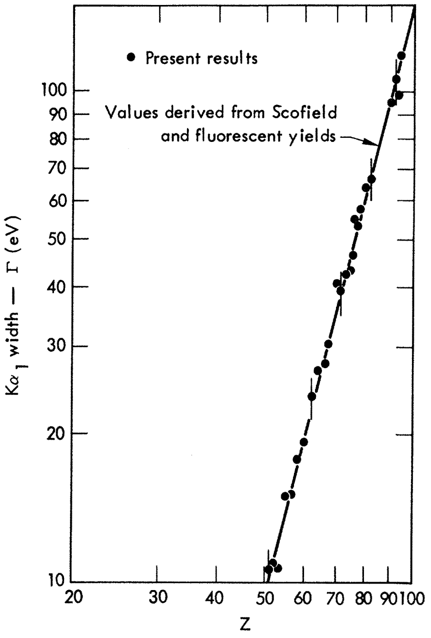

FIG. 2. Width of the $K\alpha_1$ x-rays as a function of Z.

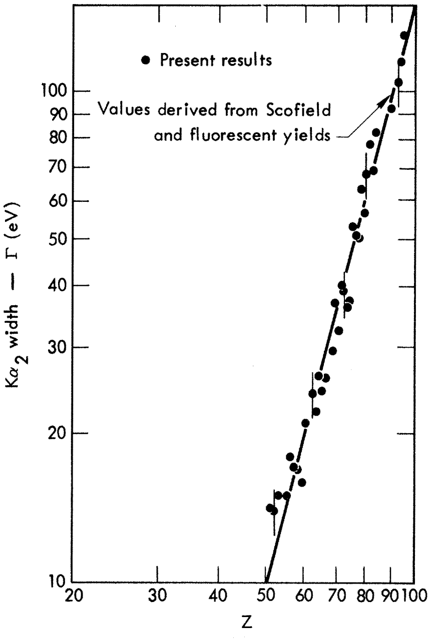

FIG. 3. Width of the $K\alpha_2$ x-rays as a function of Z.

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*Work performed under the auspices of the U. S. Atomic Energy Commission.

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[2] O. I. Sumbayev, in *Government Committee on the Uses of Atomic Energy* (Government Publishers of Literature on Atomic Science and Technology, Moscow, 1963) (English transl.: University of Colorado, Department of Physics and Astrophysics).

[3] J. H. Scofield, Phys. Rev. 179, 9 (1964).

PHYSICAL REVIEW A VOLUME 2, NUMBER 2 AUGUST 1970

Sound Velocity, Density, and Grüneisen Constant in Liquid ^{4}He: Comparison of Experiment with Theoretically Calculated Results*

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An experimental determination of the pressure dependence of the sound velocity $c(P)$, the density $\rho(P)$, and the Grüneisen constant $u(P)$, of liquid ^{4}He has been reported recently.[1] It is straightforward to deduce the ground-state energy from these data:

$$[E(\rho)-E(\rho_0)]/N=\int_{\rho_0}^{\rho}[P(\rho')/\rho'^2]\,d\rho' \quad , \tag{1}$$

where $\rho_0 = 0.021\,85$ Å^{-3} is the experimental density at zero pressure, and $E(\rho_0)/N$ is taken to be -7.14 °K. We find the following expression to give a very precise fit of the results:

$$\frac{1}{N}E(\rho) = -7.14+13.65\left(\frac{\rho-\rho_0}{\rho_0}\right)^2+7.67\left(\frac{\rho-\rho_0}{\rho_0}\right)^3 \quad , \tag{2}$$

where all coefficients (hereafter) are in °K.

Theoretical calculations based on variational wave functions of the Jastrow type

$$\psi(1, 2, \cdots, N) = \prod_{i<j=1}^{N} e^{u(r_{ij})/2} . \qquad (3)$$

have previously been reported.[2,3] The evaluation of the energy expectation value employs either some integral-equation methods or molecular dynamics. We shall compare the experimental energies of Eq. (2) to two sets of theoretical results: one by Massey and Woo [2] and one by Schiff and Verlet.[3]

