propagate and are parametrically unstable at wide angles to the magnetic field. In any event, this is not an important point since n_{HOT} is determined by v_1, and v_1 is determined by $I(0)$, the spectrum along the pump and magnetic field. As for convection, we will find that $v_1 < 3v_e$, which is sufficiently small that convection may not be important. Furthermore, the spectrum we have used does give reasonable agreement with the rate of anomalous absorption observed at large P[6] Let us then calculate n_{HOT} with (21) for $P = 32$ at $\omega_e^2/\omega^2 = 0.94$, and $P = 14$ at $\omega_e^2/\omega^2 = 0.77$. Both cases qualify for perturbed-orbit saturation since in the former case, the wave energy is not much less than the electron thermal energy and in the latter case $k_{\mathrm{D}}/k_m \approx 4$. In the former case we substitute $P = 32$ and $k_m/k_{\mathrm{D}} = 0.15$ into (15), (18), and (16) and simultaneously solve to obtain $I(0)(4\pi nKT_e)^{-1} = 0.375$, $\omega_d/k_m = 0.81v_e$, $v_1 = 2.7v_e$ In this calculation we have taken $\omega_e/\nu = 2\times 10^4$ since $\omega_e/\nu_c \approx 10^3$ and, for $v_1 = 2.7v_e$, $\nu_c/\nu \approx 20$. Using (22) we find that $v_c = 2.3v_e$ so that the modified f will not change the spectral energy. Substituting $v_1 = 2.7v_e$ into (21) we have $n_{\mathrm{HOT}}/n \approx 0.36 \times 10^{-2}$ which is about half the experimental value of 0.77×10^{-2}. For the case $P = 14$, $\omega_e^2/\omega^2 = 0.77$, $k/k_{\mathrm{D}} = 0.25$ we solve (15), (18), and (16) to obtain $I(0)(4\pi nKT_e)^{-1} \approx 0.056$, $\omega_d/k_m \approx 0.31v_e$, $v_1 = 2.73v_e$. This gives, with (21), $n_{\mathrm{HOT}}/n \approx 0.33\times 10^{-2}$, compared to the experimental value of 0.75×10^{-2}. In this case we find that $v_c \approx 3.0v_e$ so that v_c and v_1 differ by only one trapping velocity and f cannot change $I(0)$ by much.

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Character of the Pair Interaction in Solid and Gaseous H_2†

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Existing theoretical H_2 pair potentials are investigated. We develop a spherically symmetric potential applicable to solid H_2. It yields a ground-state energy of -98.7 K (experimental values range from -93.5 to -101 K). Pressure-volume data are also in excellent agreement with experiment between 0 and 25 kbar. Second virial coefficients using this potential are consistently too low. When an anisotropic pair potential is used, agreement becomes very good.

Representations of the intermolecular potential have only recently become adequate for theoretical descriptions of the quantum solids ^{3}He and ^{4}He in both the solid and gas phases.[1] Major discrepancies remain for molecular H_2.[2] It is apparent that molecular H_2 properties cannot be predicted in terms of any known phenomenological potential.[2-4] If the potential form and/or its parameters are adjusted to fit one set of experimental properties, other properties are poorly predicted.

The work reported in this Letter is directed toward this discrepancy and the problem of predicting ground state properties in solid H_2. We employ *ab initio* calculations of the pair potential, and thus make no assumptions regarding anisotropy. The potential separates into four parts,

$$U = U_{QQ} + U_{DD} + U_{QD} + U_V, \qquad (1)$$

where

$$U_{QQ}=0.048\,05 f(\theta_1,\theta_2,\varphi_1-\varphi_2)/r^5 \qquad (2)$$

is the quadrupole energy[5] with

$$f=1-5(\cos^2\theta_1+\cos^2\theta_2+3\cos^2\theta_1\cos^2\theta_2)$$
$$+2[4\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)]^2;$$

