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## Short-range correlations in quantum crystals and motional renormalization of anisotropic interactions in solid hydrogen as a function of density

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Using moment constraints, pair-distribution functions for solid fcc H<sub>2</sub> and D<sub>2</sub> are calculated and the motional renormalization of the electric quadrupole interaction is obtained. Horner's basic concepts are followed but are improved by introducing a simpler form for the distribution function, which then allows the procedure to be carried out at high densities. Two differential equations for the short-range asymptotic behavior are investigated. Some implications of the results concerning the theory of quantum crystals are discussed.

### I. INTRODUCTION

The anisotropic interaction between hydrogen molecules is responsible for a variety of phenomena associated with the orientational degrees of freedom of these molecules. By virtue of the large zero-point motion of solid H<sub>2</sub> and D<sub>2</sub>, the translational motion has a considerable influence on the orientational dynamics. This can often be expressed in terms of orientational quantities which are renormalized by averaging over the pair distribution function of the center of mass motion.<sup>1,2</sup> However, the computation of the pair distribution function of quantum crystals is not trivial because of their large vibrational amplitude and because of short-range correlations induced by the highly repulsive anharmonic core of the intermolecular potential. The knowledge of the value of the motional renormalization (which in some cases can be high as a factor of 3) is essential for the proper interpretation of experimental data, which in turn can be used to obtain information on the bare interactions.

Horner<sup>3</sup> has recently formulated a theory for short-range correlations where the pair distribution function is parametrized so as to bear the (presumably known) short-range asymptotic behavior and constrained to produce moments of the displacements which are consistent with the lattice dynamics up to the second moment. Luryi and Van Kranendonk<sup>4</sup> have made use of the moments to obtain certain renormalizations. However, their treatment is best suited to deal with effects due to vibrational anisotropy and does not yield a pair-distribution function. The study of the density dependence of the renor-

malizations would enhance our knowledge concerning the radial dependence of the interactions; however there are no results yet available for renormalizations involving short-range correlations at pressures other than zero.

In this paper pair distribution functions as well as selected renormalizations are presented for solid H<sub>2</sub> and D<sub>2</sub> for densities up to 10 cm<sup>3</sup>/mole (~20 kbar). Horner's concepts are basically followed but are further developed by eliminating the use of the multiplicative polynomial in the pair distribution function which we found to limit the applicability of the method at high densities. Furthermore, a differential equation (proposed by Brueckner and Froberg<sup>5</sup>) which better describes the short-range asymptotic behavior is used in the calculation.

### II. ANHARMONIC PAIR DISTRIBUTION FUNCTION

The pair distribution  $g(\bar{r})$  can formally be defined

$$g(l\kappa; l'\kappa'|\bar{r}) = \langle \delta^3(\bar{r} - \bar{x}(l\kappa) + \bar{x}(l'\kappa')) \rangle,$$

where  $\bar{x}(l\kappa)$  is the position of the particle labeled by the  $l$ th unit cell and  $\kappa$ th sublattice, and  $\langle \rangle$  denotes averaging over a canonical ensemble. The second moment  $\bar{\lambda}$  of  $g(\bar{r})$  defined below

$$\bar{\lambda}(l\kappa; l'\kappa') = \int [\bar{r} - \bar{R}(l\kappa) + \bar{R}(l'\kappa')] \times [\bar{r} - \bar{R}(l\kappa) + \bar{R}(l'\kappa')] g(l\kappa; l'\kappa'|\bar{r}) d^3r$$

can be related<sup>6</sup> to the one-phonon spectral function  $\chi''(\bar{q}jj'; \omega)$  via the fluctuation-dissipation theorem

$$\lambda_{\alpha\beta}(l\kappa; l'\kappa') = \frac{1}{N} \sum_{\bar{q}jj'} [e^{i\bar{q}\cdot\bar{R}(l)} e_{\alpha}(\kappa|\bar{q}j) - e^{i\bar{q}\cdot\bar{R}(l')} e_{\alpha}(\kappa'|\bar{q}j)] \times [e^{-i\bar{q}\cdot\bar{R}(l)} e_{\beta}^*(\kappa|\bar{q}j') - e^{-i\bar{q}\cdot\bar{R}(l')} e_{\beta}^*(\kappa'|\bar{q}j')] \int_{-\infty}^{\infty} \chi''(\bar{q}jj'; \omega) [1 + n(\omega)] \frac{d\omega}{\pi}. \quad (1)$$