It is clear from the curves in Fig. 1 that a direct comparison of experimental and theoretical results is not illuminating. The reason is that variational calculations always give rise to energies higher than the exact eigenvalue, and furthermore, the equilibrium densities differ. To effect a meaningful comparison, we postulate that corrections to theoretical results can be expanded in power series of $(\rho-\rho_0)/\rho_0$. The leading terms in the correction series will be determined by forcing the equilibrium density and energy to agree with experiment. It is expected that the series converges rapidly, so that terms beyond the second need not be included. Thus, we write

$$E_{\mathrm{corr}}(\rho) = E_{\mathrm{calc}}(\rho) + \Delta E(\rho), \qquad (4)$$

where

$$(1/N)\,\Delta E(\rho) = a + b(\rho-\rho_0)/\rho_0 + \cdots . \qquad (5)$$

The coefficients a and b are determined by

$$E_{\mathrm{corr}}(\rho_0) = E(\rho_0) \qquad (6)$$

and $$\left.\frac{dE_{\mathrm{corr}}(\rho)}{d\rho}\right|_{\rho=\rho_0} = 0. \qquad (7)$$

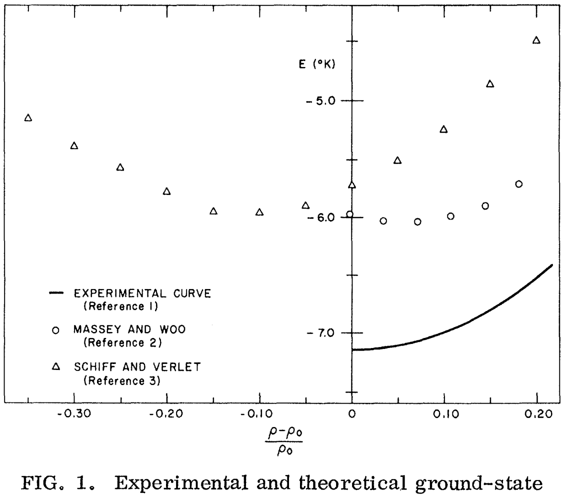

FIG. 1. Experimental and theoretical ground-state energies.

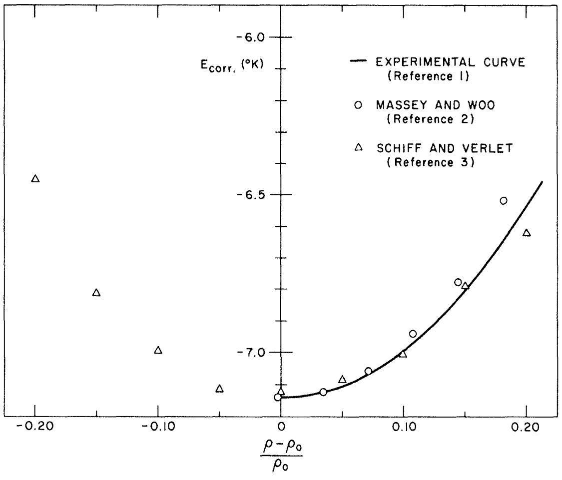

FIG. 2. Experimental energies and theoretical values after linear correction.

Finally, $E_{\mathrm{corr}}(\rho)$ will be compared to $E(\rho)$. The coefficients still free for comparison are those which determine the sound velocity and the Grüneisen constant.

For the Massey-Woo (MW) calculation the correction series turns out to be

$$(1/N)\Delta E^{\mathrm{MW}}(\rho) = -1.17 + 2.00(\rho-\rho_0)/\rho_0 \quad , \qquad (8)$$

while the resulting energy fits well the following expression:

$$(1/N)\,E^{\mathrm{MW}}_{\mathrm{corr}}(\rho) = -7.14 + (16.0 \pm 0.6)\,(\rho-\rho_0)^2/\rho_0^2 + (10.2 \pm 4.5)(\rho-\rho_0)^3/\rho_0^3 . \qquad (9)$$

For the Schiff-Verlet (SV) calculation, the corresponding expressions are

$$(1/N)\Delta E^{\mathrm{SV}}(\rho) = -1.40 - 3.62(\rho-\rho_0)/\rho_0$$

and

$$(1/N)E^{\mathrm{SV}}_{\mathrm{corr}}(\rho) = -7.14 + (14.9 \pm 0.4)(\rho-\rho_0)^2/\rho_0^2 + (2.6 \pm 2.8)(\rho-\rho_0)^3/\rho_0^3 \qquad (10)$$

Note that for $(\rho-\rho_0)/\rho_0 \lesssim 20\%$, both the MW and the SV correction series, indeed, appear to converge rapidly. Figure 2 compares $E(\rho)$, $E^{\mathrm{MW}}_{\mathrm{corr}}(\rho)$, and $E^{\mathrm{SV}}_{\mathrm{corr}}(\rho)$.

