Two-dimensional molecular para-hydrogen and ortho-deuterium at zero temperature

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We study molecular para-hydrogen (p-H\textsubscript{2}) and ortho-deuterium (o-D\textsubscript{2}) in two dimensions and in the limit of zero temperature by means of the diffusion Monte Carlo method. We report energetic and structural properties of both systems like the total and kinetic energy per particle, radial pair distribution function, and Lindemann's ratio in the low pressure regime. By comparing the total energy per particle as a function of the density in liquid and solid p-H\textsubscript{2}, we show that molecular para-hydrogen, and also ortho-deuterium, remain solid at zero temperature. Interestingly, we assess the quality of three different symmetrized trial wave functions, based on the Nosanow-Jastrow model, in the p-H\textsubscript{2} solid film at the variational level. In particular, we analyze a new type of symmetrized trial wave function which has been used very recently to describe solid \textsuperscript{4}He and found that also characterizes hydrogen satisfactorily. With this wave function, we show that the one-body density matrix $g_1(r)$ of solid p-H\textsubscript{2} possesses off-diagonal long range order, with a condensate fraction that increases sizably in the negative pressure regime.

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I. INTRODUCTION

Quantum crystals like helium and hydrogen are intriguing systems of fundamental physical interest. Due to the light mass of their constituents and relatively weak interparticle attraction, quantum solids exhibit large kinetic energy and Lindemann's ratio even in the limit of zero temperature ($T \sim 10^0 - 10^{-3}$ K). In consequence, anharmonic effects and atomic quantum exchanges are of importance in this class of crystals. Moreover, in the last few years a series of ultra-low temperature experiments performed in solid $^4$He by different groups has led to a renewed interest on the possibility of superfluidity and/or Bose-Einstein condensation (BEC) in quantum solids\textsuperscript{1,2,3,4}. Essentially, these experiments analyze the quantum behavior of the helium crystal upon rotation or seek for some thermodynamic and/or structural anomaly signalizing a possible normal-to-superfluid phase transition. Despite that most of the observations fairly agree in locating the onset of superfluidity ($75-150$ mK), there is a large dispersion in the value of the measured superfluid fraction $\rho_s/\rho$ ($\approx 0.3-0.005$%). At present, there is lack of conclusive arguments for explaining these discrepancies but it is widely accepted that the purity of the sample and the presence of crystalline defects play on it a relevant role.\textsuperscript{5,6} On the other hand, there is overall agreement among microscopic full quantum calculations in practically ruling out superfluidity in the perfect (free of defects) bulk configuration. It is worth noticing that usual techniques devised to study classical crystals (that is crystals composed of heavier elements and with larger cohesive energies), like for instance harmonic based approaches, are not longer suitable for quantum solids and calculations on them are in most cases challenging.\textsuperscript{7,8}

In the present work, we present a theoretical study of two-dimensional (2D) molecular para-hydrogen (p-H\textsubscript{2}) and ortho-deuterium (o-D\textsubscript{2}) at zero temperature by means of the diffusion Monte Carlo (DMC) method\textsuperscript{9,10,11} and the semi-empirical radial pair interaction due to Silvera and Goldman.\textsuperscript{12} Hydrogen is a very interesting and challenging system which has been investigated very intensively during the last half century. As a matter of fact, hydrogen is the most abundant element in the universe and from a technological point of view it is considered among the most promising green combustibles of the near future. Very interestingly, hydrogen has been predicted to exhibit a new state of matter at very high pressures ($P \sim 400$ GPa) in which superfluidity and superconductivity might coexist.\textsuperscript{13,14}

In this work, we restrict our analysis of molecular hydrogen and deuterium to the low pressure regime ($P \sim 0$) and zero temperature. Contrarily to what occurs in helium, molecular hydrogen freezes at a temperature of 13.96 K in spite of its lighter mass, given that the interactions between particles are more attractive (the minimum of the interaction between hydrogen molecules amounts to $\sim -37$ K while in helium is $\sim -10$ K). One of our motivations for carrying out the present study was to unravel whether liquid p-H\textsubscript{2} could be stabilized or not at zero temperature by reducing the dimensionality with respect to the bulk. This possibility appears to be very appealing since it would provide a chance for superfluidity and Bose-Einstein condensation (BEC) to be observed in a quantum liquid different from helium. In fact, p-H\textsubscript{2} in one dimension and inside a carbon nanotube has already been studied in the zero-temperature limit and predicted to be liquid at its equilibrium density.\textsuperscript{15} Also, small drops
with a number of molecules $N \lesssim 26$ present superfluid character. On the other hand, it has been reported recently an experiment performed on molecular ortho-deuterium pre-plated on krypton at very low temperatures ($T \sim 1$ K) in which it is claimed evidence for the existence of a reentrant $\sz{D}2$ liquid phase. As it will be presented in short, our results show that no first order solid-liquid phase transition occurs in two-dimensional $\sz{H}2$ at zero temperature. On account of this result, we straightforwardly reject this possibility also for $\sz{D}2$ since deuterium molecules are heavier and their intermolecular interactions are considered equal to the $\sz{H}2-\sz{H}2$ ones. Consequently, most of the effort done in this work has been devoted to achieve an accurate description of the ground state of two-dimensional solid $\sz{p-H}2$ and $\sz{o-D}2$.

