

Static energy of a molecular hydrogen crystal with allowance for three-particle interactions

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The static energy and the energy of the zero-point oscillations of a molecular hydrogen crystal are calculated with allowance for ternary interactions between the molecules. It is shown that the three-particle correction to the energy and to the pressure is negative and becomes comparable with the energy of the pair interaction at densities on the order of 0.8 g/cm^3 .

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In connection with the study of the transition of hydrogen into the metallic state, a number of workers have calculated the thermodynamic functions of molecular solid hydrogen at zero temperature and at pressures in the megabar range (see^[1-5]). A common shortcoming of these studies is the use of the approximation of the pair-interaction between molecules to calculate the crystal energy. This approximation is obviously incorrect near the transition point; but even far enough from the transition point, as will be seen from the results reported here, the pair-approximation is quite crude. This circumstance, as well as the need for estimating the limits of applicability of the calculations based on the pair approximation, calls for taking into account the next higher terms in the expansion of the energy over clusters containing three, four, and more molecules.^[6] In this paper, this expansion is continued to include three-molecule clusters. The calculations were performed for two crystal lattices: hexagonal close packed, and a lattice of the α -nitrogen type.

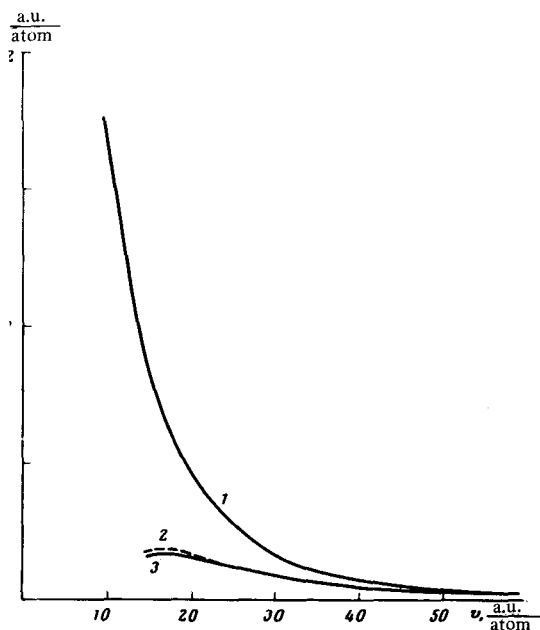


FIG. 1. Static energy for hcp lattice: 1—pair approximation with allowance for nearest neighbors only; 2—three-particle approximation with allowance for nearest neighbors only; 3—three-particle approximation with allowance for the next-nearest neighbors.

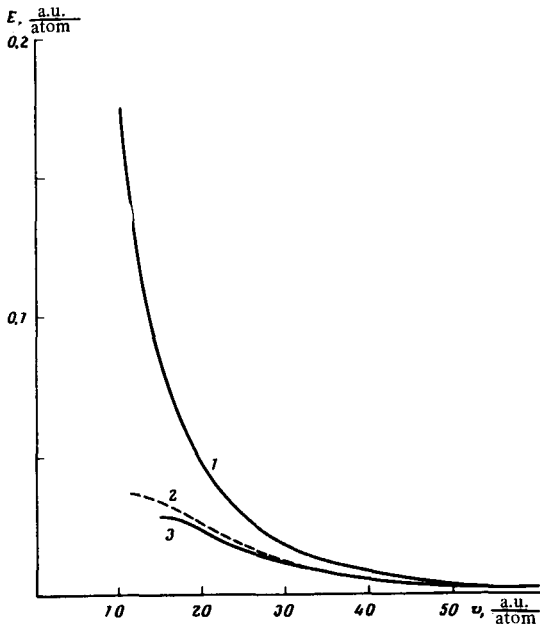


FIG. 2. Static energy for lattice of α -nitrogen type: 1—pair approximation with allowance for nearest neighbors only; 2—three-particle approximation with allowance for nearest neighbors; 3—three-particle approximation with allowance for next-nearest neighbors.

Allowance for the three-particle interactions results in an energy and a pressure lower than in the pair approximation. At a density on the order of 0.8 g/cm^3 , the correction due to the three-particle interaction becomes comparable with the energy of the pair interactions. Generally speaking, four-particle and higher-order interactions should become significant here, so that the proposed calculation ceases to be corrected. At lower densities, the equations of state obtained with account taken of the ternary forces is in better agreement with experiment^[7] than the equations of state in^[1-5].

