the values of the parameters A and K as a function of R. We have included these results because this extremely simple form for the wave function gives remarkably good results and may be useful for future calculations.

In Fig. 5 we plot E_0 as a function of V_m, the molar volume, and the appropriate experimental values[26] for comparison. It is seen that our values for ^{4}He are about 8 cal/mole higher than the experimental ones. These results may be compared with those of Nosanow and Shaw[4] which are about 25 cal/mole higher than the experimental ones. Unfortunately, the values for E_0 for ^{3}He have not yet been determined, although it is estimated that they are about -1 cal/mole at the lowest densities. Thus, it is probable that our values for ^{3}He are approximately 10 cal/mole too high. In this case the results of Nosanow and Shaw[4] are about 34 cal/mole too high.

An important feature of the calculations of E_0 is that the energy of the bcc phase is lower than the energy of the corresponding hcp phase in every case. Such a result would be impossible in the classical case because of the spherical symmetry of the pair interaction. In our opinion, this result shows clearly that the existence of the bcc phase in ^{3}He and ^{4}He is due to the effect of correlations in the motion of the atoms, an effect which is large only because of the large zero-point energy in the system. Of course, our results, if taken literally, would predict that the hcp phase could not exist. Clearly, the theory is not sufficiently accurate that it can be trusted to 1%. However, we feel that it is significant that the bcc energy is approximately the same as the hcp energy and not several cal/mole higher as had been obtained previously.[4]

Our results for the ground-state pressure and compressibility are given in Figs. 6 and 7, respectively, along with the appropriate experimental work[27–30] for comparison. The most interesting feature of these results is that, in contrast to the calculation of E_0 they agree with experiment to within about 10%. This result can be understood on the basis of a simple physical argu-

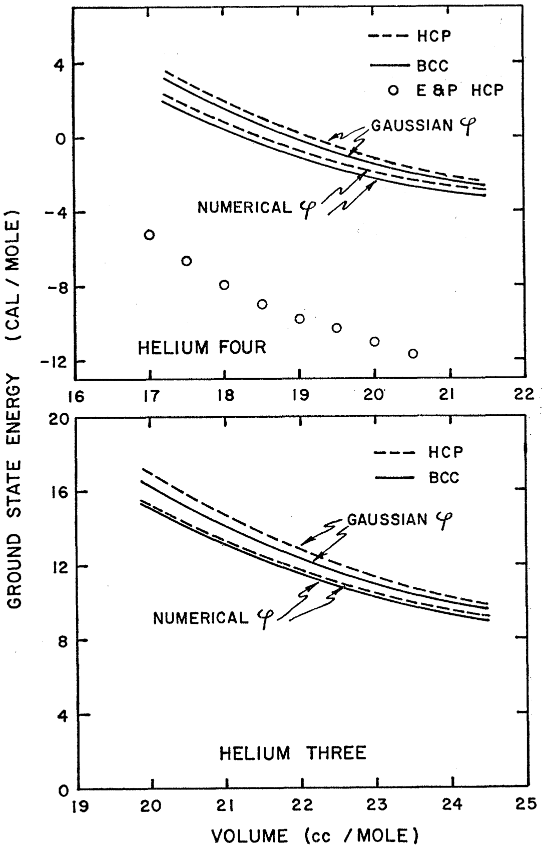

FIG. 5. Plot of E_0 (in units of cal/mole) as a function of molar volume for the bcc and hcp structures of both ^{3}He and ^{4}He. The experimental data for ^{4}He are those of Edwards and Pandorf (Ref. 26).

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[26] D. O. Edwards and R. C. Pandorf, Phys. Rev. **140**, A816 (1965).

[27] D. O. Edwards and R. C. Pandorf (unpublished report).

[28] S. G. Sydoriak, R. L. Mills, and E. R. Grilly, Phys. Rev. Letters **4**, 495 (1960).