In this work, we calculate by means of the diffusion Monte Carlo method (DMC) some energetic and structural properties of both hydrogen and deuterium films near equilibrium. Quantities like the kinetic energy per particle and Lindemann’s ratio have been computed within the pure estimator approach in order to remove any possible bias coming out from the trial wave function used for importance sampling. In this way, we quote quantum isotopic effects in hydrogen directly and only within the statistical uncertainty. Previous to the DMC results, we present a variational Monte Carlo (VMC) study of the $\sz{p-H}2$ crystal in which we have tested the quality of several symmetrized and unsymmetrized trial wave functions. With this analysis, we determine the effect of symmetrization on the total energy and the relevance of molecule exchanges along the simulation. Moreover, we analyze which symmetrized wave functions can be implemented in DMC to the end of estimating the possible superfluidity and Bose-Einstein condensation (BEC) of the solid with simultaneous accurate description of their energetic and structural properties. In particular, we have studied in detail a symmetrized trial wave function, named $\psi_{JG}$ in this work (the notation will become clear later), which has been proposed and used recently to study bulk solid $\sz{^3He}$. Here, we find that $\psi_{JG}$ also characterizes solid hydrogen in two dimensions accurately.

Interestingly, we assess the behavior of the one-body density matrix $\varrho_{i}(r)$ of $\sz{p-H}2$ with density by means of the symmetric trial wave function $\psi_{JG}$. In all cases, a very small condensate fraction $n_0$ is observed. For densities below the equilibrium one, and near the spinodal point, a significant increase of $n_0$ is observed pointing to the emergence of a finite superfluid density.

This paper is organized as follows. In Sec. II we present a brief description of the semiempirical pair potential and techniques used throughout this work. Next, in Sec. III and IV we report our variational and diffusion Monte Carlo results for $\sz{p-H}2$ and $\sz{o-D}2$ in two dimensions, respectively. Sec. V is devoted to the examination of the one-body density matrix $\varrho_{i}(r)$ obtained with $\psi_{JG}$ and its dependence with the density. Finally, in the Sec. VI we summarize the main results presented in this work.

II. MOLECULAR INTERACTION AND METHOD

The $\sz{H}2$ ($\sz{D}2$) molecule is composed of two hydrogen (deuterium) atoms linked by a covalent bond, which in the para-hydrogen (ortho-deuterium) state possesses spherical symmetry (total angular momentum zero). The energy scale involved in electronic excitations ($\sim 10^5$ K) is orders of magnitude larger than the intermolecular one ($\sim 10^4$ K), thus to model the $\sz{H}2-\sz{H}2$ (or $\sz{D}2-\sz{D}2$) interaction by means of a radial pair-potential and consider the molecules as point-like turns out to be justified upon the condition of low or moderate pressures. In this work, we have adopted the well-known and commonly used semiempirical Silvera-Goldman pair potential. This potential has proved to perform excellently at low temperature and at the pressure regimes in which we are interested.

The ground state of para-$\sz{H}2$ and ortho-$\sz{D}2$ is determined using the DMC method. DMC is a zero-temperature method which provides the exact ground-state energy of many-boson interacting systems within some statistical uncertainty. This technique is based on a short-time approximation for the Green’s function corresponding to the imaginary time ($\tau$)-dependent Schrödinger equation. Despite this method is algorithmically simpler than domain Green’s function Monte Carlo, it presents some ($\Delta\tau$) bias coming from the factorization of the imaginary time propagator $e^{-\Delta\tau\hat{H}}$. Our implementation of DMC is quadratic, hence the control of the time-step bias is efficiently controlled given that the required $\Delta\tau$ extrapolation is nearly eliminated by choosing a sufficiently small time step.

The Hamiltonian $\hat{H}$, describing our system is

$$H = \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j}^{N} V(r_{ij}) , \quad (1)$$

and the corresponding Schrödinger equation in imaginary time $(it \equiv \tau)$,

$$-\hbar \frac{\partial \Psi(R, \tau)}{\partial \tau} = (H - E) \Psi(R, \tau) , \quad (2)$$

with $E$ an arbitrary constant. Equation (2) can be formally solved by expanding the solution $\Psi(R, \tau)$ in the basis set of the energy eigenfunctions $\{ \Phi_n \} \ (\Phi_n \equiv \{ r_1, r_2, \ldots, r_N \})$. It turns out that $\Psi(R, \tau)$ tends to the ground-state wave function $\Phi_0$ of the system for an infinite imaginary time as well as the expected value of the Hamiltonian tends to the ground-state value $E_0$. The hermiticity of the Hamiltonian guarantees the equality

$$E_0 = \frac{\langle \Phi_0 | H | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = \frac{\langle \Phi_0 | H | \psi_T \rangle}{\langle \Phi_0 | \psi_T \rangle} = \langle H \rangle_{\text{DMC}} , \quad (3)$$

where $\psi_T$ is a convenient trial wave function. As a consequence, the ground-state energy of the system can be
computed by calculating the integral
\[ \langle H \rangle_{_{\text{DMC}}} = \lim_{\tau \to \infty} \int_V E_L (\mathbf{R}) f (\mathbf{R}, \tau) \, d\mathbf{R} \, , \]  
(4)
where \( f (\mathbf{R}, \tau) = \Psi (\mathbf{R}, \tau) \psi_T (\mathbf{R}) \), and \( E_L (\mathbf{R}) \) is the local energy defined as \( E_L (\mathbf{R}) = \mathbf{H} \psi_T (\mathbf{R}) / \psi_T (\mathbf{R}) \). The introduction of \( \psi_T (\mathbf{R}) \) in \( f (\mathbf{R}, \tau) \) is known as importance sampling and its use is important to reduce the variance of Eq. (1) to a manageable level (for instance, by imposing \( \psi_T (\mathbf{R}) = 0 \) when \( r_{ij} \) is smaller than the core of the pair interaction).

