

- DAGENS, L., 1971, *J. Phys.*, at press.
 GELDART, D. J. W., and TAYLOR, R., 1970, *Can. J. Phys.*, **48**, 155-65.
 GELDART, D. J. W., and VOSKO, S. H., 1966, *Can. J. Phys.*, **44**, 2137-71.
 HARRISON, W. A., 1969, *Pseudopotentials in the Theory of Metals* (New York: Benjamin).
 HERMAN, F., VAN DYKE, J. P., and ORTENBURGER, I. B., 1969, *Phys. Rev. Lett.*, **22**, 807-11.
 HOHENBERG, P., and KOHN, W., 1964, *Phys. Rev.*, **136**, B 864-71.
 HUBBARD, J., 1957, *Proc. R. Soc. A*, **243**, 336-52.
 KLEINMAN, L., 1967, *Phys. Rev.*, **160**, 585-90.
 KOHN, W., and SHAM, L. J., 1965, *Phys. Rev.*, **140**, A 1133-38.
 SINGWI, K. S., TOSI, M. P., LAND, R. H., and SJÖLANDER, A., 1968, *Phys. Rev.*, **176**, 589-99.
 SHAW, R. W. JR., 1970, *J. Phys. C: Solid St. Phys.*, **3**, 1140-58.
 SLATER, J. C., 1951, *Phys. Rev.*, **81**, 385-91.

The ground state energy, pressure and compressibility of solid ^3He at high pressures.

Abstract. The ground state energy, pressure and compressibility of solid ^3He were calculated in the molar volume range 12 to 18 cm³ using the improved selfconsistent phonon theory of Goldman *et al.* A soft core potential due to Beck was used and relatively good agreement was obtained with experiment for the pressure and compressibility.

In a recent paper (Chell 1970, to be referred to as I) we calculated the compressibility of solid ^3He and ^4He in the molar volume range 12 to 18 cm³. Selfconsistent phonon theory (SCP) was used and short range correlations (src) were omitted. A nearest neighbour interaction, face centred cubic model was used. We gave reasons for believing that for isotropic crystal properties this model reproduces the main features of a hexagonal close packed model. In this letter we wish to report on the extension of the calculations for solid ^3He .

First, instead of the Lennard-Jones (12-6) (L-J) potential a new potential, $\phi(r)$, due to Beck (1968) was used in the calculations where

$$\phi(r) = A \exp(-ar - \beta r^6) - \frac{0.869}{(r^2 + a^2)^3} \left(1 + \frac{2.709 + a^2}{r^2 + a^2} \right)$$

with $a = 0.675 \text{ \AA}$, $\alpha = 4.390 \text{ \AA}^{-1}$, $\beta = 3.746 \times 10^{-4} \text{ \AA}^{-6}$ and $A = 398.7 \text{ eV}$.

This potential has several advantages over the L-J potential. It has a nonsingular core at the origin which made accurate calculations possible over the complete molar volume range considered. The difficulties arising from the singular core in the L-J potential have been discussed in I.

The ground state energy of body centred cubic ^3He has been computed by Glyde (1971) using both the Beck and L-J potentials. The former gave a lower ground state energy than did the latter. Lastly, but not least, the Beck potential was fitted to experimental and theoretically determined potentials down to an internuclear separation of 0.5 Å and thus reproduces the repulsive part of the He-He potential more accurately than the L-J. Secondly, the calculations were extended to include all neighbour interactions, a necessary step if the ground state energy is to be determined accurately over the volume range considered. Thirdly, the leading second order correction, ΔF , to the first order SCP energy, F_{sc} , was included in the calculations using the improved selfconsistent approximation (ISC) introduced by Goldman *et al.* (1968). In this letter the notation and definitions of I and Goldman *et al.* (1968) are used wherever possible. We have