Using the thermodynamic relations

$$P(\rho) = \rho^2 \frac{d}{d\rho}\left(\frac{E(\rho)}{N}\right) , \qquad (11)$$

$$mc^2(\rho) = \frac{d}{d\rho}\, P(\rho) , \qquad (12)$$

$$u(\rho) = \frac{\rho}{c(\rho)}\, \frac{d}{d\rho}\, c(\rho) , \qquad (13)$$

we find $c^{\mathrm{MW}}(\rho_0) = 257$ m/sec and $c^{\mathrm{SV}}(\rho_0) = 248$ m/sec, in comparison with the experimental velocity of sound $c(\rho_0) = 238$ m/sec, and $u^{\mathrm{MW}}(\rho_0) = 2.96$ and $u^{\mathrm{SV}}(\rho_0) = 2.26$, in comparison with the experimental Grüneisen constant $u(\rho_0) = 2.84$.

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*Work supported in part by the U.S. Atomic Energy Commission, the National Science Foundation through Grant No. GP-11054, and the Advanced Research Projects Agency through the Materials Research Center of Northwestern University.

[1] B. M. Abraham, Y. Eckstein, J. B. Ketterson, M. Kuchnir, and P. R. Roach, Phys. Rev. A1, 250 (1970). Table III of this reference is wrong in the fifth column. The value for $w = (\rho^2/c)(d^2c/d\rho^2)$ should be corrected by subtracting the square of the entry for u in column 4.

[2] W. E. Massey and C-W. Woo, Phys. Rev. Letters 19, 301 (1967); 19, 622(E) (1967).

[3] D. Schiff and L. Verlet, Phys. Rev. 160, 208 (1967).

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Inhomogeneity Correction to Exchange Potential

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It is pointed out that the inhomogeneity correction term to the Gaspar-Kohn-Sham exchange potential proposed recently by Herman, Van Dyke, and Ortenburger follows, to within a numerical factor, from a similar correction to the statistical energy derived previously by Hohenberg and Kohn. The numerical coefficient in the latter case, obtained from Hubbard's work on electronic polarizabilities, is about four times larger than the average variational value of Herman, Van Dyke, and Ortenburger.

In a recent letter, Herman, Van Dyke, and Ortenburger[1] have used the so-called statistical model of the atom to propose the following local approximation to the nonlocal Hartree-Fock (HF) exchange potential:

$$V_X = -c_X^{(1)}[\rho(r)]^{1/3} - c_X^{(2)}G_X(\rho)\,\rho^{1/3}\,. \tag{1}$$

The novel feature of their proposal is the inclusion of the inhomogeneity correction term

$$G_X(\rho) = \rho^{-2/3}\left[\tfrac{4}{3}(\nabla\rho/\rho)^2 - 2\nabla^2\rho/\rho\right]. \tag{2}$$

In their work, Herman, Van Dyke, and Ortenburger take $c_X^{(2)}$ (and, initially $c_X^{(1)}$) to be a variational parameter determined by minimizing the total HF energy. They find that for the ground states of the atoms considered (Ar, Cu$^+$, Kr, and Xe), $c_X^{(1)}$ turns out to be essentially $(3/\pi)^{1/3}e^2$, the value obtained from statistical energy extremization by Gaspar[2] and Kohn and Sham,[3] while $c_X^{(2)}$ is about $\frac{3}{2}(0.005)\,c_X^{(1)}$ for the above cases. Herman, Van Dyke, and Ortenburger suggest that as far as the local approximation to the HF exchange potential is concerned, the Gaspar-Kohn-Sham value can be assumed to be a first-principles result derivable from independent considerations. But, they suggest, in the absence of a first-principles value of $c_X^{(2)}$, it should be treated as a variable or empirical parameter.

Herman, Van Dyke, and Ortenburger arrive at their form for V_X by adding the inhomogeneity correction

$$c_X^{(2)}\int\left[(\nabla\rho)^2/\rho^{4/3}\right]d^3r \tag{3}$$

to the usual statistical expression for the total energy, analogously to the addition of the Weizsäcker inhomogeneity correction[4,5]

$$c_K^{(2)}\int\left[(\nabla\rho)^2/\rho\right]d^3r$$

to the kinetic energy term. We wish to point out that the form for V_X suggested by these authors is, in fact, implicit in the work of Hohenberg and Kohn,[6] who derive, in an approximate way, the form of the kinetic and exchange inhomogeneity corrections given above [Eq. (92) of Ref. 6] from Hubbard's work on electronic polarizability.[7] Furthermore, the constant $c_X^{(2)}$, extracted from their expression, turns out to be $\pi(3\pi^2)^{-4/3}e^2 = \frac{3}{2}(0.023219)\,c_X^{(1)}$, about four times larger than the variational value of Herman, Van Dyke, and Ortenburger. Albeit, this fundamental value of $c_X^{(2)}$ has inherent in it the inaccuracies associated with the approximations made in deriving (3), but then the