In this work, all the operators diagonal in real-space which do not commute with the Hamiltonian, that is \( [\mathbf{H}, \hat{O}] \neq 0 \), have been sampled using the pure estimator technique based on forward walking. Essentially, with this method the possible bias introduced by \( \psi_T \) in the mixed estimator \( \langle \hat{O} \psi_T \rangle \) are removed by proper weighting of the configurations generated along the simulation.

III. MOLECULAR PARA-HYDROGEN

A. Variational Monte Carlo results

In this section, we present a variational Monte Carlo (VMC) study of two-dimensional p-H$_2$, which provides us with the most convenient trial wave function (twf) to be used in subsequent DMC calculations and valuable physical insight on the system itself. In brief, the VMC method relies on the variational principle which states that given a Hamiltonian the energy difference \( E_L - E_0 \) averaged over the probability density distribution \( |\psi_T|^2 \) is always positive and it decreases as the overlapping between \( \psi_T \) and the true ground-state wave function increases (\( E_L \) and \( E_0 \) are the local energy defined in the previous section and the ground-state energy, respectively). In the present work, the main variational effort has been devoted to achieve an accurate description of the 2D solid phase. We have checked by means of VMC and DMC that in both p-H$_2$ and o-D$_2$ systems the triangular configuration is the stable one at all the studied densities. The energies reported in this section have been calculated at the density \( \rho = 0.060 \, \text{Å}^{-2} \), which corresponds to the variational equilibrium density of the solid.

In order to determine the nature of the ground-state of the system we have also carried out simulations for the liquid phase. In this case, the trial wave function is of Jastrow type,
\[ \psi_J (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \prod_{i<j} f_2 (r_{ij}) \, , \]  
(5)
where the two-body factors \( f_2 \) account for the molecular correlations arising in the system due to pair interactions. These two-body correlation factors have been chosen of McMillan form, \( f_2 = e^{-\frac{3}{2} (z_0)^2} \), and as best value of the variational parameter \( b \) we obtain 3.70 Å.

For the solid phase, an additional one-body factor is introduced \textit{ad hoc} in the trial wave function to the end of reproducing the periodic order of the system and so making the sampling over the space of configurations more efficient (Nosanow-Jastrow model). Such one-body factor consists in a production of localizing functions centered on the positions that define the perfect crystal configuration (sites), given by the family of vectors \( \{ \mathbf{R}_i \} \)
\[ \psi_{N,J} (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \psi_J \prod_{i} g_3 (|\mathbf{r}_i - \mathbf{R}_i|) \, . \]  
(6)

We have explored two different trial wave functions based on \( \psi_{N,J} \), each one consisting in a different choice for \( g_3 (r) \). The first model corresponds to the standardly used Gaussian function,
\[ g_G (r) = \exp \left( -\frac{a_G}{2} r^2 \right) \, , \]  
(7)
while the second is a Padé function, defined as
\[ g_P (r) = \exp \left( -\frac{a_P r^2}{1 + c_P r} \right) \, , \]  
(8)
where \( a_G \), \( a_P \) and \( c_P \) are variational parameters to be optimized. Even though \( g_G (r) \) and \( g_P (r) \) are analytically quite similar, the asymptote of \( g_G \) can be choosen as to decay to zero less abruptly than that of \( g_G \) (see Fig. 1). This feature can be used in the simulations for increasing somewhat the degree of delocalization of the molecules at the expense, however, of an increase of the kinetic energy within the surroundings of the equilibrium positions (where \( g_P (r) \) varies more rapidly than \( g_G (r) \) ). In Table I, we report the best energies obtained in the optimization process of \( \psi_{N,J} \) with Gaussian and Padé functions for \( g_3 (r) \) as well as the optimal set of parameters. As one can see, in both cases the lowest energy obtained is \(-21.3(1) \, \text{K} \). It is worthwhile noticing that when the asymptotes of the Padé factors are widened (that is, the value of \( c_P \) is increased), or equivalently, when the molecules are left to move more freely around the equilibrium positions, the energy of the system increases. Given the variational equivalency between \( g_G (r) \) and \( g_P (r) \) , we opt for \( \psi_{N,J} \) with Gaussian factors and optimal parameters \( b_G = 3.45 \, \text{Åand} \, a_G = 0.67 \, \text{Å}^{-2} \) in our subsequent DMC calculations.

It is well known that \( \psi_{N,J} \) is not symmetric under the permutation of particles (that is, \( \psi_{N,J} (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \neq \psi_{N,J} (\mathbf{r}_2, \mathbf{r}_1, \ldots, \mathbf{r}_N) \)). This property is manifestly incorrect for a system of indistinguishable bosons. Nevertheless, the use of the Nosanow-Jastrow model is widely spread within the field of microscopic calculations since it is assumed that the effect of symmetrization on the total and partial energies of quantum solids is practically negligible. In fact, we will show in brief that this is also the case for two-dimensional hydrogen. To this end, we
have tested the quality of several symmetrized trial wave functions in the variational study of 2D solid p-H$_2$. As mentioned in the Introduction, our motivation for this analysis is twofold: estimate the influence in the energy of molecular quantum exchanges, and chiefly, study the possibility of its use as importance sampling in DMC to determine the possible existence of Bose-Einstein condensation (BEC) and superfluidity.