In the above  $N$  is the number of unit cells,  $\bar{R}(l\kappa) = \langle \bar{x}(l\kappa) \rangle$ ,  $n(\omega) = (e^{\hbar\omega/\kappa T} - 1)^{-1}$ , and  $e_\alpha(\kappa|\bar{q}j)$  is an eigenvector for the  $(\bar{q}j)$  mode.

The anharmonic one-phonon spectral function can generally be expressed as<sup>7</sup>

$$\chi''(\bar{q}j; \omega) = \frac{\hbar}{M} \frac{2\omega_{\bar{q}j}\Gamma(\bar{q}j; \omega)}{[\omega^2 - \omega_{\bar{q}j}^2 - 2\omega_{\bar{q}j}\Delta(\bar{q}j; \omega)]^2 + 4\omega_{\bar{q}j}^2\Gamma^2(\bar{q}j; \omega)} \quad (2)$$

where  $M$  is the mass,  $\{\omega_{\bar{q}j}\}$  is some suitable set of basis frequencies, and  $2\omega_{\bar{q}j}[\Delta(\bar{q}j; \omega) - i\Gamma(\bar{q}j; \omega)] \equiv \Sigma(\bar{q}j; \omega)$  is the complex phonon self-energy.

In the present work the parametrized form of  $g(\bar{r})$  is given by

$$g(l\kappa; l'\kappa'|\bar{r}) = Af(r)\exp\left\{-\frac{1}{2}[\bar{r} - \bar{\xi}(l\kappa; l'\kappa')] \cdot \bar{\gamma}^{-1}(l\kappa; l'\kappa') \cdot [\bar{r} - \bar{\xi}(l\kappa; l'\kappa')]\right\} \quad (3)$$

The Gaussian parameters  $A$ ,  $\bar{\xi}$  (peak position of Gaussian), and  $\bar{\gamma}$  (width) are determined from the moment constraints defined below

$$\int g(l\kappa; l'\kappa'|\bar{r}) d^3r = 1 \quad (4a)$$

(normalization),

$$\int g(l\kappa; l'\kappa'|\bar{r}) \bar{r} d^3r = \bar{R}(l\kappa) - \bar{R}(l'\kappa') \quad (4b)$$

(lattice structure),

$$\int g(l\kappa; l'\kappa'|\bar{r}) [\bar{r} - \bar{R}(l\kappa) + \bar{R}(l'\kappa')]^2 d^3r = \bar{\lambda}(l\kappa; l'\kappa') \quad (4c)$$

Unlike the harmonic case,  $\bar{\xi}$  and  $\bar{\gamma}$  do not in general coincide with  $\bar{R}$  and  $\bar{\lambda}$ . The function  $f(r)$  should ensure the proper asymptotic behavior at short distances and is given here by the solution to the differential equation

$$\left\{-\frac{\hbar^2}{M}\nabla^2 + v(r) - \epsilon_p\right\}\psi(r) = 0 \quad (5a)$$

with<sup>8</sup>

$$f(r) = |\psi(r)|^2 \exp\left\{\frac{3}{2}[\bar{r} - \bar{R}(l\kappa) + \bar{R}(l'\kappa')]^2 / \text{Tr}\bar{\lambda}\right\} \quad (5b)$$

$$f(r) = f(r_{\max}), \quad r > r_{\max} \quad (5b)$$

$v(r)$  is the bare potential interaction (isotropic part),  $\epsilon_p$  is an eigenvalue representing the effective pair energy in the solid, and  $r_{\max}$  is the distance at which  $\psi(r)$  reaches its first maximum. This differential equation, which was originally proposed by Brueckner and Froberg<sup>5</sup> for quantum crystals, can be derived from a variational procedure on the two-body cluster contribution to the ground-state energy and should thus give a good approximation to the short-range asymptotic behavior of  $g(\bar{r})$ .