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The exact effective wave function ϕ_k is then used as a trial function in the variational formula (4). The two $T\{\}$ terms cancel each other and (4) becomes simply $E_X \leq \mathcal{E}_X$. \mathcal{E}_X is first expressed in terms of $a_q(k)$ ($q \neq 0$), deleting third and higher order terms. The result is $E_X^0 + E_A + E_B$ with

$$E_A = -2\Omega \sum_{kk'q}^{\text{occ}} a_q^*(k) a_q(k') \{v(k+k'+q) + v(k-k')\} \quad (8)$$

$$E_B = -2\Omega \sum_{kk'q}^{\text{occ}} |a_q(k)|^2 \{v(k+k'+q) - v(k-k')\}.$$

The approximation (7) is then substituted in equation (8), the resulting expression being exact up to $O(\lambda^2)$. \mathcal{E}_X then has the form (5), with the same E_X^0 . The inequality (4) (with $\psi_k \equiv \phi_k$) must be true for every value of λ and n_q/λ . We then get the important result

$$X(q) \leq X_I(q) \equiv -\frac{\pi_{AB}(q)}{\pi_0(q)^2} \quad (9)$$

with

$$\pi_{AB} = \pi_A + \pi_B$$

and

$$\pi_A = \left[\frac{4m}{\hbar^2}\right]^2 \sum_{kk'}^{\text{occ}} \frac{v(k+k'+q) + v(k-k')}{(q^2 + 2q \cdot k)(q^2 + 2q \cdot k')} \quad (10)$$

$$\pi_B = \left[\frac{4m}{\hbar^2}\right]^2 \sum_{kk'}^{\text{occ}} \frac{v(k+k'+q) - v(k-k')}{(q^2 + 2q \cdot k)^2}$$

The integrals $\pi_{A,B}$ are identical to the two first order polarization graphs (exchange and self energy graphs). The numerical values of $\pi_{AB}(q)/\pi_{AB}(0)$ were given by Geldart and Taylor (1970) for $q \leq 2k_F$. Their method is used in I to obtain π_{AB} in the range $q > 2k_F$. The screening function π_I corresponding to X_I is identical to the expression proposed by Geldart and Taylor, who use first order perturbation theory, with an arbitrary interpolation procedure to include the effect of the higher HF graphs. This interpolation is done here in a natural way when solving the HFKS equations.

Another advantage of the present variational method is that it leads to the useful inequality (9). Bounds for $\epsilon(q)$ and $\tilde{\epsilon}(q)$ follow from the exact formulas (1) and (2)

$$\epsilon(q) \geq \epsilon_I(q) \quad (11)$$

$$\tilde{\epsilon}(q) < \tilde{\epsilon}_I(q) \quad (12)$$

where ϵ_I and $\tilde{\epsilon}_I$ are given in terms of X_I by the same formulas.

The behaviour of $X_I(q)$ is established in I. $X_I(<0)$ is exact when $q \rightarrow 0$ and $q \rightarrow \infty$, and presents a sharp minimum for $q \sim 1.9 k_F$. The exact $X(q)$ has necessarily the same behaviour, in qualitative disagreement with the approximations proposed by Hubbard (1957), Kleinman (1967) and many other authors. The very interesting method of Singwi *et al.* (1968), also used by Shaw (1970), leads to an incorrect behaviour in the range $q < 2k_F$, when applied in the HF framework (formula (22) of Singwi *et al.*). Herman *et al.* (1969) introduced an inhomogeneity correction to V_{XKS} in a semiempirical way. It is shown in I that the corresponding effective exchange interaction is in qualitative agreement with our results in the range $q < 2k_F$ but is quite wrong, of course, when $q \geq 2k_F$, which is a quite significant range in solid state calculations.

system. This method will be referred to as the HFKS method. It involves a local effective exchange potential $V_X = \delta E_X[n]/\delta n(\mathbf{r})$ where the effective exchange energy E_X is a universal functional of the electron density $n(\mathbf{r})$. Only approximate forms of E_X and V_X are known. The Kohn and Sham approximation V_{XKS} ($= 2/3$ Slater's potential) is valid for electron systems with slowly varying density (as in heavy atoms) but cannot be used in principle in band calculations where wave numbers q larger than k_F are quite significant (Geldart and Vosko 1966).

The HF test particle static dielectric function $\epsilon(q)$ and the HF electron dielectric function $\tilde{\epsilon}(q)$ of a homogeneous electron gas (Kleinman 1967, Shaw 1970) are directly related to the HF density response to an external potential. They are exactly given by the linearized HFKS equations, since the Kohn and Sham method allows an exact calculation of the ground state HF energy functional and its derivatives, such as the density and the Fermi level. A simple calculation (Harrison 1969) gives

$$\epsilon(q) = 1 + \frac{v(q)\pi_0(q)}{1 + X(q)\pi_0(q)} \quad (1)$$

$$\tilde{\epsilon}(q) = 1 + \{v(q) + X(q)\}\pi_0(q) \quad (2)$$

where $v(q)$ is the direct interaction function $4\pi e^2/q^2$, $\pi_0(q)$ the RPA static screening function and $X(q)$ the effective exchange interaction defined by equation (5) below.