We have studied three different symmetrized trial wave functions. The first model consists in a permanent of monoparticular functions containing the $N$ possible permutations $\{P\}$ of the $N$ particles among the different lattice sites, expressed as

$$
\psi_{JL}^{S1}(r_1, r_2, \ldots, r_N) = \psi_J \sum_{\{P\}} g_1 (r_i - R_{Pi}).
$$

(9)

Due to the algebraic difficulties arising in the implementation of permanents (contrarily to what occurs with determinants), the sampling of $\psi_{JL}^{S1}$ must be divided into two different parts, one performed in the space of spatial configurations and the other in the space of permutations. The acceptance probability for a proposed change of position of the particle labeled $i$, $r_i \rightarrow r_i'$, corresponds to

$$
q = \min \left( 1, \frac{\psi_J (r_i')^2 g_1 (r_i' - R_{P1}) g_1 (r_i - R_{Pj})}{\psi_J (r_i)^2 g_1 (r_i - R_{P1}) g_1 (r_i' - R_{Pj})} \right),
$$

(10)

where the subindex $Pi$ can take any of the $N$ possible lattice sites. On the other side, the acceptance probability for a proposed site permutation between the $i$ and the $j$ particles, $R_{Pi} \leftrightarrow R_{Pj}$, is

$$
Q_2 = \min \left( 1, \frac{g_1 (r_j - R_{Pj}) g_1 (r_i - R_{Pj})}{g_1 (r_j - R_{Pj}) g_1 (r_i' - R_{P1})} \right).
$$

(11)

Notice that permutations involving more than two particles are not sampled since the acceptance level for swap permutations is already extremely low.

The optimal results obtained with $\psi_{JL}^{S1}$, using Gaussian and Padé $g_1 (r)$ functions, are reported in Table I. By comparing the variational energies obtained with $\psi_{NJ}$ and $\psi_{JL}^{S1}$, we show that symmetrizing $\psi_{NJ}$ with the above prescription has not appreciable effects on the total energy of p-H$_2$. Nevertheless, it must be said that one should not draw other conclusive statements about the effects of a full symmetrization based on the approximation of the permanent by a reduced sampling in the permutation space of the type $\{\{\}\}$. In fact, the acceptance rate of permutations is already extremely low.

The second model of symmetrized trial wave function $\psi_{JL}^{S2}$ consists in a productory of sums in the form

$$
\psi_{JL}^{S2}(r_1, r_2, \ldots, r_N) = \psi_J \prod_{i=1}^{N} \left( \sum_{j=1}^{N} g_1 (r_i - R_{ij}) \right).
$$

(12)

This trial wave function has been proposed very recently by Zhai and Wu and has been suggested to be of possible relevance for the study of the supersolid. In fact, $\psi_{JL}^{S2}$ avoids any explicit sampling in permutation space hence turns out to be well-suited for being used as importance sampling in DMC simulations. However, as one can see in Table I the best variational energy obtained with this model is sizably larger than the ones obtained with $\psi_{NJ}$ and $\psi_{JL}^{S1}$, in both Gaussian and Padé cases. In fact, the variational energy obtained with $\psi_{JL}^{S2}$ is very similar to the one calculated with $\psi_J$ for the liquid ($\sim -17.4$ K). In doing the simulation with this wave function it is observed that particles diffuse excessively within the container giving place to glassy-like configurations; we have checked this feature by monitoring the radial pair distribution function (see Fig. 2 and mean squared displacement (which grows steadily with time). The reason for this excessive atomic diffusion is that the way in which the one-body factor is symmetrized in $\psi_{JL}^{S2}$ does not penalize multiple occupation of a same lattice site. This feature will be illustrated in short by means of a simple example involving two particles moving in one dimension. Moreover, if the width of $g_1 (r)$ is narrowed in order to avoid such unrealistic molecular diffusion, the total energy of the system is worsened because of the rapid increase of kinetic energy.

The third type of symmetrized trial wave function reads

$$
\psi_{JG}^{S3}(r_1, r_2, \ldots, r_N) = \psi_J \prod_{j=1}^{N} \left( \sum_{i=1}^{N} g_1 (r_i - R_{ij}) \right),
$$

(13)

and it is also straightforward to implement in DMC codes. This type of trial wave function has been proposed very recently by Cazorla et al. and has been used to set an upper bound of $10^{-5}$ for the superfluid fraction of perfect crystalline bulk $^4$He at zero temperature. $\psi_{JL}^{S3}$ and $\psi_{JL}^{S2}$ look similar, the difference being that the pro-
We have studied the energetic and structural properties of p-H$_2$ using the DMC method and $\psi_{N,J}$ as trial wave function. We have verified that the DMC energy and diagonal properties obtained with $\psi_{N,J}$ are statistically indistinguishable from the ones obtained using the symmetric wave function $\psi_{JG}^{S3}$. The results presented in this section have been obtained for a rectangular plane containing 90 particles with periodic boundary conditions in the two spatial directions. Internal parameters of the simulations, namely the averaged population of walkers and time step, are 250 and $5 \cdot 10^{-4}$ K$^{-1}$, respectively; these parameters have been adjusted in order to reduce any possible bias to the level of the statistical uncertainty ($\sim 0.05$ K).