Horner<sup>3</sup> has suggested the following parametrization for  $g(\bar{r})$ :

$$g(l\kappa; l'\kappa'|\bar{r}) = [a + b(r - R') + c(r - R')^2] f(r) \times \exp\left[-\frac{1}{2}(\bar{r} - \bar{R}') \cdot \bar{\lambda}^{-1}(l\kappa; l'\kappa') \cdot (\bar{r} - \bar{R}')\right] \quad (6)$$

with  $\bar{R}' \equiv \bar{R}(l\kappa) - \bar{R}(l'\kappa')$  and  $f(r)$  satisfying the differential equation

$$\left\{-\frac{\hbar^2}{M}\nabla^2 + v(r)\right\}\psi(r) = 0 \quad (7)$$

with

$$f(r) = |\psi(r)|^2, \quad r \leq r_{\max}$$

$$f(r) = f(r_{\max}), \quad r > r_{\max}$$

Here the Gaussian parameters are fixed and the parameters  $a$ ,  $b$ , and  $c$ , in the multiplicative spherically symmetric polynomial are varied to obey the moment constraints [Eqs. (4)].

With this procedure, we encountered pathologies at high densities where  $g(\bar{r})$  displayed oscillations and took negative values. No pathological behavior was encountered with the use of Eqs. (3) and (4). Furthermore, the form for  $g(\bar{r})$  expressed in Eq. (3) can be adapted to the symmetry of the lattice and allows for the satisfaction of constraints on all the tensor components of the moments. This is important for the renormalization of the electric quadrupole interaction where vibrational anisotropy plays an important role<sup>2</sup> and is not possible with a spherically symmetric term. Horner<sup>9</sup> had originally introduced the multiplicative polynomial as a general (nonspherically symmetric) quadratic form. With this form, however, the moments constraints forced  $g(\bar{r})$  into negative regions even at low densities.

### III. RESULTS

The normal mode contribution to  $\bar{\lambda}$  in Eq. (1) can be expressed in terms of effective frequencies<sup>10</sup>  $\hat{\omega}_{\bar{q}j}$  defined below

$$\frac{\hbar}{M} \frac{[n(\hat{\omega}_{\bar{q}j}) + \frac{1}{2}]}{\hat{\omega}_{\bar{q}j}} \equiv \int_{-\infty}^{\infty} \chi''(\bar{q}j; \omega) [n(\omega) + 1] \frac{d\omega}{\pi} \quad (8)$$

The anharmonic spectral functions for  $H_2$  and  $D_2$  which are used here have been calculated recently<sup>11</sup>

and good agreement with experiment was obtained. There, the basis frequencies  $\{\omega_{\vec{q}j}\}$  in Eq. (2) were determined from the standard self-consistent phonon approximation and the self-energy  $\Sigma(\omega)$  included cubic three-phonon decay processes and higher order anaharmonic terms. A higher order approximation for  $\chi''(\omega)$  would require the  $\{\omega_{\vec{q}j}\}$  and other vertices to be renormalized iteratively via the calculated  $g(\vec{r})$ . However, it is important to keep in mind that the  $\bar{\lambda}$ 's utilized here contain cubic and higher anharmonic corrections which tend to compensate for different kinds of vertex renormalizations. Such an iterative procedure may be important for highly quantum crystals such as low-pressure solid helium, but we do not expect it to substantially change the present results which, as we will show, are more sensitive to the form of  $f(r)$  in Eqs. (3) and (6) rather than  $\bar{\lambda}$ .

The frequencies  $\hat{\omega}_{\vec{q}j}$  defined in Eq. (8) have to be calculated for various points in the Brillouin zone via  $\chi''(\vec{q}j; \omega)$ . For computational economy we make the numerical approximation where the  $\hat{\omega}_{\vec{q}j}$  are calculated only for the (100) zone boundary  $X$  point and, with the help of the calculated isothermal elastic constants, a five force-constants fit is produced in order to extrapolate to other wave vectors in the Brillouin zone.