We use a new variational method for $E_X[n]$ (Dagens 1971; this paper will be referred to as I), to derive an upper bound for $X(q)$ and, as a consequence, a lower bound for $\epsilon(q)$ and upper bound for $\tilde{\epsilon}(q)$, which are exact in the HF scheme.

An inequality verified by $E_X[n]$ is given first. The derivation is given in I. The exact solution of the HFKS equation is known to be a functional $\phi_k[n]$ of $n(\mathbf{r})$ (Hohenberg and Kohn 1964) which satisfies identically equation (3). Let $\psi_k[n]$ be a trial wave function which satisfies

$$\sum_{k\sigma}^{\text{occ}} |\psi_k[n]|^2 \equiv n \equiv \sum_{k\sigma}^{\text{occ}} |\phi_k[n]|^2. \quad (3)$$

We denote by $\mathcal{E}_X\{\psi_k\}$ the well known expression of the true exchange energy and by $T\{\psi_k\}$ the total kinetic energy. The fundamental formula is then

$$E_X[n] \leq \mathcal{E}_X\{\psi_k[n]\} + T\{\psi_k[n]\} - T\{\phi_k[n]\}. \quad (4)$$

The equality is obtained when the trial wave function is identical (as a functional of n) to the exact HF wave function. The second member is then stationary. It must be noted that the value of E_X is generally not equal to the true exchange energy.

We consider an electron gas perturbed by a small external potential $\lambda V_0(\mathbf{r})$. The effective exchange energy $E_X[n]$ can be written (Harrison 1969) as

$$E_X[n] = E_X^0(n_0) + \frac{\Omega}{2} \sum_q' |n_q|^2 X(q) + O(\lambda^3) \quad (5)$$

where $E_X^0(n_0)$ is the exchange energy of the homogeneous system and $X(q)$ the effective exchange interaction. The summation is over all nonzero wave vectors q , and n_q is the Fourier coefficient of the density (mean value of $n(\mathbf{r}) \exp(-i\mathbf{q}\cdot\mathbf{r})$). Let $a_q(k)$ be the Fourier coefficient of $\phi_k \exp(-i\mathbf{k}\cdot\mathbf{r})$, with the following normalization

$$a_0(k)^2 = 1 - \sum_q' |a_q(k)|^2. \quad (6)$$

$a_q(k)$ and n_q are known to be first order quantities in λ . A simple calculation leads to

$$a_q(k) = \frac{2m}{\hbar^2} \frac{1}{|\mathbf{k} + \mathbf{q}|^2 - k^2} \frac{n_q}{\pi_0(q)} + O(\lambda^2) \quad (7)$$

when $q \neq 0$.

example, by comparing the calculations of Hurst (1959) for LiH with the observed structure factors, Calder *et al.* (1962) obtained $R = 0.02$ which shows an order of magnitude better agreement.

Phillips and Weiss (1969) measured the Compton profile of LiH using Mo K α X rays scattered along three different crystallographic directions. Since they did not obtain appreciable anisotropy, they averaged their results over the three directions. The Compton profile is the projection of the electron momentum distribution on the direction of the momentum transfer. It is given by

$$J(p_{0z}) = 2\pi \int_{p_{0z}}^{\infty} |\chi(p_0)|^2 p_0 dp_0 \quad (4)$$

where p_{0z} is the projection of the initial electron momentum p_0 on the momentum transfer direction z . Assuming s like wave functions, we have

$$\chi(p_0) \propto \int_0^{\infty} P(r) j_0(p_0 r) r dr \quad (5)$$

We calculated the Compton profile of LiH using equation (4) and (5), and the wave functions of Kunz. In figure 1 we compare these calculations with the experimental curve of Phillips and Weiss. It is seen again that there is marked disagreement between experiment and the wave functions calculated by Kunz.

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ADAMS, W. H., 1962, *J. chem. Phys.*, **37**, 2009–18.