$$U_{DD}=-[g(\theta_1,\theta_2,\varphi_1-\varphi_2)+11.133]/r^6 \qquad (3)$$

is the Van der Waals energy[6] with

$$g=0.2002[\sin\theta_1\sin\theta_2\cos(\varphi_1-\varphi_2)$$
$$-2\cos\theta_1\cos\theta_2]^2+1.672(\cos^2\theta_1+\cos^2\theta_2);$$

$$U_{DQ}=116/r^8 \qquad (4)$$

is the induced dipole-quadrupole energy,[5] and U_V is the valence energy. The quantities (θ_1,φ_1) and (θ_2,φ_2) are the angular orientations of molecules 1, 2 with respect to r, the separation between their centers of mass. All quantities are in atomic units.

Equations (2)-(4) are the most recent multipole determinations. The valence energy U_V, which comes from the overlap of the wave function, dominates at short range. The atomic-orbital calculations investigated were by Evett and Margenau (EM),[7] Mason and Hirschfelder (MH),[8] Magnasco and Musso,[9] Tapia, Bessis, and Bratos (self-consistent field),[10] and de Boer.[11] Spherical averages of these theoretical valence potentials, obtained using the method of EM,[7] are shown in Fig. 1 along with the Lennard-Jones (6-12) potential obtained from second virial coefficients.[3] There are two important observations: (1) All theoretical averages are remarkably similar (the agreement is even more striking if MH is discounted, which is not unreasonable since MH state in their paper that EM is probably more accurate), and (2) 6-12 has a much more repulsive core than any of the other potentials.

Figure 2 shows several empirical potentials[12,13] and the spherically averaged theoretical potential obtained using the EM valence energy. It is again apparent that the 6-12 is much harder than any of the others.

Figure 3 shows P-V results calculated with 6-12.[14] As can be seen, the agreement with experiment[15,16] is poor except at low pressures. Similar results are obtained with an exp-6 potential.[17] The 6-12 ground-state energy is − 85.47 K.[14] Experimental values range from − 93.47[15] to − 101 K[18] with the former number probably most reliable. There is ample evidence[2,14,17] that the problem is with the potential rather than the theory, although there has been some question about experiment until recently.[16] An unambiguous resolution of this discrepancy requires calculations using *ab initio* potentials that can be understood theoretically.

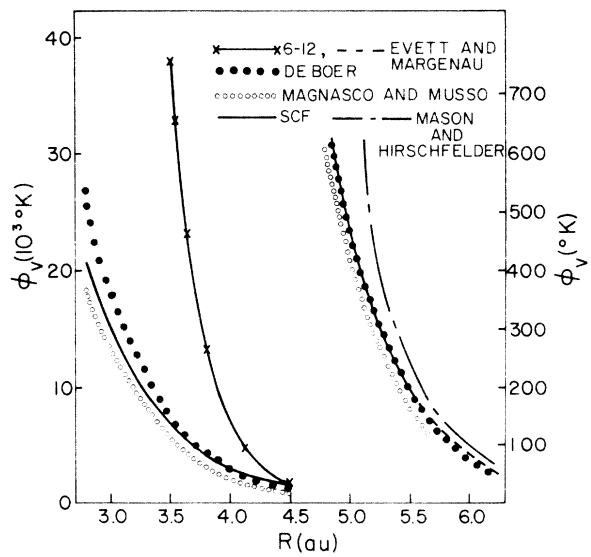

FIG. 1. Comparison of theoretical valence potentials. The left- (right-) hand ordinate applies to the left- (right-) hand side of the figure.