In Table II, we report the total ground-state energy per particle, $E/N$, corresponding to 2D solid p-H$_2$ at some densities. The pure (unbiased) estimation of the potential, $V/N$, and kinetic energies, $T/N$, are also quoted therein. The energy results have been corrected for the finite size of the simulation plane by assuming the radial

### Table I: Optimal variational total energy per particle obtained at the density $\rho = 0.060$Å$^{-2}$ with different trial wave function models. Values appearing on the left(right)-side of the table correspond to one-body factors $g_1(r)$ adopted in the form $g_1(r) = \langle g_1(r) \rangle$.

| $\psi_{N,J}$ | $a_2$ (Å$^{-2}$) | $E/N$ (K) | $Q_2$ (%) |
|--------------|-----------------|-----------|-----------|
| $\psi_{S1}$  | 3.45            | 0.67      | -21.3(1)  |
| $\psi_{S2}$  | 3.45            | 0.67      | -21.3(1)  |
| $\psi_{S3}$  | 3.58            | 0.38      | -17.9(1)  |
| $\psi_{JG}$  | 3.45            | 0.61      | -20.4(1)  |

We have studied the energetic and structural properties of p-H$_2$ using the DMC method and $\psi_{N,J}$ as trial wave function. We have verified that the DMC energy and diagonal properties obtained with $\psi_{N,J}$ are statistically indistinguishable from the ones obtained using the symmetric wave function $\psi_{JG}^{S3}$. The results presented in this section have been obtained for a rectangular plane containing 90 particles with periodic boundary conditions in the two spatial directions. Internal parameters of the simulations, namely the averaged population of walkers and time step, are 250 and $5 \cdot 10^{-4}$ K$^{-1}$, respectively; these parameters have been adjusted in order to reduce any possible bias to the level of the statistical uncertainty ($\sim 0.05$ K).


| ρ (Å⁻²) | E/N (K) | V/N (K) | T/N (K) |
|---------|---------|---------|---------|
| 0.053   | −19.42(2) | −35.73(3) | 16.30(3) |
| 0.060   | −22.21(2) | −43.67(3) | 21.46(3) |
| 0.065   | −23.27(2) | −49.23(4) | 25.96(4) |
| 0.067   | −23.42(2) | −51.68(4) | 28.26(4) |
| 0.070   | −23.19(2) | −54.83(4) | 31.64(4) |
| 0.076   | −21.30(2) | −59.22(5) | 37.92(5) |
| 0.083   | −14.23(2) | −62.40(7) | 48.17(7) |

**TABLE II**: Ground-state energy E/N, potential energy V/N, and kinetic energy T/N, per particle of solid 2D p-H₂. Potential and kinetic energies are obtained with pure estimators.

The pair distribution function \( g(r) \) to be one beyond the distance \( R_{\text{max}} = L/2 \), with \( L \) being the size of the plane. Assuming \( g(r) \sim 1 \) beyond \( R_{\text{max}} \) could seem a crude approximation for crystals since this function shows periodic structure (see for instance Fig. 5). However, the periodic oscillations of \( g(r) \) around unity might suggest that in average this approximation is essentially correct.

In order to test the reliability of this finite size correction we have calculated the total energy per particle in a plane containing 90, 120 and 168 molecules at the density \( \rho = 0.0597 \, \text{Å}^{-2} \); we obtain \( E/N = -22.19(2) \), \(-22.16(2)\) and \(-22.15(2)\) K, respectively, thus achievement of convergence within the present statistical uncertainty is proved.

The energy per particle corresponding to liquid and solid 2D p-H₂ at zero temperature is plotted in Fig. 4 as a function of the density. The simulation of the metastable liquid phase uses a Jastrow wave function \( \psi_J \) as importance sampling. The lines in Fig. 4 correspond to polynomial fits to our results in the form

\[
E/N = e(\rho) = e_0 + B \left( \frac{\rho - \rho_0}{\rho_0} \right)^2 + C \left( \frac{\rho - \rho_0}{\rho_0} \right)^3. \tag{14}
\]

The pressure, compressibility and speed of sound (averaged for all the directions) are then easily derived from Eq. (14) through the expressions,

\[
P(\rho) = \rho^2 \frac{\partial e(\rho)}{\partial \rho}, \tag{15}
\]

\[
\kappa(\rho) = \frac{1}{\rho} \left( \frac{\partial P}{\partial \rho} \right)_T, \tag{16}
\]

\[
c(\rho) = \left( \frac{1}{m \kappa} \right)^\frac{1}{2}. \tag{17}
\]

The optimal value of the parameters for the solid phase are \( e_0 = -23.453(3) \) K, \( \rho_0 = 0.0673(2) \, \text{Å}^{-2} \), \( B = 121(2) \) K, and \( C = 152(8) \) K, where \( e_0 \) and \( \rho_0 \) are the equilibrium energy per particle and density, respectively. According to these figures, the compressibility and speed of sound at the equilibrium density are

\[
k(\rho_0) = 0.0615(8) \, \text{Å}²/\text{K} \quad \text{and} \quad c(\rho_0) = 998.6(1) \, \text{m/s},
\]

The numbers quoted within parentheses being the statistical errors. The equation of state of the liquid phase is also well described by the polynomial form (14) with optimal parameters \( e_0 = -21.43(2) \) K, \( \rho_0 = 0.0633(3) \, \text{Å}^{-2} \), \( B = 75(7) \) K, and \( C = 69(9) \) K.