CALDER, R. S., COCHRAN, W., GRIFFITHS, D., and LOWDE, R. D., 1962, *J. Phys. Chem. Solids*, **23**, 621–32.

GILBERT, T. L., 1964, *Molecular Orbitals in Chemistry, Physics and Biology*, Eds P. O. Löwdin and B. Pullman (New York: Academic Press).

HURST, R. P., 1959, *Phys. Rev.*, **114**, 746–51.

KUNZ, A. B., 1969, *Phys. Stat Solidi*, **36**, 301–9.

PHILLIPS, W. C., and WEISS, R. J., 1969, *Phys. Rev.*, **182**, 923–5.

WYCKOFF, R. W. G., 1963, *Crystal Structures*, Vol. 1, 2nd Edn. (New York: Wiley).

Bounds for the Hartree-Fock effective exchange interaction and the static dielectric constants

Abstract. We use a variational form of the Kohn and Sham general effective exchange energy to derive an upper bound for the effective exchange interaction. Exact bounds (within the Hartree-Fock scheme) are deduced for the usual (test particle) static dielectric constant and the electron-dielectric constant.

Kohn and Sham (1965) showed that a Hartree-Fock-Slater like method (Slater 1951) allows an exact calculation of the Hartree-Fock (HF) ground state energy of an electron

Anisotropy of the cubic Fe_3S_4 induced in an electrostatic field

Abstract. A synthetic iron sulphide of spinel type became anisotropic when immersed in an electrostatic field. Analysis of the electron diffraction patterns observed from the Fe_3S_4 specimens showed that a preferred induction took place at about 313 K along the [111] axis in the crystal. This anisotropy became negligibly small over about 373 K.

An aqueous suspension of synthetic iron sulphide (Fe_3S_4 , space group: $Fd3m$, spinel structure, $a_0 = 9.87 \text{ \AA}$) was smeared on a smooth surface of mica lamina, about $3 \times 3 \times 0.1 \text{ mm}^3$ in size. The thickness of the sulphide layer deposited was about one micron. The specimen was then investigated in terms of electron diffraction. The disposition of the experiment is illustrated in figure 1. A monoenergetic electron beam served for charging up the

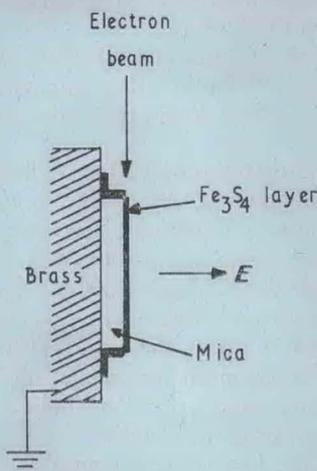


Figure 1. This shows the Fe_3S_4 layer deposited on a mica surface. A monoenergetic electron beam plays three roles, to charge up the mica layer, to heat the sulphide film and to undergo diffraction at it. E is the electrostatic field.

specimen with electrons (Yamaguchi 1966), for heating it by means of electron bombardment (Yamaguchi 1962), and for carrying out the diffraction experiments (Yamaguchi 1968).

The diffraction patterns observed are shown in figures 2 and 3, which correspond to the

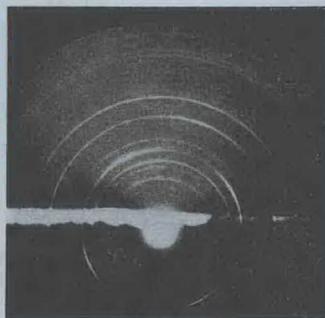


Figure 2. This shows the diffraction pattern from the sulphide specimen in figure 1. At a temperature of about 313 K. The reference pattern of gold is superimposed on the specimen pattern, and the (333) reflection from the sulphide shows a preferred displacement. Wavelength of the electrons: 0.0440 \AA (75 kV), camera length: 50 cm.

Also included in the figures are the theoretically calculated values of Horner (1970), who used a L-J potential and summed ladder diagrams to all orders to produce src, and the results of experiments.

