

## Diffusion Monte Carlo study of the equation of state of solid para-H<sub>2</sub>

Francesco Operetto

*Dipartimento di Fisica and INFN, Università di Trento, via Sommarive, 14 I-38050 Povo, Trento, Italy*

Francesco Pederiva

*Dipartimento di Fisica and INFN, Università di Trento, via Sommarive, 14 I-38050 Povo, Trento, Italy  
and CNR/INFN DEMOCRITOS National Simulation Center, Trieste, Italy*

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The diffusion Monte Carlo method is used to exactly solve the  $N$ -body Schrödinger equation for a system of para-H<sub>2</sub> molecules at different densities described as pointlike particles interacting via an effective potential. We compare the results obtained using two of the most used model interactions, i.e., the Silvera-Goldman and the Buck potentials in order to assess their validity. We also discuss the role of explicit three-body forces by adding a term of the Axilrod-Teller kind. This term corrects the large underestimation of the pressure given by the standard two-body interactions commonly employed.

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### I. INTRODUCTION

The interest about the low- and high-pressure behavior of molecular solid parahydrogen has recently increased due in particular to two important findings. Experiments on rotational spectra of linear molecules embedded in He droplets, and coated with a small number of  $p$ -H<sub>2</sub> molecules show a sudden drop of the momentum of inertia of the molecule-hydrogen compound when lowering the temperature of the system, indicating the onset of a sort of local superfluidity of the  $p$ -H<sub>2</sub> molecules.<sup>1</sup> This discovery gave rise to a series of theoretical studies carried out by means of Monte Carlo techniques, in particular with the path integral Monte Carlo (PIMC) technique which samples the quantum density matrix at finite temperature,<sup>2</sup> and variants of the diffusion Monte Carlo technique.<sup>3</sup> PIMC has also been used in the past to study the onset of solidification as a function of the number of  $p$ -H<sub>2</sub> molecules in a droplet,<sup>4</sup> and to study effects of the reduced dimensionality on the onset of superfluidity in  $p$ -H<sub>2</sub> films<sup>5</sup> and two-dimensional droplets.<sup>6</sup> In all these studies the molecules of  $p$ -H<sub>2</sub> have been treated as point particles interacting by means of an effective two-body potential. Several model interactions are available for  $p$ -H<sub>2</sub>, and some of them, in particular the Buck<sup>7,8</sup> potential and the Silvera-Goldman (SG) (Ref. 9) potential, have been used indifferently in theoretical works. These interactions either completely neglect or treat in an effective way the possible three-body interactions acting among the molecules. The usual argument for neglecting such terms, which are expected due to the nonspherical nature of the molecule, is that the  $p$ -H<sub>2</sub> molecule ground state has total angular momentum  $J=0$ , and therefore the average interaction must have spherical symmetry. Three-body interactions should therefore be a second order effect. Another important issue that was recently discovered by computer simulations of  $p$ -H<sub>2</sub> at very high pressure is the possibility of the occurrence of a phase transition between the crystal phase and a fluid dissociated phase at about 400 GPa.<sup>10</sup> In this context it is interesting to test the limit of validity of the intermolecular interactions to see how fast the quality of the description of the equation of state decays when increasing the density. Clearly for high pres-

ures the influence of many-body terms in the interaction will become more and more important, as it was shown in similar quantum crystals like solid <sup>4</sup>He or solid <sup>3</sup>He.<sup>11</sup>

In this paper we present the results of a systematic study of the equation of state of solid  $p$ -H<sub>2</sub> for pressures ranging from 0 (and slightly below) up to 400 MPa using highly optimized variational functions and projecting from them the ground state energy by means of the diffusion Monte Carlo algorithm, which gives for many Bosons the exact eigenvalue of the system. This means that results depend only on the particular choice of the potential.