Another magnitude of interest in the study of bulk systems is the spinodal density \( \rho_S \). \( \rho_S \) sets the limit for the system to remain in a homogeneous phase since at this density the compressibility grows to infinite (or equivalently, the speed of sound becomes zero); in case of going below this point (\( \rho < \rho_S \)) the system breaks down into clusters. According to our DMC calculations, this low-limit density amounts to \( \rho_S = 0.0548(1) \, \text{Å}^{-2} \) in solid p-H₂.

A glance at Fig. 4 shows that the solid phase is the stable one overall the regime of positive pressures. Nevertheless, by looking at our results one could suggest a first order liquid-solid phase transition occurring at negative pressures, where the two equations of state cross each other. Needless to be said, that this possibility deserves detailed exploration since it could provide a chance for superfluidity to be observed in a quantum liquid different from helium. Aimed at this, we have simulated 2D liquid p-H₂ down to densities of \( 0.039 \, \text{Å}^{-2} \), (the spinodal density of the liquid is \( \rho_S = 0.0519(1) \, \text{Å}^{-2} \)) and searched for that transition by means of the Maxwell double-tangent construction. Our results show that a liquid-solid transition is not possible within the range set by the spinodal densities, and thus the possibility of liquid p-H₂ in two dimensions must be rejected.

Our results for the equation of state of p-H₂ can be compared with two previous PIMC studies carried out on the same system. In Ref. 23, Gordillo and Ceperley obtained \( \rho = 0.064 \, \text{Å}^{-2} \) for the equilibrium density of 2D solid p-H₂ at \( T = 1 \) K; the authors of that work reported a figure with the energy per particle as a function of the density, and the minimum of the curve is located at \( \sim -22.0 \) K. A more systematic analysis of the

**FIG. 4**: Total ground-state energy per particle of liquid (dotted line) and solid (dashed line) 2D p-H₂ at zero temperature. The lines correspond to polynomial fits of our results (empty and filled circles); the statistical errors bars are smaller than the symbol size.
extrapolation of the low temperature results to absolute 
squared displacement
TABLE III: Lindemann’s ratio $\gamma$, kurtosis $\zeta$, and mean 
squared displacement $\langle u^2 \rangle$ of 2D solid p-H$_2$ at different 
densities close to equilibrium (pure estimations).

| $\rho (\text{Å}^{-2})$ | $\gamma_{u^2}$ | $\zeta(20)$ | $\zeta(50)$ | $\langle u^2 \rangle (\text{Å}^2)$ |
|------------------------|----------------|-------------|-------------|-------------------------------|
| 0.058                  | 0.121(1)       | 0.00(2)     | 0.00(2)     | 0.19(1)                       |
| 0.060                  | 0.197(1)       | 0.02(2)     | 0.00(2)     | 0.15(1)                       |
| 0.065                  | 0.183(1)       | 0.02(2)     | 0.02(3)     | 0.12(1)                       |
| 0.067                  | 0.178(1)       | 0.01(1)     | 0.02(2)     | 0.11(1)                       |
| 0.070                  | 0.170(1)       | 0.02(1)     | 0.00(2)     | 0.09(1)                       |
| 0.076                  | 0.158(1)       | 0.00(2)     | 0.01(1)     | 0.07(1)                       |
| 0.083                  | 0.146(1)       | 0.01(2)     | 0.01(1)     | 0.06(1)                       |

same system was performed later on by Boninsegni.$^{20}$
In that work, the total energy per particle and chemical 
potential are calculated at several densities and within 
the temperature range $T = 1 - 8$ K. Subsequently, an 
extrapolation of the low temperature results to absolute 
zero was performed, leading to $\rho_0^{\text{PIMC}} = 0.068(5) \text{ Å}^{-2}$, 
$e_0^{\text{PIMC}} = -23.25(5)$ K and $\rho_S^{\text{PIMC}} = 0.0585(10) \text{ Å}^{-2}$. We 
note that the agreement between those zero-temperature 
extrapolated PIMC values and our DMC results is fairly 
good, specially in the case of the equilibrium density $\rho_0$.