From the results several conclusions and comments can be made. Although ΔF changes the SCP ground state energy considerably (see figure 1) it produces very little change in the volume derivatives of the free energy (the SCP pressure and compressibility are not shown in figures 2 and 3 as their difference between the ISC values is so small that their inclusion would only detract from the clarity of the graphs). The pressure and compressibility are in relatively good agreement with experiment. We found that the compressibility curve calculated in this work lay virtually on top of the ^3He curve that was calculated in I using the L-J potential. For this reason that curve is not reproduced here. The SCP ground state energy is far too high. ΔF is of the right sign and magnitude to lower the energy and produce a value closer to Horner's (1970) result. It must be noted, however, that since ΔF is large compared with F_{sc} (nearly half its value at 18 cm^3) the original philosophy of ISC of treating it like a perturbation on the SCP free energy is questionable. The contribution of the next to the leading term of the second order theory, involving the fourth order force constant squared, might also be substantial. It is interesting to note, however, that this term is also likely to contribute a negative energy and lower the ISC ground state energy even more.

The use of the soft core Beck potential removed the computational difficulties involved in the hard core L-J potential calculations. Accurate numerical results could be obtained over the full volume range considered without recourse to src. Nevertheless the deep penetration of the SCP Gaussian wavefunction into the core of the repulsive part of the helium potential is physically unrealistic, and, we believe, is one of the major reasons for the very high value obtained for the ground state energy using SCP. SCP theories that include src (see for example Koehler 1967) lower the ground state energy considerably. These theories clearly contain greater anharmonicities than are involved in SCP alone and this is illustrated somewhat in the present work where higher order anharmonic terms have been included in SCP within the framework of ISC.

I wish to thank Professor G. K. Horton for suggesting the present work and for many helpful discussions concerning it. Acknowledgements are also due to Dr V. V. Goldman for use of his computer programme to calculate ΔF . I also wish to thank Dr G. C. Straty for drawing my attention to the experimental 18 cm^3 molar volume compressibility data. Financial support of the US Air Force Office of Scientific Research under grant No. AFOSR 68-1372 and the Rutgers Research Council under grant No. Quantum Crystals 07-2180 is also gratefully acknowledged.

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- BECK, D. E., 1968, *Mol. Phys.*, **14**, 311-5.
CHELL, G. G., 1970, *J. Phys. C: Solid St. Phys.*, **3**, 1861-5.
GLYDE, H. R., 1971, *Can. J. Phys.*, **49**, 761-75.
DUGDALE, J. S., and FRANCK, J. P., 1964, *Phil. Trans. R. Soc.*, **257**, 1-29.
GOLDMAN, V. V., HORTON, G. K., and KLEIN, M. L., 1968, *Phys. Rev. Lett.*, **21**, 1527-9.
HORNER, H., 1970, *Phys. Rev.*, **1**, A 1722-29.
KOEHLER, T. R., 1967, *Phys. Rev. Lett.*, **18**, 654-6.
STRATY, G. C., and ADAMS, E. D., 1968, *Phys. Rev.*, **169**, 323-40.

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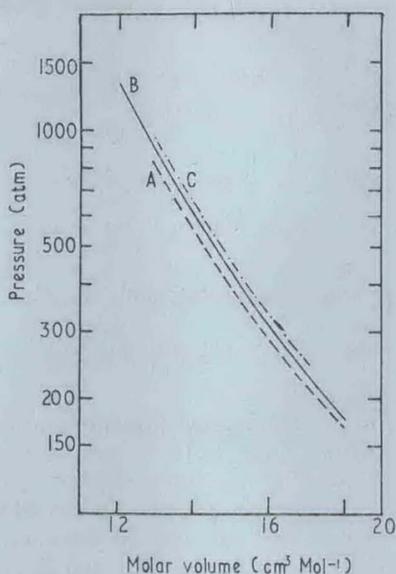


Figure 2. Pressure against molar volume for ³He. Curve A, Horner (1970); curve B, P_{ISC} , present paper; curve C, Experiment (Dugdale and Franck 1964).