The eigenvalue  $\epsilon_p$  in Eq. (5a) represents essentially the pair expectation of the potential and kinetic energy

$$\epsilon_p = \frac{1}{2} \left\langle \frac{[\bar{p}(l\kappa) - \bar{p}(l'\kappa')]^2}{2M} \right\rangle + \langle v(\bar{x}(l\kappa) - \bar{x}(l'\kappa')) \rangle,$$

which is also evaluated using the self-consistent phonon basis.

With the spectral functions  $\chi''(\omega)$  and elastic constants calculated in Ref. 11, and the procedure outlined above, pair distribution functions in the form of Eq. (3) were calculated for nearest-neighbors fcc  $H_2$  and  $D_2$  at  $T=0$  K for densities ranging up to 10  $cm^3/mole$ . For comparison both Brueckner-Frohberg's (BF) differential equation [Eq. (5a)] and Horner's [H, Eq. (7)] were used; however, in the latter case (H) the numerical method (Newton-Raphson) used to obtain  $A$ ,  $\bar{\xi}$ , and  $\bar{\gamma}$  became unstable for molar volumes smaller than 12  $cm^3/mole$ .

Figure 1 shows  $g(\vec{r})$  along the nearest-neighbor pair axis for (a)  $H_2$  at 22.73  $cm^3/mole$  ( $P \approx 0$ ) and for (b)  $D_2$  at 12  $cm^3/mole$ . Plotted are a correlated Gaussian distribution and the distribution functions obtained using the BF and H differential equations [Eqs. (5) and (7)]. For a given density all three distribution functions plotted have identical 0th, 1st, and 2nd moments of the displacements. One should note in Fig. 1(a) the difference in the short-range behavior of the BF and H results. This will in turn be reflected in the renormalizations shown in Figs. 2 and 3. The electric quadrupole interaction reduction

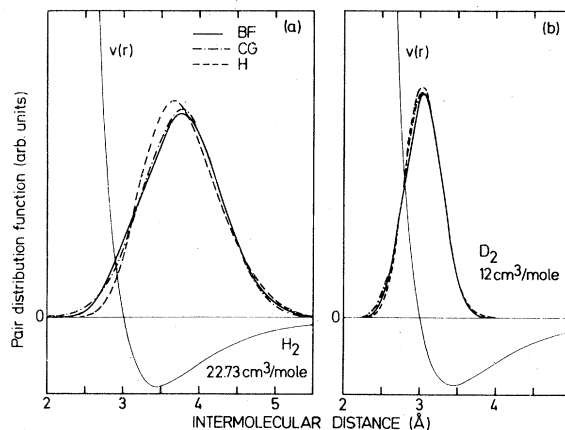


FIG. 1. Pair distribution functions with short-range asymptotic behavior calculated with Eq. (5): BF, and Eq. (7): H. Correlated Gaussian without short-range correlations: CG. The pair distribution functions are shown relative to the isotropic intermolecular potential  $v(r)$  of Silvera and Goldman (Ref. 17).

factor

$$\xi_{54} = \left( \frac{4}{9\pi} \right)^{1/2} \left\langle \frac{Y_4^0(l)}{(r/R_0)^5} \right\rangle, \quad (9)$$

where  $R_0$  is the nearest-neighbor distance, is shown in Fig. 2 as a function of density for the various approximations. The quantity  $g_{00} = \langle (r/R_0)^{-10} \rangle$  which

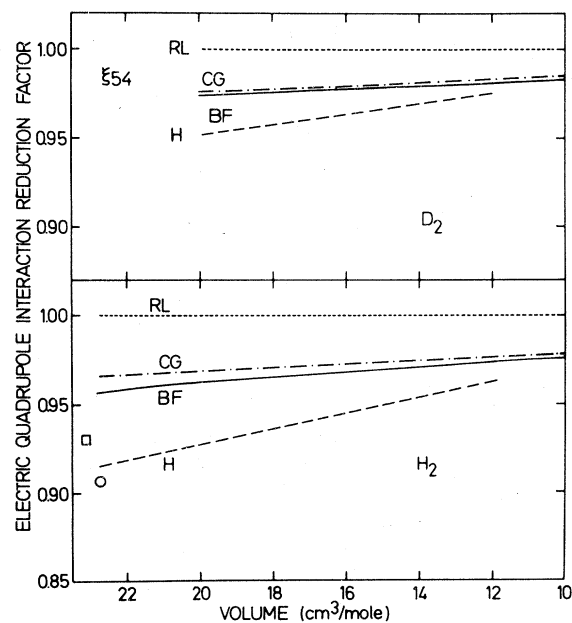


FIG. 2. Density dependence of the electric quadrupole interaction reduction factor for various pair distribution functions as labeled in Fig. 1. RL denotes the rigid lattice value. □: Ref. 4; ○: Two-body cluster Nosanow-Koehler Jastrow method.