We have analyzed the structure of the 2D solid by 
calculating the radial pair distribution function $g(r)$,
$$g(r) = \frac{N - 1}{\rho} \int \frac{|\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N}{\int |\Psi(\mathbf{r})|^2 d\mathbf{r}} ,$$
and the Lindemann’s ratio $\gamma_{u^2}$,
$$\gamma = \frac{1}{a} \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i - \mathbf{R}_e)^2} = \frac{\langle u^2 \rangle^{\frac{1}{2}}}{a} ,$$
where $a$ is the distance between nearest neighbors in 
the perfect crystalline configuration. In Fig. 5 we plot $g(r)$ 
at the density 0.068 Å$^{-2}$ which, as it is expected in 
crystals, exhibits a pattern of periodic order. At low 
temperatures, the Lindemann’s ratio $\gamma$ around the equilibrium 
density tends to zero in classical solids while in quantum 
crystals it is finite due to the zero-point motion of particles, 
hence this quantity is regarded as a good quantum 
indicator. Furthermore, the Lindemann’s ratio (or equivalently, 
the mean squared displacement) is related to the 
Debye-Waller factor $M_Q$, which describes the attenuation 
of the emergent radiation in coherent scattering experiments 
according to the formula $I(Q,T) \propto e^{-2M_Q}$
(where $I(Q,T)$ is the intensity of the outgoing radiation 
scattered by the target and $Q$ is the modulus of the transfer 
wave vector). By means of a cumulant expansion, the 
Debye-Waller factor can be expressed as
$$2M_Q = \langle u^2 \rangle Q^2 - \frac{1}{12} \left( \langle u^4 \rangle - 3 \langle u^2 \rangle^2 \right) Q^4 + O(Q^6) ,$$
where $\langle u^2 \rangle$ is the mean squared displacement along the direction $\mathbf{Q}$. It is easy to see that when the distribution 
of particles around the equilibrium positions is well-
described by a Gaussian function, the quantity within parentheses 
in the second right-term of Eq. (20) is known as kurtosis $\zeta_Q$, 
vanishes. In such a case, the Debye-Waller factor reduces to 
the simple formula $2M_Q = \langle u^2 \rangle Q^2$ . In Table III , we report the Lindemann’s ratio, kurtosis and mean 
squared displacement of two-dimensional p-H$_2$ at different densities. We have calculated $\langle u^2 \rangle$ and $\zeta_Q$ along two orthogonal directions and not 
found appreciable differences in the results. Moreover, 
the kurtosis is null in all the studied cases. Consequently, 
we may conclude that the distribution of hydrogen 
molecules around the equilibrium positions is isotropic and 
can be accurately reproduced by a Gaussian, contrarily to what it is 
found to occur in $^4$He.$^{20}$
Regarding the value of $\gamma$, it can be said that solid H$_2$ is 
less quantum than $^4$He since $\gamma_{u^2} \sim 0.18$ at $\rho_0$ whereas in 
solid helium $\gamma_{He} \sim 0.24$ near melting. Also it is worth 
noticing that the trend of $\gamma_{u^2}$ is to increase with decreasing 
density, therefore quantum exchange effects in the crystal would become of 
greater relevance at small densities.

IV. MOLECULAR ORTHO-DEUTERIUM

The ground-state properties of o-D$_2$ (with total angular 
momentum zero) have been also studied using the DMC 
method and the same radial pair potential (Silvera-
Goldman) than in p-H$_2$. The larger mass of D$_2$ makes one to expect that two-dimensional bulk D$_2$ is solid at 
zero temperature, so in this case we have restricted our 
study to the solid phase.

In our simulations, the equilibrium positions of the 
o-D$_2$ molecules are arranged according to a triangular 
lattice and the particles are assumed point-like. In this case, 
we use the trial wave function
$$\psi_{N,J}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \prod_{i<j} e^{-\frac{1}{2}(b/r_{ij})^2} \prod_{i} e^{-\frac{1}{2}(|\mathbf{r}_i - \mathbf{R}_e|)^2} ,$$
(21)
FIG. 6: Ground-state energy per particle of 2D solid o-D$_2$ (solid line and filled circles), and 2D solid p-H$_2$ (dotted line and empty triangles) which is shown for comparison.

which differs slightly from $\psi_{NJ}$ in Eq. (6) (now the pair correlation factors $f_2$ depend on the extra variational parameter $c$). The variational parameters in Eq. (21) have been optimized using VMC; the best values are $b = 3.32$Å, $c = 7$, and $a = 0.67$Å$^2$. All the DMC simulations have been performed in a rectangular plane containing 120 particles and applying periodic boundary conditions. The target averaged population of walkers, $n_w$, is 250 and the time step, $\Delta \tau$, $5 \times 10^{-4}$ K$^{-1}$. Finite size effects have been corrected with the same approach than used for hydrogen (see Sec. III B).

In Fig. 6, we plot the total ground-state energy per o-D$_2$ molecule as a function of the density; the solid line represents the best fit to our data following the polynomial function expressed in Eq. (14). The best value of the parameters are $B = 241(3)$ K, $C = 324(10)$ K, $c_0 = -42.305(5)$ K and $\rho_0 = 0.0785(2)$ Å$^{-2}$, which lead to a spinodal density $\rho_{s} = 0.0641(2)$ Å$^{-2}$. By comparing with p-H$_2$, we show that o-D$_2$ is denser at equilibrium and appreciably more bounded (the total energy decreases substantially). The heavier mass of the o-D$_2$ molecules, makes the solid to reduce its kinetic energy and mean squared displacement at any density (see Tables II, III, IV and V), thus allowing the system to increase its equilibrium density in order to take advantage of the attractive interparticle interaction.

Concerning the structural properties of 2D solid o-D$_2$, we have calculated the radial pair distribution function at the equilibrium density (see Fig. 6), and the Lindemann’s ratio and kurtosis at different points (see Table V). As it is shown in Fig. 6, the peaks of the radial pair distribution function of 2D o-D$_2$ are sharper and somewhat closer than in molecular hydrogen at equilibrium since the density and degree of localization of the particles are larger in the first case. This statement is also corroborated by the results contained in Table V, where the Lindemann’s ratio is invariably some tenths smaller than in p-H$_2$ at the same density. As a matter of comparison, the Lindemann’s ratio of o-D$_2$ at equilibrium is about 1.3 times smaller than that of p-H$_2$ and 1.7 than in two-dimensional $^4$He. Furthermore, as it could be expected from our previous study of 2D p-H$_2$ (Table III B), the kurtosis in two-dimensional o-D$_2$ is practically null in both the two orthogonal directions for which it has been calculated.