Taking into account the three-particle interactions, the crystal energy per atom, reckoned from the energy of the free molecule, is written in the form

$$E = \frac{1}{2n} \sum_{\alpha=1}^n \left\{ \frac{1}{2} \sum_{\alpha \neq j} U_{\alpha j}^{(2)} + \frac{1}{3} \sum_{\substack{j \neq \alpha \neq k \\ j \neq k}} U_{\alpha j k}^{(3)} \right\}.$$

Here n is the number of molecules per unit cell, $U_{\alpha j k}^{(3)}$ is the three-particle contribution to the interaction energy of the molecules α , j , and k and is equal to the difference between the total energy of the three-particle complex and the sum of the single-particle energies and the energies of the pair interactions:

$$U_{\alpha j k}^{(3)} = E_{\alpha j k} - U_{\alpha j}^{(2)} - U_{\alpha k}^{(2)} - U_{j k}^{(2)} - 3E_0.$$

Analogously, the pair contribution is the difference between the total energy of the molecule pair and the sum of their single-particle energies:

$$U_{\alpha j}^{(2)} = E_{\alpha j} - 2E_0.$$

The total energies of the two- and three-particle complexes were calculated by us by the method of variation of the valence bonds with Slater orbitals of the $1S$ type. Account was taken here of all the independent covalent structures and of all such polarization structures in which the electrons of any molecule are both located at one of its nuclei. For the case of two molecules, this yields 10 basis functions; for the case of three molecules the number of basis functions is 37. The static energy of

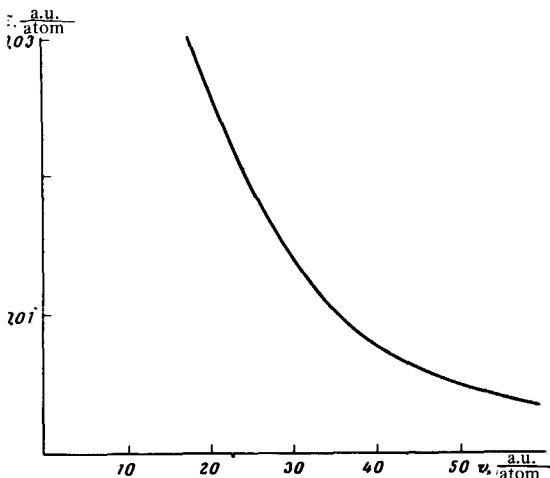


FIG. 3. Sum of static energy and zero-point oscillation energies for hcp lattice.

The crystal was calculated for a hexagonal close packed (hcp) lattice with molecule axes along the principal axis and for the structure of α nitrogen, in which the centers of the molecules form a face-centered cube, and their axes are directed along the body diagonals of this cube. In each of the lattices, the molecules have 12 nearest neighbors each. In the calculation of the three-particle interactions, account was taken of only such molecule groups in which not more than one distance between the centers of the molecules exceeds the distances between the nearest neighbors. The remaining three-particle clusters make a negligibly small contribution to the three-particle correction. For each of the lattices, we took into account 150 principal triads, among which the most substantial contribution comes from 24 triads in which all the distances are equal to the distance between the nearest neighbors. The symmetry conditions decrease the number of different configurations of the triads to 8 in the hcp lattice and 12 in the α -nitrogen lattice. For the hcp structure, in the pair-interaction approximation, we varied the ratio c/a of the height of the lattice to the length of its base. With increasing specific volume from 10 to 60 atomic units per atom, the ratio increases from 2.00 to 1.78, i.e., when the density is increased the lattice is stretched along the principal axis.

The static energy per atom as a function of the specific volume is shown in Figs. 1 and 2 for hcp and α -nitrogen lattices, respectively. The three-particle correction is negative and increases in absolute magnitude with increasing density. At $v < 15$ at.u./atom it is necessary to take into account the higher terms in the expansion of^[6]. Figure 3 shows the volume dependence of the crystal energy with allowance for the zero-point oscillations. The latter were calculated in analogy with^[1] in the Debye approximation.

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