[29] D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, *Helium Three* (Ohio State University Press, Columbus, 1960).

[30] E. D. Adams, G. C. Straty, and E. L. Wall, Phys. Rev. Letters **15**, 549 (1965).

Table I. Values of the parameters A and K as a function of molar volume for both the bcc and hcp structures of ^{3}He.

	bcc ^{3}He			hcp ^{3}He		
R (Å)	V (cm^3/mole)	A (Å^{-2})	$\log_{10}K$	V (cm^3/mole)	A (Å^{-2})	$\log_{10}K$
3.45	19.0	1.65	−0.75			
3.55	20.7	1.54	−0.75	19.1	1.75	−0.75
3.65	22.5	1.42	−0.75	20.7	1.64	−0.75
3.75	24.5	1.30	−0.75	22.5	1.48	−0.75
3.85				24.3	1.36	−0.75

ment. A typical value of E_0 for bcc ^{3}He is about 10 cal/mole. This is the sum of approximately 35 cal/mole of kinetic energy and −25 cal/mole of potential energy. Thus, the kinetic and potential energies are individually determined to the order of 10%. Since the kinetic energy changes more rapidly with pressure than does the potential energy, it is more important in determining the pressure and compressibility. Therefore, since we can calculate the kinetic energy to 10%, it is quite reasonable that we can obtain the pressure and compressibility to 10%.

In Tables I and II, we give the values of the parameters A and K which minimize E_0 for ^{3}He and ^{4}He, respectively. We have determined $\log_{10}K$ to within ±0.05 and A to within ±0.02. We note that the value of A for the hcp case is a bit larger than that for the bcc case at the same density. This reflects the fact that there are more near neighbors in the hcp case which causes an atom to be more confined and hence to have a smaller root-mean-square deviation from its equilibrium position. Again the value of K is largely insensitive to changes in the density.

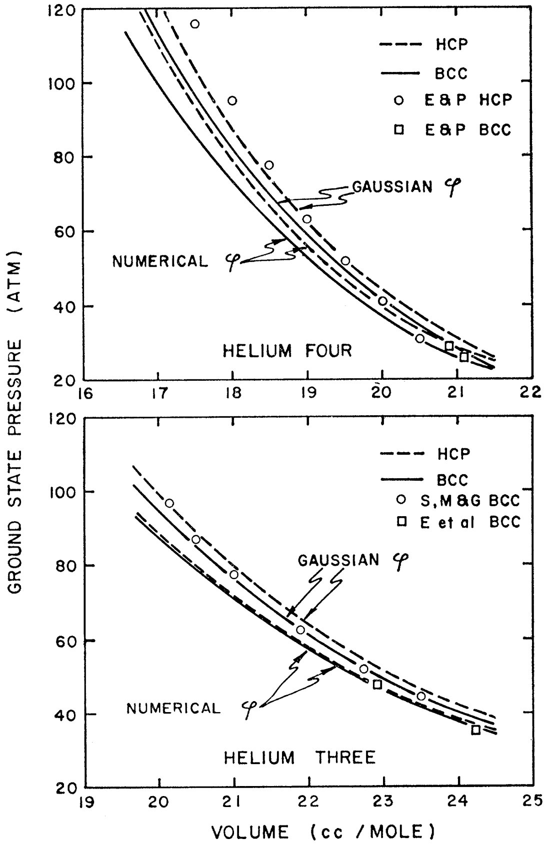

Fig. 6. Plot of P (in units of atmospheres) as a function of molar volume for the bcc and hcp structures of both ^{3}He and ^{4}He. The data for ^{4}He are those of Edwards and Pandorf (Refs. 26 and 27). The data for ^{3}He were obtained along the melting curve and approximate the ground-state data to within a few percent. These data are those of Sydoriak, Mills, and Grilly (Ref. 28) and Edwards, Baum, Brewer, Daunt, and McWilliams (Ref. 29).