Two earlier papers partially addressed the same question. Cheng and Whaley,<sup>12</sup> and previously Cocker and Watts<sup>13</sup> performed diffusion Monte Carlo (DMC) calculations at the saturation density, using the Silvera-Goldman and the Buck potentials, respectively. Our work extends this analysis to higher and lower densities, in order to have a better assessment of the quality of the potentials. The results for pressure computed in our simulations show a rather large discrepancy compared to the experimental measurements. We tried to assess the importance of explicit three-body potentials by introducing in the calculation a simple triple-dipole Axilrod-Teller (AT) form. This term, while making the estimate of the energy per particle higher, substantially improves the estimate of the pressure.

The next section of the paper will describe the methods used in our analysis. Section III will present the results on energies, pressures, and other ground state properties in  $p$ -H<sub>2</sub>. Section IV is devoted to conclusions.

### II. METHODS

The  $N$   $p$ -H<sub>2</sub> molecules are described by the following Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j} v_2(r_{ij}) + \sum_{i<j<k} v_3(r_{ij}, r_{jk}, r_{ik}), \quad (1)$$

where  $R = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ . As already mentioned, we use two different molecule-molecule interaction  $v_2$ , i.e., the Silvera-

Goldman and the Buck potentials. In the calculations including the three-body interaction it was chosen as a simple triple-dipole potential of the Axilrod-Teller form, already used in calculations for He (Ref. 15)

$$v_3(r_{ij}, r_{jk}, r_{ki}) = A \left[ \frac{1 + 3 \cos(\theta_{ij}) \cos(\theta_{jk}) \cos(\theta_{ki})}{(r_{ij} r_{jk} r_{ki})^3} \right]. \quad (2)$$

In the diffusion Monte Carlo (DMC) algorithm,<sup>16</sup> the ground state of the Hamiltonian  $H$  is projected starting from a variational ansatz for the many-body wave function. In our case we chose a function of the Jastrow-Nosanow form

$$\psi(R) = f(r_{ij}) e^{-C(\mathbf{r}_i - \mathbf{S}_i)^2}, \quad (3)$$

where the  $\{\mathbf{S}_i\}$  are the coordinates of the lattice sites around which the molecules are confined. This form of the wave function does not respect the required Boson symmetry. However, it has been shown in the case of He solids that the low-exchange frequency makes contributions to the total energy from the symmetrization very small.<sup>17,18</sup> Solid parahydrogen is even more localized than He, and this justifies the assumption of our ansatz. The projection is achieved by sampling the evolution of a population of  $N_w$  points in configuration space (*walkers*) according to the importance sampled Green's function

$$G(\mathbf{R}, \mathbf{R}', \Delta\tau) = G_0(\mathbf{R}, \mathbf{R}', \Delta\tau) \frac{\psi(\mathbf{R}')}{\psi(\mathbf{R})}, \quad (4)$$

where

$$G_0(\mathbf{R}, \mathbf{R}', \Delta\tau) = e^{-\Delta\tau/2V(\mathbf{R})} e^{-(\mathbf{R} - \mathbf{R}')^2/2D\Delta\tau} e^{-\Delta\tau/2V(\mathbf{R}')}. \quad (5)$$

The propagation has to be iterated in order to achieve a propagation for an imaginary time  $\tau$  such that the density of walkers becomes  $\psi(R)\psi_0(R)$  where  $\psi_0$  is the ground state of the Hamiltonian considered. In this situation the expectation value of the Hamiltonian itself computed as the average of the local energy  $\hat{H}\psi(R)/\psi(R)$  on the sampled walkers becomes

$$\langle \hat{H} \rangle = \frac{\int dR \psi(R) \psi_0(R) \hat{H} \psi(R) / \psi(R)}{\int dR \psi(R) \psi_0(R)} = E_0, \quad (6)$$

the lowest eigenvalue of the Hamiltonian. The computed estimate is exact at order  $\Delta\tau$ .

