

tion of V_{ani} to the crystal energy. Indeed, that contribution to ΔE_a which is most important in the quantum calculation actually vanishes as a consequence of the crystal symmetry if the molecules are pinned precisely at lattice sites. We shall discuss this and related points further below.

The remainder of the paper is organized as follows: Section 2 contains a review of the quantum crystal formalism and of the anisotropic potential, while section 3 describes those modifications of our formalism which are necessary to handle V_{ani} ; finally, in section 4 we present and discuss the results, assuming the crystal is 100% parahydrogen.

2. Review

2.1. Quantum crystal formalism

The self-consistent calculation given by EBNER and SUNG (1971b) of the ground state properties of quantum crystals can be summarized with several basic equations. First, the single-particle wave function $\varphi_i(1)$ of a particle localized around lattice position \mathbf{R}_i is determined from the equation*

$$\left[-\frac{\nabla_1^2}{2m} + u_i(1) \right] \varphi_i(1) = \varepsilon \varphi_i(1), \quad (1)$$

where m is the mass of a hydrogen molecule and $u_i(1)$ is the single-particle self-consistent field which is taken in the harmonic approximation

$$u_i(1) = u_0 + \frac{\alpha^4}{2m} (\mathbf{r}_1 - \mathbf{R}_i)^2. \quad (2)$$

The symbols 1, 2, etc. stand for r_1, r_2, \dots . The constants u_0 and α^2 are found by expanding the relation

$$u_i(1) = \sum_j' \int V(1, 2) \chi_{ij}(1, 2) \varphi_j^2(2) d^3r_2 \quad (3)$$

in powers of $\mathbf{r}_i - \mathbf{R}_i$. The prime on the summation sign denotes that the summation is over all $j \neq i$; $V(1, 2)$ is the interparticle interaction, and $\chi_{ij}(1, 2)$ is the two-particle correlation function for particles 1 and 2 localized around sites i and j . This function is found from the two-particle equation

$$\left\{ -\frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} + u_i(1) + u_j(2) + V(1, 2) - W_{ij}(1, 2) + \Delta_{ij}(1, 2) - \lambda_0 \right\} \varphi_i(1) \varphi_j(2) \chi_{ij}(1, 2) = 0, \quad (4)$$

* The units are such that $\hbar = k = 1$.

where

$$W_{ij}(1, 2) = \int V(1, \bar{2}) \chi_{ij}(1, \bar{2}) \varphi_j^2(\bar{2}) d^3\bar{r}_2 + \int V(\bar{1}, 2) \chi_{ij}(\bar{1}, 2) \varphi_i^2(\bar{1}) d^3\bar{r}_1, \quad (5)$$

and $\Delta_{ij}(1, 2)$ contains some three-body correlation effects. It is approximated by $p(r_{12} - R_{ij})$, where p is chosen so that the condition

$$\int (\mathbf{r}_{12} - \mathbf{R}_{ij}) \cdot \mathbf{R}_{ij} \chi_{ij}(1, 2) \varphi_i^2(1) \varphi_j^2(2) d^3r_1 d^3r_2 = 0 \quad (6)$$

is satisfied. Here $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$ and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$. The parameter p turns out to be non-zero only for nearest neighbors. Finally, the normalization of $\varphi_i(1)$ and $\chi_{ij}(1, 2)$ is specified:

$$\int \varphi_i^2(1) d^3r_1 = 1 \quad (7)$$

and

$$\int \chi_{ij}(1, 2) \varphi_i^2(1) \varphi_j^2(2) d^3r_1 d^3r_2 = 1. \quad (8)$$

Using eq. (1) and making some simple approximations, we may write the two-particle equation for χ_{ij} in the form

$$H_{00}\chi_{ij}(\xi) \equiv \left[-\frac{1}{m} \frac{d^2}{d\xi^2} + v(\xi) + \frac{\alpha^2}{m} (\xi^2 - R_{ij}^2) \frac{d}{d\xi} - W_{ij}(\xi) + p(\xi - R_{ij}) \right] \chi_{ij}(\xi) = \lambda_1 \chi_{ij}(\xi), \quad (9)$$

where $\xi = r_{12}$, $v(\xi) = V(1, 2)$, and $W_{ij}(\xi)$ is an approximation form of $W_{ij}(1, 2)$ in which it is averaged over all motions of particles 1 and 2 which can occur at constant r_{12} . These equations are solved simultaneously for χ_{ij} , φ_i and u_i .