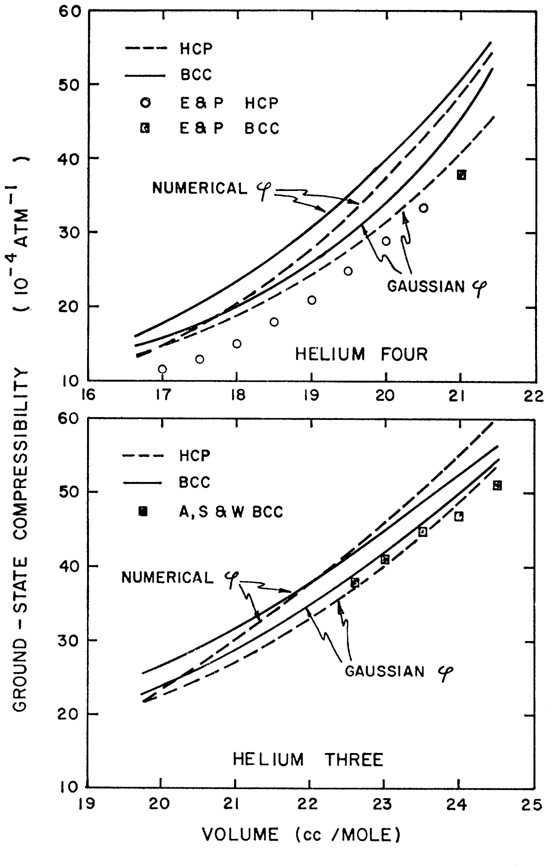

Fig. 7. Plot of κ (in units of 10^{-4} inverse atmospheres) as a function of molar volume for the bcc and hcp structures of both ^{3}He and ^{4}He. The data for ^{4}He are those of Edwards and Pandorf (Refs. 26 and 27). The data for ^{3}He are those of Adams, Straty, and Wall (Ref. 30).

TABLE II. Values of the parameters A and K as a function of molar volume for both the bcc and hcp structures of ^{4}He.

	bcc ^{4}He			hcp ^{4}He		
R (Å)	V (cm^3/mole)	A (Å^{-2})	$\log_{10}K$	V (cm^3/mole)	A (Å^{-2})	$\log_{10}K$
3.35	17.4	2.19	−0.75			
3.40	18.2	2.09	−0.75	16.7	2.42	−0.75
3.50	19.9	1.89	−0.75	18.3	2.23	−0.75
3.60	21.6	1.71	−0.65	19.9	1.99	−0.75
3.70				21.6	1.80	−0.75

VII. DISCUSSION

The basic objective of this work has been to obtain a better understanding of the effects of correlations in quantum crystals. We have introduced these effects in a crude fashion via a trial correlation function of the form (2.10). It is a very remarkable result of our calculations that, within the context of approximation (5.1), the energy minimum occurs for a very small value of K, namely $K\simeq 0.178$. Thus for $r\geq\sigma$, $f(r)$ turns out to be very close to unity. Fundamentally, it is this result which leads to the very rapid convergence of the cluster expansion and the good agreement of our calculations with experiment.

It is quite clear that these results depend strongly on the choice of the analytic form for $f(r)$. For example, had we chosen the form

$$f(r)=\exp(-C/r^{10}), \tag{7.1}$$

we would *not* have found a minimum within the approximation (5.1). The physical reason for this is that as C is increased the kinetic energy is continually lowered until the particles are no longer localized. Thus it is clear that it is not possible to make an *arbitrary* variation of $f(r)$ within the context of the approximation (5.1). This result has been emphasized by Brueckner,[12,31] and is due to the omission of the higher terms of the expansion. However, it does not affect the validity of the results obtained with an $f(r)$ given by (2.10).