In order to reduce the variance on the estimate of the eigenvalue in the DMC calculation the importance function  $\psi$  must be variationally optimized. A series expansion of the function  $f(r)$  in Eq. (3) was used to obtain an accurate description of the two-body correlations in the system. The functions  $f$  are written in terms of pseudopotentials

$$f(r) = \exp \left[ -\frac{1}{2} u(r) \right]. \quad (7)$$

The function  $u = u_0 + u_c$  is the sum of a standard McMillan pseudopotential

$$u^0(r) \equiv \left( \frac{b}{r} \right)^5, \quad (8)$$

and of a correction term which has been expanded in terms of suitable basis functions

$$u_c(r_{ij}) = \sum_n a_n \chi_n(r_{ij}). \quad (9)$$

The basis functions  $\chi_n$  (about 40) have been chosen to be similar to the ones introduced by Moroni *et al.*<sup>19</sup> for analogous calculations in He

$$\chi_n(r) \equiv \begin{cases} \left\{ 1 - \cos \left[ \frac{2\pi n}{L/2 - r_c} (r - L/2) \right] \right\} r^{-5} & r > r_c \\ 0 & r \leq r_c. \end{cases} \quad (10)$$

The cut-off radius  $r_c$ , if small enough, does not influence the value of the energy. In our calculations it has been taken equal to 1 Å. All the free parameters have been determined by minimizing a linear combination of the variance of the expectation value of the Hamiltonian, and of the expectation value itself.<sup>3</sup> This is obtained by cycling through steps of variational Monte Carlo calculations of  $\langle \hat{H} \rangle$  and minimization of the variance/energy combination on a set of sampled configurations using the Levenberg-Marquardt minimization code by C. J. Umrigar and P. Nightingale. Diffusion Monte Carlo calculations have been performed for different imaginary time steps and populations of walkers, and the results have been extrapolated in the limit of  $\Delta\tau=0$  and  $N_w \rightarrow \infty$ . Calculations were performed for crystals of different densities both for the face centered cubic (fcc) structure and the hexagonal close-packed (hcp) lattices. In the first case a periodic system of 108  $p$ -H<sub>2</sub> molecules was used, corresponding to  $3 \times 3 \times 3$  elementary cubic cells. For the hcp lattice calculations we used 108  $p$ -H<sub>2</sub> molecules filling  $5 \times 3 \times 3$  elementary cells. In this case the box is not cubic, but the ratio of the three sides to each other is as close as possible to 1. The potential energy was truncated at a distance corresponding to  $L/2$ , where  $L$  is the length of the shortest side of the cell. In order to avoid discontinuities in the Green's function used to sample the walkers, the potential was also shifted of a quantity  $v(L/2)$ . The error due to the cutoff has been corrected by integrating the potential in the  $(L/2, +\infty)$  interval, assuming therefore a uniform distribution of molecules beyond  $L/2$ . The same procedure has been used for correcting the error due to the shift in the sphere of radius  $L/2$ .

### III. RESULTS

In Fig. 1 we report the results obtained for the equation of state in the density interval  $0.0194 \text{ \AA}^{-3} < \rho < 0.0430 \text{ \AA}^{-3}$ , for the SG and the Buck potentials. In the inset we report the expanded curves for density near the equilibrium one. The curves report the DMC results, which are found to be only slightly lower than the corresponding results obtained by