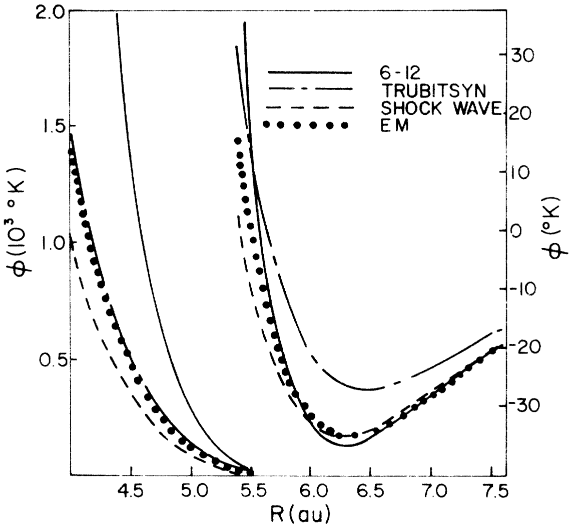

FIG. 2. Comparison of empirical potentials with the theoretical spherically averaged potential. Trybitsyn's potential reproduces experimental P-V results and 6-12 reproduces experimental second virial coefficients. The ordinates are used as in Fig. 1.

For the orientationally disordered solid, a spherical average of the EM valence potential and Eqs. (2)–(4) is a good representation of the effective pair interaction. The method of calculation[19] is a local-field variational approximation with a trial wave function

$$\Phi(\vec{r}) = \prod_{i=1}^{N} \varphi(\vec{r}_i) \prod_{j<k}^{N} f(r_{jk}),$$

where N is the total number of molecules. The φ's reflect spatial order in the solid and the $f(r)$ account for short-range pair correlations. An analytic form used previously[20] is found to be quite satisfactory. We calculate the energy of all pairs (λ, k) in the molecular field (MF) produced by the $N-2$ other molecules. Correlations between the $N-2$ other molecules and (λ, k) are contained in the MF, but it does not contain correlations $f(r_{ij})$ between MF molecules themselves. In practice only correlations from the two nearest-neighbor shells around λ and k are needed, and then only when λ and k are themselves first, second, or third nearest neighbors. Correlations from more remote shells are calculated by assuming the MF molecules are fixed on their fcc lattice sites. The theory gives almost the same results as earlier Monte Carlo work on ^{3}He, ^{4}He, and H_2.[14,20] (For further details see Ref. 19.) The calculated ground-state energy, -98.7 ± 2 K, and the P-V results (Fig. 3) are in good agreement with experiment.

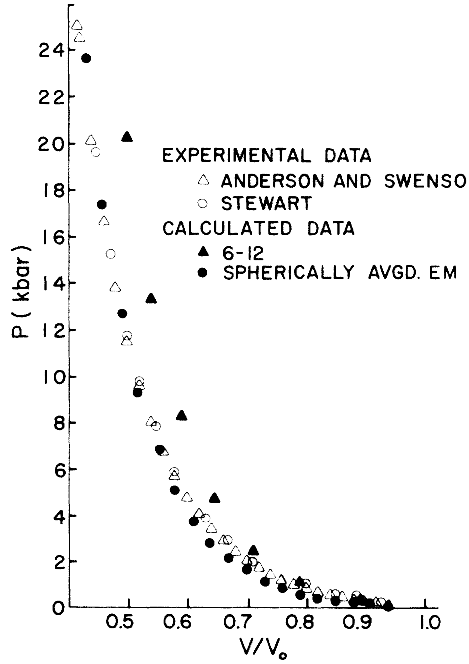

FIG. 3. Comparison of empirical and theoretical P-V results.