As we mentioned in Sec. V, our approximation is equivalent to a Hartree calculation in which $v(r)$ is replaced by $v_{\mathrm{eff}}(r)$ given by (5.14). These potentials are both pictured in Fig. 8. It is seen that $v_{\mathrm{eff}}(r)$ differs from $v(r)$ in that it has a "soft" core and a slightly displaced minimum. One of the main deficiencies of the $f(r)$ given by (2.10) is that it "softens" the hard core too much. This effect shows up clearly in Figs. 6 and 7, since, in the main, we calculate *lower* pressures and *higher* compressibilities than those observed experimentally. This inadequacy of (2.10) is consistent with the fact that it gives an $f(r)$ which vanishes too rapidly for small r [cf. (2.8a)].

Further, we feel that it is this inadequacy in our choice of $f(r)$ that limits the density range in which we are able to calculate. As we noted in Sec. V, the calculation fails when there is no longer a bound state in the effective well. This behavior is also due to the fact that the hard core has been "softened" too much. Further, it is consistent with the fact that our calculations of the pressure and compressibility are worse at high densities than they are low densities. We also feel that it is this inadequacy in $f(r)$ which contributes to the poor agreement between the observed and calculated density dependence of the exchange integral[15] and the various sound velocities.[17]

We wish to point out that, although the calculations with the numerical ϕ's yield the lowest energies, those with the Gaussian ϕ's yield better pressures and compressibilities. In our opinion this result is due to the fact that the analytic form for ϕ does not adjust properly to a change in density. Hence, the single-particle wave function compensates a bit for the fact that the $f(r)$ "softens" the "hard" core too much and therefore, the Gaussian ϕ's yield better values for the pressure and compressibility.

We feel that our assumption of a spherically symmetric $\phi(r)$ is probably quite good in the bcc phase, but may not be sufficient in the hcp phase. In the bcc phase, the Wigner-Seitz unit cell is very nearly spherical and $\phi(r)$ is certainly spherical for sufficiently small r. However, in the hcp phase, $\phi(r)$ is never spherical, even for sufficiently small r. Further, the agreement between theory and experiment in *all* of our calculations is worse for the hcp phase than for the bcc phase. This question can be studied by assuming a trial wave function of the form

$$\phi(r)=\exp(-\tfrac{1}{2}Ar^2-\tfrac{1}{2}BZ^2), \tag{7.2}$$

where Z is the component of r along the c axis of the crystal and B is another variational parameter.

We wish to discuss briefly the possible effect of the higher terms of the cluster expansion. On a basis of the calculation of E_{03V} at $R=3.65$ Å it seems reasonable to suppose that the cluster expansion converges rapidly at this density. To understand this result physically, we note that an important parameter is clearly $a=r_{\mathrm{min}}/R$. For the above-mentioned calculation $a=0.79$; whereas, for a classical crystal $a\simeq 1.0$. Since the cluster expansion is inherently a low-density one, it is not so startling that it converges rapidly when $a^3\ll 1$. However, as the density increases, it is quite possible that the cluster expansion will no longer be a good approximation. This possibility has been con-

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[31] K. A. Brueckner (private communication).

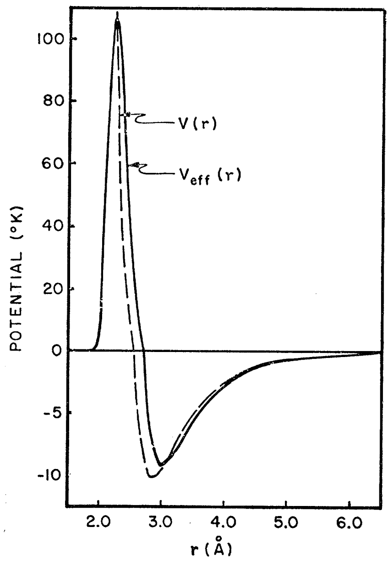

FIG. 8. Plot of $v(r)$ and $v_{\mathrm{eff}}(r)$ (both in units of degrees). The maximum in $v_{\mathrm{eff}}(r)$ is approximately 106°K and is very sensitive to the precise form of $f(r)$.

sidered in a preliminary way by Mullin[10] and may also be partly responsible for the inadequacy of our results in the high-density region.