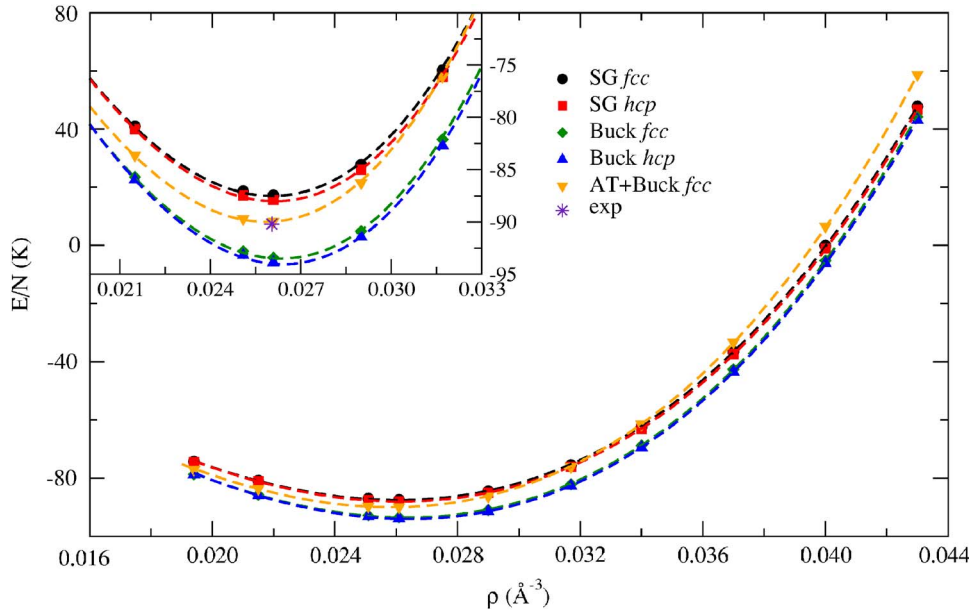


FIG. 1. (Color online) Energy per particle (in Kelvin) in solid  $p$ -H<sub>2</sub> as a function of the density  $\rho$ , computed with different interactions. The curves represent the fits to the DMC results with a Murnaghan-like curve. In the inset the region around the equilibrium density is expanded. The experimental point is taken from Ref. 14.

optimizing the Jastrow factor in the wave function (between 1 and 7 % depending on the density). This suggests that the importance function used is already quite accurate. The results for the binding energy at saturation density can be compared with the estimate of the sublimation heat at 0 K for pure  $p$ -H<sub>2</sub>, found in Ref. 14 to be  $-89.9$  K. The computed DMC values for the fcc and hcp crystals using the Buck potential are  $E/N = -93.42(1)$  K and  $E/N = -93.87(2)$  K, respectively, about 3 K below the experimental result. On the other hand, the SG potential gives a result which is about 10 K higher, as shown in Table I. This discrepancy is due to the effective triple-dipole term proportional to  $1/r^9$ , which is repulsive, and which tends therefore to increase the energy per particle. The hcp lattice turns out to be always stable with respect to the fcc one. The agreement with the experimental finding of the equilibrium energy is substantially improved by adding to the Buck potential the explicit three body term discussed below.

In Table II we also reported some results of simulations performed in the fcc crystal using 256 molecules arranged on  $4 \times 4 \times 4$  elementary cells. Effects due to the finite size of the simulation box have been found negligible in comparison

with the effects due to the choice of different potentials. Energetic differences between fcc and hcp lattice seem to slightly increase if the fcc lattice with 256 sites is taken into account.

In order to compute the pressure as function of  $\rho$  and the equilibrium density of the system, we fitted the results of the energy per particle by means of a Murnaghan-like curve

$$\epsilon(\rho) = \epsilon_0 + a\rho + b\rho^\gamma. \quad (11)$$

The coefficients and the minimum of the curves in the fcc and hcp crystal are reported in Table III. The pressure as a function of the density was then obtained from the following expression:

$$P = \rho^2 \left[ \frac{\partial \epsilon(\rho)}{\partial \rho} \right]_T. \quad (12)$$

The computed curves for the pressure are reported in Fig. 3, and compared with the experimental results of Ref. 20. It can be noticed how in this case the agreement with the experiment is much less satisfactory. Both the Buck and SG potentials seem to be not capable of describing correctly the

TABLE I. Energy per particle (in Kelvin) in solid  $p$ -H<sub>2</sub> computed with different interaction for fcc and hcp crystalline structure.