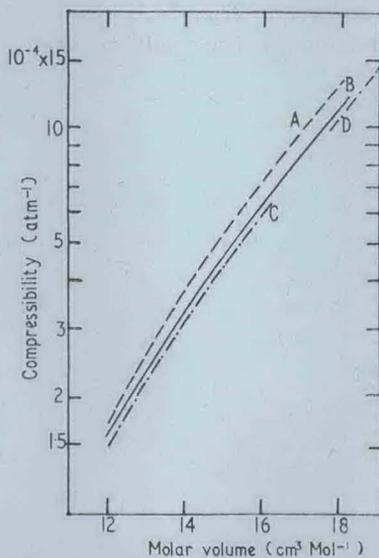


Figure 3. Compressibility against molar volume for ³He. Curve A, Horner (1970); curve B, X_{ISC} , present paper; curve C, Experiment (Dugdale and Franck, 1964); curve D, Experiment (Straty and Adams 1968).

$$F_{sc} = \frac{1}{2}N \sum_k \langle \phi^k \rangle_{sc} + \sum_{qs} (f_{qs} - \frac{1}{2}u_{qs}) \quad (1)$$

and

$$\Delta F = - \frac{\hbar^2}{48M^3N} \sum_{1,2,3} \frac{\Delta(q_1 + q_2 + q_3)}{\omega_1\omega_2\omega_3} W_{123} |\Psi(1,2,3)|^2 \quad (2)$$

where

$$W_{123} = (n_1n_2 + n_2n_3 + n_3n_1 + n_1 + n_2 + n_3) (\omega_1 + \omega_2 + \omega_3)^{-1} \\ + 3(n_2n_3 + n_3n_1 - n_1n_2 + n_3) (\omega_1 + \omega_2 - \omega_3)^{-1}$$

and

$$\Psi(1,2,3) = -4i \sum_k \exp \{i(q_1 + q_2 + q_3) \cdot \mathbf{R}_k/2\} \sin(\frac{1}{2}q_1 \cdot \mathbf{R}_k) \\ \times \sin(\frac{1}{2}q_2 \cdot \mathbf{R}_k) \sin(\frac{1}{2}q_3 \cdot \mathbf{R}_k) e_{\alpha}(1)e_{\beta}(2)e_{\gamma}(3) \langle \phi_{\alpha\beta\gamma}^k \rangle_{sc}$$

The ISC free energy, $F_{ISC} = F_{sc} + \Delta F$.

With these changes the ground state energy, pressure and compressibility of solid ^3He were calculated in the molar volume range 12 to 18 cm^3 . In the computations it was found necessary to smear up to and including the third neighbours only, the effects of smearing the force constants beyond this point were negligible. ΔF was calculated using the frequencies of the all neighbour model but including only nearest neighbours in the lattice sums.

The contribution, ΔP , of ΔF to the pressure, P_{ISC} , and ΔB , to the bulk modulus, B_{ISC} , and hence the compressibility χ_{ISC} , were determined by numerical differentiation using the expressions

$$P_{ISC} = - \left(\frac{\partial F_{ISC}}{\partial V} \right)_T = P_{sc} + \Delta P$$

and

$$B_{ISC} = V \left(\frac{\partial^2 F_{ISC}}{\partial V^2} \right)_T = -V \left(\frac{\partial P_{ISC}}{\partial V} \right)_T \\ = B_{sc} + \Delta B = \chi_{ISC}^{-1}. \quad (3)$$

Subscript ISC refers to quantities calculated using the improved selfconsistent theory. P_{sc} was determined from the expression given in equation (2.2) of I, and B_{sc} by numerical differentiation of P_{sc} using equation (3). The results are shown graphically in figures 1 to 3.

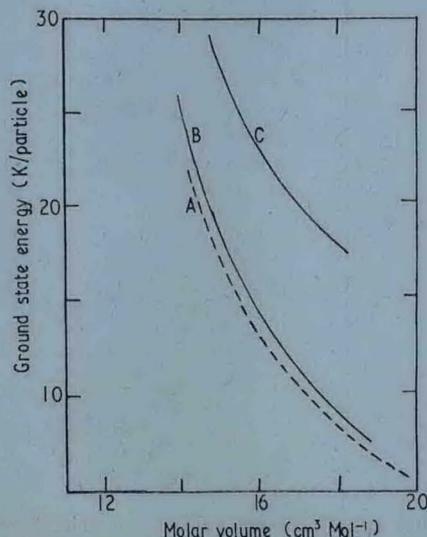


Figure 1. Ground State energy of ^3He against molar volume. Curve A, Horner, (1970); curve B, $F_{ISC} = F_{sc} + \Delta F$, present paper; curve C, F_{sc} , present paper.