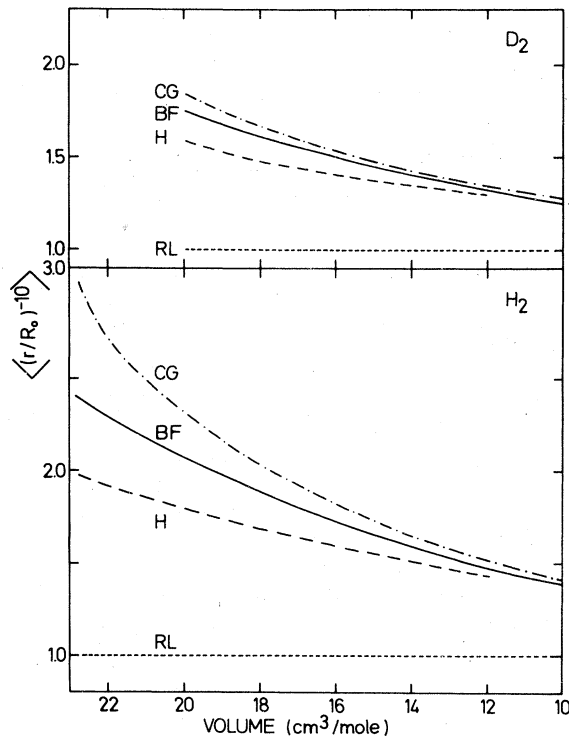


FIG. 3. Density dependence of the motional renormalization of  $(R_0/r)^{10}$  for various pair distribution functions as labeled in Fig. 1. RL denotes the rigid lattice value.

enters in the total integrated intensity of the far infrared absorption line shape<sup>12</sup> is plotted in Fig. 3. The rigid lattice (RL) value of  $\xi_{54}$  value of  $g_{00}$  is unity for all densities. The difference between the  $H$  and BF solutions for the short-range part of  $g(\vec{r})$  is clearly reflected in these figures.

In Fig. 2 we also show a value for  $\xi_{54}$  we obtained using the Nosanow-Koehler<sup>13</sup> two-body cluster variational method, and a value calculated by Luryi and Van Kranendonk.<sup>4</sup> Hardy *et al.*<sup>14</sup> experimentally ob-

tain an *effective* quadrupole reduction factor of 0.856 for  $H_2$  at zero pressure. However a direct comparison with theory requires taking into account [besides  $\xi_{54}$  defined in Eq. (9)], nonquadrupolar valence and dispersion terms which are poorly known. With this data the BF renormalization implies a deviation of  $-10.5\%$  from (motionally renormalized) ideal quadrupolar behavior, and  $-6.5\%$  from the  $H$  renormalization, at  $P=0$ .

#### IV. CONCLUDING REMARKS

Using moment constraints, pair-distribution functions, and motional renormalizations of electric quadrupole interactions in the solid hydrogens have been obtained as a function of density. The new form for the pair distribution function introduced here allows the procedure to be carried out at high densities and the marked differences between results obtained from the Horner and Brueckner-Frohberg differential equations point to the necessity of a good *a priori* knowledge of the asymptotic short-range behavior for the Horner scheme. Because it is derived variationally we expect the BF equation results to be more realistic. However, some improvement might be achieved by taking into account three-body terms<sup>15</sup> or applying methods from the theory of inhomogeneous liquids.<sup>16</sup> Of all previous treatments involving short-range correlations, the BF solution yields the weakest renormalization of the electric quadrupole interaction. The implementability of the present method to high densities can now allow for a better interpretation of high-pressure experiments in the solid hydrogens.

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turn out to be small we do not expect this substitution to appreciably affect the results.

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