$\rho$	SG fcc	SG hcp	Buck fcc	Buck hcp	AT+Buck fcc
0.01940	-74.33(3)	-74.44(4)	-78.65(3)	-78.70(4)	-77.10(4)
0.02150	-80.85(2)	-81.13(2)	-85.70(2)	-85.96(2)	-83.63(2)
0.02509	-87.06(2)	-87.48(2)	-92.79(2)	-93.19(2)	-89.70(3)
0.02609	-87.45(2)	-87.90(2)	-93.42(1)	-93.87(2)	-89.94(1)
0.02900	-84.52(3)	-85.00(2)	-90.89(2)	-91.43(3)	-86.28(3)
0.03170	-75.50(4)	-76.13(1)	-82.10(2)	-82.70(1)	-76.11(4)
0.03400	-62.30(2)	-62.98(2)	-68.77(2)	-69.51(2)	-61.49(3)
0.03700	-36.51(2)	-37.34(2)	-42.57(2)	-43.41(1)	-33.22(3)
0.04000	-0.14(2)	-1.09(3)	-5.25(2)	-6.20(2)	6.49(4)
0.04300	47.77(2)	46.70(2)	44.18(4)	43.14(2)	58.71(2)

TABLE II. Energy per particle (in Kelvin) in solid  $p$ -H<sub>2</sub> computed in fcc crystal using different number of molecules interacting via the Buck potential. Densities are in  $\text{\AA}^{-3}$ .

	108	256
0.01940	-78.65(3)	-78.26(4)
0.02609	-93.42(1)	-93.26(2)
0.04300	44.18(4)	44.65(4)

pressure-volume curve in the system. In particular, the pressure is almost constantly underestimated of about 50 MPa over all the range of densities considered. For densities  $\rho > 0.037 \text{\AA}^{-3}$  the Buck potential provides a slightly better agreement with the experimental data. It can be expected that at such high densities the effects of many-body potentials become important. However, the triple-dipole effective term in the SG potential is practically ineffective in terms of pressure at low densities, and it seems not to give a significant contribution at higher pressures. In order to explore the effects of explicit three-body contributions to the potential energy, we performed DMC calculations adding a three-body potential  $V_3$  of the Axilrod-Teller form (2), that describes the triple-dipole effects, and can be parametrized with a single coefficient  $A$ , to the Buck potential, which seems to give an overall slightly better agreement with the experiment when used by itself and does not include the effective triple-dipole term proportional to  $1/r^9$ . The value  $A = 23\,914.946 \text{ K}\text{\AA}^9$  was fixed as follows: The mean value of  $V_3$  as function of the density was calculated by means of DMC simulations. From the curve  $\langle V_3 \rangle(\rho)$  we estimated the contribute of the three-body potential to the pressure  $P_3(\rho)$  and fitted the experimental values of the pressure in order to fix the value of the multiplicative coefficient  $A$ . The result was checked by repeating the DMC simulations using the fitted value of  $A$ . The results for both the energy and the pressure in the fcc lattice are displayed in Figs. 1 and 2. As it can be seen, the energies computed with the AT+Buck potential almost overlap with the SG results at low densities, as expected. The behaviors tend to depart more at higher densities. On the other hand the gap in the estimate of the pressure at low densities is almost completely removed, and the agreement becomes better also at higher densities, although the density dependence of the pressure indicates that the pressure would tend to be overestimated at higher densities. This result strongly indicates that effects of explicit many-body interactions in  $p$ -H<sub>2</sub> on the energy are already very strong at low densities, and they

TABLE III. Coefficients of the equation of state [Eq. (11)] fitted to DMC simulation results. The energy is given in Kelvin; the computed equilibrium density  $\rho_0$  is given in  $\text{\AA}^{-3}$ .

	$\epsilon_0$	$a$	$b$	$\gamma$	$\rho_0$
SG fcc	45.6939	-7129.73	$2.08446 \cdot 10^7$	3.53405	0.02606
SG hcp	48.1222	-7278.12	$1.99851 \cdot 10^7$	3.51769	0.02613
Buck fcc	46.8125	-7375.50	$2.62068 \cdot 10^7$	3.60038	0.02647
Buck hcp	52.4309	-7741.95	$2.14537 \cdot 10^7$	3.52809	0.02640
AT+Buck fcc	46.9315	-7363.65	$2.47129 \cdot 10^7$	3.56850	0.02583