In conclusion, we wish to discuss briefly the possibility of extending the work described in this paper. The central problem is certainly to obtain an improved correlation function. It is clearly possible to derive a differential equation for $f(r)$ by varying E_0 with respect to $f(r)$. Since it is not possible to make an arbitrary variation of $f(r)$ within the approximation (5.1), it will either be necessary to introduce an appropriate constraint or to include higher terms of the cluster expansion.[12,31] In either case, the solution of the equations will probably be extremely difficult.

ACKNOWLEDGMENTS

The author wishes to thank Dr. William J. Mullin for many useful conversations and also for critically reading the manuscript. He also wishes to thank Professor Keith A. Brueckner for illuminating conversations and for his hospitality during the summer of 1964 at the University of California, San Diego, where part of this work was done. Further, the author wishes to thank the Numerical Analysis Center of the University of Minnesota for its assistance in computing. He wishes to thank Hugh Seidman for his help in writing the necessary computer programs. Finally, he wishes to thank the Graduate School of the University of Minnesota for a grant which made it possible to start this research.

APPENDIX

In this Appendix we shall discuss some of the numerical details of solving (5.9) by iteration. In principle, the problem is straightforward; however, in practice it is quite complicated due to the difficulty of computing $w(r)$. It is numerically convenient to calculate $w(r)$ differently for three regions: (i) $r<R/2$, (ii) $R/2<r<R$, and (iii) $r>R$. We find that $u(r)$ is sufficiently small in region (iii) so that we can replace the boundary condition at infinity by

$$u(R)=0. \tag{A1}$$

Further, it is necessary to calculate F_1 and F_2. We shall now show how the calculation of these functions can be reduced to the computation of the sum of two single integrals and how they may be tabulated in terms of a few one-dimensional arrays. We are interested in integrals of the form

$$I=(16\pi^2)^{-1}\int d\Omega_1\int d\Omega_2\, F([\boldsymbol{\varrho}_1-\boldsymbol{\varrho}_2+\mathbf{R}_{12}]^2)\,. \tag{A2}$$

Because of the spherical symmetry, the integrations over the angles φ_1 and φ_2 can be carried out explicitly, so that

$$I=(8\rho_1\rho_2R_{12})^{-1}\int_{|R_{12}-\rho_2|}^{R_{12}+\rho_2}dx\int_{(x-\rho_1)^2}^{(x+\rho_1)^2}dz\,F(z)\,. \tag{A3}$$

After integration by parts, we have

$$\begin{aligned}(8\rho_1\rho_2R_{12})I=&\,G(R_{12}+\rho_1+\rho_2)\\ &-G(|R_{12}-\rho_2|+\rho_1)-\epsilon_2G(\epsilon_2[R_{12}+\rho_2-\rho_1])\\ &+\epsilon_1G(\epsilon_1[|R_{12}-\rho_2|-\rho_1])\,,\end{aligned} \tag{A4}$$

where

$$G(y)=\int_0^{y^2}dz\,(y-\sqrt{z})F(z)\,, \tag{A5}$$

and there are three cases:

$$\begin{aligned}&\text{(a)}\ \rho_1<|R_{12}-\rho_2|\,, && \epsilon_1=1,\ \epsilon_2=1;\\ &\text{(b)}\ |R_{12}-\rho_2|<\rho_1<R_{12}+\rho_2\,, && \epsilon_1=-1,\ \epsilon_2=1;\\ &\text{(c)}\ R_{12}+\rho_2<\rho_1\,, && \epsilon_1=-1,\ \epsilon_2=-1.\end{aligned}$$

Thus to calculate F_1 or F_2 we have only to tabulate $G(y)$ and use (A4) with a straightforward interpolation scheme. These formulas reduce to those of Nosanow and Shaw[4] when $\rho_1\leq R/2$ and $\rho_2\leq R/2$. For the present calculations we need only cases (a) and (b), since case (c) is eliminated by (A1).