Let us compare our method with three other recent calculations of the ground state energy in solid hydrogen. The first is the semi-classical approach of POLLOCK *et al.* (1972) in which the molecules are initially fixed on lattice sites \mathbf{R}_j for the purpose of calculating the effective field around an individual site \mathbf{R}_i . This is

$$u_i^0(1) = \sum_j' v(|\mathbf{r}_1 - \mathbf{R}_j|).$$

The next step is to put in zero-point motion, which is done using the Domb-Salter approximation for the normal modes of the system. This method has the virtue of being very simple and is also such that finite temperature can be taken into account. At the same time, because of the rather extreme approximations made, the method should be checked against more sophisticated (and presumably more accurate) calculations. This has been done by the Cornell group who find it to be reliable at sufficiently small molar volume.

KRUMHANSL and WU (1972) have given a variational calculation of E in which short-range correlations are included by introducing a Jastrow-type pair-correlation function into the trial wave function. The expectation value of the Hamiltonian and the normalization integral are evaluated using a cluster expansion, a technique used in the quantum crystal problem by NOSANOW (1966). Nosanow chooses a two-particle correlation function $f(r_{12})$ such that the peak in the function is independent of molar volume; Krumhansl and Wu, on the other hand, choose a function such that the peak moves to a smaller value of r_{12} as the volume is decreased. In our formalism, the condition expressed by eq. (6) has the same effect on our correlation function χ_{ij} . As an example, in fig. 1 we plot $\chi_{ij}(r)$ for nearest neighbors at molar volumes of 10 and 23 cm³ corresponding to nearest neighbor distances of 2.88 Å and 3.78 Å, respectively. Krumhansl and Wu introduce this behavior not only because it is physically reasonable, but also because it maintains good convergence of the cluster expansion at small molar volumes.

Finally, we mention the work of BRUCE (1972) which is also a variational calculation of E using a Jastrow-type pair correlation function in the trial wave function. Uncertainties associated with the cluster expansion are avoided by using Monte-Carlo methods to evaluate many-dimensional integrals. The procedure is the same as originally applied to solid helium by HANSEN and LEVESQUE (1968). From a theoretical point of view, it is encouraging that all of the above-described formalisms lead to comparable results for E in solid H₂ over a wide range of molar volume.

2.2. Intermolecular interaction

The interaction between a pair of parahydrogen molecules may be expanded as a sum over spherical harmonics; we shall approximate the sum by

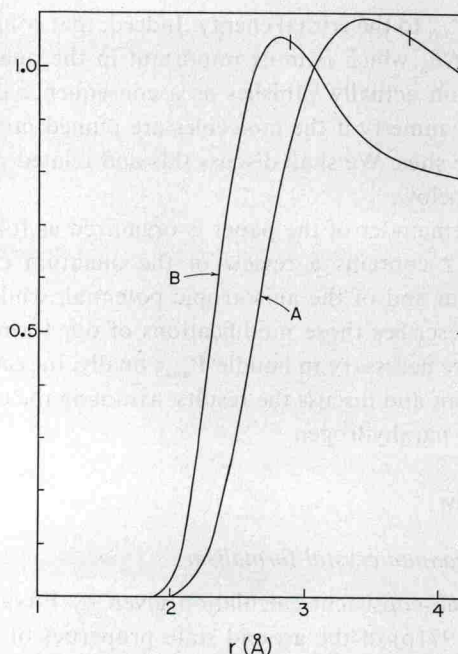


Fig. 1. Nearest-neighbor correlation functions $\chi(r)$ versus r . A: $V = 23$ cm³ corresponding to a nearest-neighbor distance $a = 3.78$ Å; B: $V = 10$ cm³ corresponding to $a = 2.88$ Å.

$$V(1, 2; \omega_1, \omega_2) = [V^{00}(1, 2) Y_0(\omega_1) Y_0(\omega_2)] \\ + [V^{02}(1, 2) Y_0(\omega_1) Y_2(\omega_2) \\ + V^{20}(1, 2) Y_2(\omega_1) Y_0(\omega_2) \\ + V^{22}(1, 2) Y_2(\omega_1) Y_2(\omega_2)], \quad (10)$$

where Y_0 and Y_2 are the spherical harmonics for $l = 0$, $m = 0$, and $l = 2$, $m = 0$; ω_1 and ω_2 refer to the directions of the interatomic axes of molecules 1 and 2 relative to the c -axis of the hcp crystal. The first term on the right-hand side of eq. (10) is just the isotropic part of the interaction,

$$(Y_0)^2 V^{00} = \frac{1}{4\pi} V^{00}, \quad V^{00} = 4\pi v(r),$$

where v is e.g. the E6 potential described in section 1.

There is no reliable empirical determination of the anisotropic part of the interaction, V_{ani} . NAKAMURA (1955) has expanded the theoretical expression of DE BOER (1942), finding for molecules in the $l = 0$ and 2 states:

$$\sqrt{\frac{1}{5}\pi} B(r) \sqrt{\frac{4}{3}\pi} \sum_m [Y_{2m}(\omega_1) Y_{2,-m}(\Omega_{12}) \\ + Y_{2m}(\omega_2) Y_{2,-m}(\Omega_{12})],$$