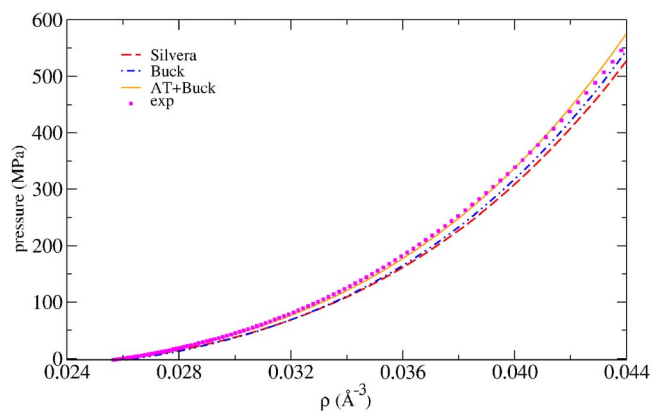


FIG. 2. (Color online) Pressure as a function of the density  $\rho$  in solid  $p$ -H<sub>2</sub> computed with different interactions. Curves for fcc and hcp are almost indistinguishable. The experimental points are taken from Ref. 20.

cannot be neglected at all when the density is increased. From the results on the equation of state it is also possible to obtain information on the compressibility, which is defined as

$$\kappa = \frac{1}{\rho} \left[ \frac{\partial \rho}{\partial P} \right]_T. \quad (13)$$

Results are reported in Fig. 3. Also in this case the effects of the inclusion of the three-body potential are relevant.

Another interesting question regards the effects of the choice of different interactions on the local structure of the crystal. In Fig. 4 we display the results for the computation of the pair distribution function  $g(r)$  in the fcc lattice at the equilibrium density using the SG, the Buck, and the AT+Buck interactions. In both cases the curves are essentially indistinguishable from each other. This means that despite the relevant difference in the energy, the structural properties are not heavily affected by the choice of the interaction. In general the results are almost independent on the particular lattice structure chosen.

#### IV. CONCLUSIONS

We presented the results of a systematic comparison of ground state properties of solid  $p$ -H<sub>2</sub> computed with the two most used interactions, the Silvera-Goldman and the Buck potential. None of the two models is capable to give a completely satisfactory description of the pressure-volume (PV)



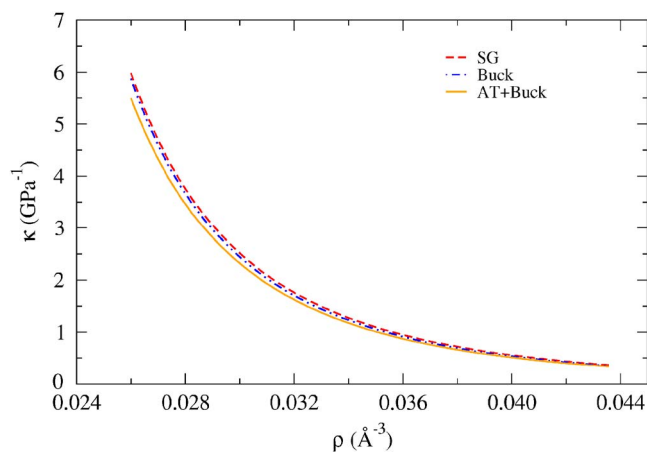


FIG. 3. (Color online) Compressibility in molecular  $p$ -H<sub>2</sub> computed using the SG, Buck and AT+Buck interactions. Curves for fcc and hcp are almost indistinguishable.

curve. We explored the effects of adding explicit three-body interactions fitting the PV curve with a simple Axilrod-Teller potential, which removes the gap in the pressure obtained with the simple two-body potentials. These results show that in order to be able to provide the most accurate theoretical prediction on  $p$ -H<sub>2</sub> it is necessary to revise and improve the available model interactions.