As shown in Fig. 4, phenomenological potentials *deduced from solid data* give poor second virial coefficients. This is investigated with the *theoretical*, anisotropic interaction given by Eqs. (2)–(4) and U_V(EM). The spherical average of Eq. (1), with U_V(EM), gives the second virial coefficients $B(T)$ (calculated using standard formulas[21]) shown as closed triangles in Fig. 4. They are consistently lower than experiment[3] over the entire range $98\text{ K} < T < 423$ K. In view of the good agreement among the spherical averages of different *theoretical* potentials, future refinements are not likely to change this result. Use of a *theoretical* spherically averaged potential implies that each molecule involved in a binary interaction undergoes sufficient rotary motion during the interaction to effect an averaging process. It is not true in the range $98\text{ K} < T < 423$ K; rotational periods are of the same order of magnitude as translational times. Angular correlations are undoubtedly important. The full anisotropy of the potential should be included. Using Eq. (1) with U_V(EM), $B(T)$ was calculated for each of the four configurations available (L, π, X, and T stand for linear, parallel, cross, and perpendicular orientations as given by EM). The angular integration was approximated by assigning random phase-space weights[7] to the $B(T)$ calculated for each EM configuration. This approximation scheme was tested using de Boer's analytical potential and it agreed with an exact angular integration to within 1–2%. The results are shown as open circles in Fig. 4. Agreement with experiment is excellent at high temperatures

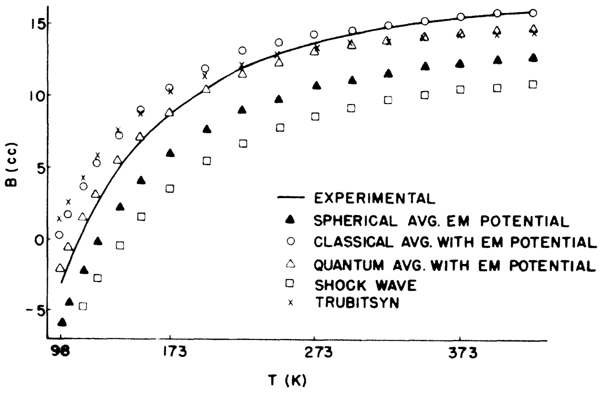

FIG. 4. Comparison of empirical and theoretical second virial coefficients.

and slowly deteriorates until $B(T)$ is 3.5 cm^3 above experiment at 98 K. This is to be expected because certain quantum effects not included in the standard formulas[21] become important at low temperatures, i.e., the discrete nature of the energy levels for $J=1$ (o-H_2) and $J=0$ (p-H_2) must be considered. It is assumed that $J=1$, 0 are good quantum numbers and that the gas exists in the statistical mixture of three parts ortho to one part para. Then,

$$B(T)=(9B_{oo}+6B_{op}+B_{pp})/16 \tag{5}$$

where B_{oo} represents $B(T)$ for interactions between two ortho molecules, etc. Since para rotational wave functions are spherically symmetric ($J=0$), B_{pp} is given by $B(T)$ for the spherical averaged potential. For two ortho molecules there are nine product states which can be labeled $|m,m'\rangle$ according to their projections. If the z axis is the quantization axis then $|0,0\rangle$ corresponds to the classical EM configuration L. We similarly identify the other cases and find the following correspondence between the other three EM configurations and quantized ortho molecules: $|T\rangle=|1,0\rangle$, $|-1,0\rangle$, $|0,1\rangle$, $|0,-1\rangle$; $|\pi\rangle=|1,1\rangle$, $|-1,-1\rangle$; $|X\rangle=|1,-1\rangle$, $|-1,1\rangle$. For the temperatures 98–423 K the nine ortho levels have equal probability, so

$$B_{oo}=(B_L+2B_\pi+2B_x+4B_T)/9, \tag{6}$$

where the subscripts refer to the EM orientations. We let $B_{op}\approx(B_{oo}+B_{pp})/2$ and Eq. (5) becomes $B=(3B_{oo}+B_{pp})/4$. If $J=1,0$ remain approximately good quantum numbers, then the quantum and classical averages should agree at high temperatures; they approximately do (see Fig. 4). Moreover, the quantum $B(T)$ are everywhere close to the experimental $B(T)$, certainly within the approximation and uncertainty in the potential itself.

To summarize, the anisotropy manifests itself in a different way in the solid, compared to the gas, and this difference is significant.

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