It was also necessary to make approximations in calculating the lattice sum in (5.12). We find that there are again three regions: (i) $\beta=1$ or 2, (ii) $3\leqslant\beta\leqslant 10$, and (iii) $\beta>10$. It is necessary to calculate the contribution from region (i) exactly. In region (ii), we find that we can use the approximations

$$Q_\beta\simeq 1\,,$$

$$\omega^{-1}\int_0^\infty d\rho\, u^2(\rho)F_2(r,\rho,R_\rho)\simeq 1\,,\quad \text{for all } r.$$

In region (iii), we use the approximations $f(r)\simeq 1$ and

$V(r)\simeq v(r)$; further, we find that we can expand $v(|\mathbf{r}-\boldsymbol{\rho}+\mathbf{R}|)$ in powers of r and ρ and retain only quadratic terms. The contribution to $w(r)$ from this region is

$$B(R)\left[r^2-\omega^{-1}\int_0^\infty dr\, r^2u^2(r)\right], \tag{A6}$$

where

$$B(R)=4\epsilon\sigma^{-2}[22C_{14}(\sigma/R)^{14}-5C_8(\sigma/R)^8], \tag{A7}$$

and

$$C_m=\sum_{\beta=11}^{\infty} n_\beta(R/R_\beta)^m. \tag{A8}$$

Our numerical procedures were sufficiently accurate to give three-place accuracy in E_0 in each iteration. A sufficient number of iterations were run so that E_0 was determined numerically to 1%.

PHYSICAL REVIEW VOLUME 146, NUMBER 1 3 JUNE 1966

Laser-Induced Prebreakdown and Breakdown Phenomena Observed in Cloud Chamber*

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(Received 23 August 1965)

Direct observation of initiating electrons below the threshold for visible breakdown discharge is reported. With the cloud-chamber techniques used, minimum detectable ionization is estimated at 5000 ion pairs/cm^3. Production of initial electrons is ascribed to photoionization, in a manner which is consistent with Phelp's model. Above the visible breakdown threshold, thermal-gradient effects overcome all other sources of droplet formation in the cloud chamber.

In this article the observation of laser-induced prebreakdown ionization[1,2] and breakdown phenomena[3–19] in a continuously sensitive cloud chamber[20–22] is reported. The nature of the cloud chamber is such that two separate and easily distinguishable effects are produced when the laser power is above and just below the breakdown threshold.

This observation of prebreakdown ionization is the first direct evidence that the breakdown-initiating electron is produced by ionization of vapor by the laser beam. Additionally, it contradicts the assumption[1,4,5,9] that if an initiating electron is present, breakdown is inevitably produced by an avalanche process. The fact that breakdown can be realized in the cloud chamber is indirect evidence that the trigger electron is not naturally present.[1,18] The specific form of the breakdown phenomena also gives indirect evidence of multimode laser characteristics.[23]

The laser system incorporated a $\frac{1}{4}$-in. diameter 3-in.-long ruby rod pumped by an E. G. & G. FX67B lamp. The Q-switched laser pulse had a peak power of approximately 10 MW, i.e., 0.2 J of optical energy was emitted in 30 nsec. Standard techniques for the operation of a continuously sensitive cloud chamber were used.[20,21] A 100-V/cm clearing field was applied. The condensable material was methanol or dimethyl methylphosphonate (DMMP).

Prebreakdown ionization was observed when the laser beam was focused into the sensitive volume of the cloud chamber. Clusters of droplets ranging in diameter from 0.1 to 0.5 cm formed and fell to the bottom of the chamber at about the same rate as the background mist.

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* This work was supported by the U. S. Army Edgewood Arsenal, under Contract DA-18-035-AMC-255(A).

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