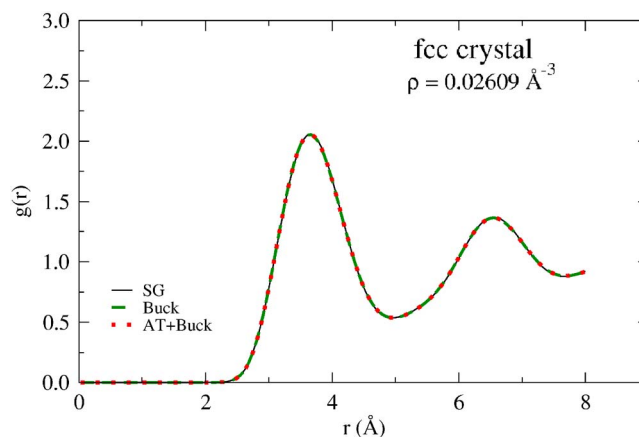


FIG. 4. (Color online) Pair distribution function in solid  $p$ -H<sub>2</sub> computed using the SG (full line) and the Buck (dashed line) and the AT+Buck (dotted line) potentials at equilibrium density  $\rho = 0.02609 \text{ \AA}^{-3}$  in the fcc crystal.

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- <sup>1</sup>S. Grebenev, B. Sarkatov, J. P. Toennis, and A. F. Vilesov, *Science* **289**, 1532 (2000).
- <sup>2</sup>Y. Kwon and K. B. Whaley, *Phys. Rev. Lett.* **89**, 273401 (2002).
- <sup>3</sup>S. Moroni, M. Botti, S. D. Palo, and A. R. W. McKellar, *J. Chem. Phys.* **122**, 094314 (2005).
- <sup>4</sup>P. Sindzingre, D. M. Ceperley, and M. L. Klein, *Phys. Rev. Lett.* **67**, 1871 (1991).
- <sup>5</sup>M. C. Gordillo and D. M. Ceperley, *Phys. Rev. Lett.* **79**, 3010 (1997).
- <sup>6</sup>M. C. Gordillo and D. M. Ceperley, *Phys. Rev. B* **65**, 174527 (2002).
- <sup>7</sup>U. Buck, F. Huisken, A. Kohlhase, D. Otten, and J. Schaefer, *J. Chem. Phys.* **78**, 4439 (1983).
- <sup>8</sup>M. J. Norman, R. O. Watts, and U. Buck, *J. Chem. Phys.* **81**, 3500 (1984).
- <sup>9</sup>I. F. Silvera and V. V. Goldman, *J. Chem. Phys.* **69**, 4209 (1978).
- <sup>10</sup>S. A. Bonev, E. Schwegler, T. Ogitsu, and G. Galli, *Nature (London)* **431**, 669 (2003).
- <sup>11</sup>S. Moroni, F. Pederiva, S. Fantoni, and M. Boninsegni, *Phys. Rev. Lett.* **84**, 2650 (2000).
- <sup>12</sup>E. Cheng and K. B. Whaley, *J. Chem. Phys.* **104**, 3155 (1996).
- <sup>13</sup>D. E. Cocker and R. O. Watts, *J. Chem. Phys.* **86**, 5703 (1987).
- <sup>14</sup>O. Schnepp, *Phys. Rev. A* **2**, 2574 (1970).
- <sup>15</sup>J. Boronat and J. Casulleras, *Phys. Rev. B* **49**, 8920 (1994).
- <sup>16</sup>P. Reynolds, D. Ceperley, B. Alder, and W. Lester, *J. Chem. Phys.* **77**, 5593 (1982).
- <sup>17</sup>D. M. Ceperley and G. Jacucci, *Phys. Rev. Lett.* **58**, 1648 (1987).
- <sup>18</sup>D. M. Ceperley and B. Bernu, *Phys. Rev. Lett.* **93**, 155303 (2004).
- <sup>19</sup>S. Moroni, S. Fantoni, and G. Senatore, *Phys. Rev. B* **52**, 13547 (1995).
- <sup>20</sup>A. Driessen, J. A. de Waal, and I. F. Silvera, *J. Low Temp. Phys.* **34**, 255 (1979).