V. ONE-BODY DENSITY MATRIX AND OFF-DIAGONAL LONG RANGE ORDER

A fundamental function in the study of quantum systems is the one-body density matrix $\rho_1(\mathbf{r}, \mathbf{r}')$, defined as

$$\rho_1(\mathbf{r}, \mathbf{r}') = \langle \Phi_0 | \hat{\psi}(\mathbf{r}) \hat{\psi}(\mathbf{r}') | \Phi_0 \rangle ,$$  

where $\hat{\psi}(\mathbf{r})$ and $\hat{\psi}(\mathbf{r}')$ are, respectively, the field operators which destroy a particle from position $\mathbf{r}'$ and create another at position $\mathbf{r}$, and $\Phi_0$ is the ground-state wave function. In particular, a finite value for $\lim_{r \to \infty} \rho_1(\mathbf{r})$ proves the existence of off-diagonal long range order (ODLRO) in the system, the measure being the condensate fraction $n_0$. In quantum Monte Carlo, the one-body density matrix can be estimated by averaging the coordinate operator $\psi_T(\mathbf{r}_1 + \mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)/\psi_T(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$. Here, we use extrapolated estimators for $\rho_1$ since the pure estimation relying on forward walking is only applicable to diagonal operators. Moreover, in order to get consistent results we have required that the two extrapolated estimators of the same accuracy, i.e. $\langle \rho_1(\mathbf{r}) \rangle = 2 \rho_1^{\text{mix}}(\mathbf{r}) - \rho_1^{\text{var}}(\mathbf{r})$ and $\rho_1(\mathbf{r}) = (\rho_1^{\text{mix}}(\mathbf{r})/\rho_1^{\text{var}}(\mathbf{r})$ (where $\text{mix}$ means obtained with DMC and $\text{var}$ with VMC), coincide within the present statistical uncertainty.

| $\rho(\text{A}^{-2})$ | $\gamma_{D_2}$ | $\zeta_{(10)}$ | $\zeta_{(01)}$ |
|-------------------|----------------|----------------|----------------|
| 0.053             | 0.204(1)       | 0.000(1)       | -0.06(2)       |
| 0.060             | 0.187(1)       | 0.011(1)       | 0.00(1)        |
| 0.069             | 0.160(1)       | 0.000(2)       | -0.01(1)       |
| 0.073             | 0.149(1)       | -0.01(1)       | 0.01(1)        |
| 0.078             | 0.139(1)       | 0.000(1)       | 0.01(1)        |
| 0.080             | 0.135(1)       | -0.02(1)       | 0.00(1)        |
| 0.088             | 0.124(1)       | 0.000(1)       | -0.03(1)       |
| 0.094             | 0.117(1)       | -0.02(1)       | 0.02(1)        |

TABLE V: Lindemann’s ratio $\gamma_{D_2}$, and kurtosis $\zeta$ of two-dimensional o-D$_2$ at different densities near the equilibrium.
In order to test the quality of this fit (which in the reduced chi-squared test leads to the value 1.59), we have calculated the atomic kinetic energy of two-dimensional p-H$_2$ through the formula

$$T/N = -\left[\frac{\hbar^2}{2m_{\text{H}_2}} \nabla^2 \rho_1(r)\right]_{r=0},$$

but assuming $G(r)$ instead of $\rho_1(r)$. In fact, it may be shown that Eq. (23) derives from the second moment of the momentum distribution $n(k)$,

$$T/N = \frac{\hbar^2}{2m_{\text{H}_2}} \frac{1}{(2\pi)^3} \rho \int dk k^2 n(k).$$

Proceeding in this way, we obtain $T/N = 19.40(30)$ K which does not agree satisfactorily with the corresponding pure (mixed) estimation 21.46(3) (20.75(2)) K. Very interestingly, Withers and Glyde have recently shown by means of simple models that anharmonic and/or particle-exchange effects in quantum solids may cause the momentum distribution $n(k)$, or equivalently $\rho_1(r)$, to deviate significantly from a Gaussian function. Therefore, on account of our variational results reported in Sec. III A which show that molecule exchanges are likely to occur at very low rate, it may be suggested that two-dimensional hydrogen presents some degree of anharmonicity.

In Fig. 8 (Top), we show DMC results similar to those enclosed in Fig. 7 but for larger distances and expressed in logarithmic scale in order to obtain the asymptote of $\rho_1$. As one observes in there, the value of $\lim_{r\to\infty} \rho_1$ in the unsymmetrized case tends obviously to zero, while for $\psi^S_{\text{JG}}$ it amounts to a small but finite value $n_0 = 6(1) \cdot 10^{-4}$. In the same figure (Bottom), we compare $\rho_1(r)$ at several densities and only for the symmetric wave function; we obtain $n_0 = 2(1) \cdot 10^{-4}$ and $8(1) \cdot 10^{-3}$ at the density 0.067 and 0.056 Å$^{-2}$, respectively. Apart from the fact that we obtain a small but finite condensate fraction for solid p-H$_2$ in all the studied cases, we note that the value of $n_0$ raises very abruptly in moving from equilibrium to densities close to the spinodal point (where $P < 0$). In a very recent work, we have analyzed the superfluid nature of solid $^4$He at zero temperature by means of $\psi^S_{\text{JG}}$. In that work, we showed that the superfluid fraction of bulk solid $^4$He lies below $1 \cdot 10^{-5}$, whereas a clear superfluid signal of $\rho_s/\rho = 3.2(1) \cdot 10^{-3}$ appears in the presence of 1% of vacancies. In the case of vacancies, we found that the condensate fraction increased by roughly a factor two with respect to that of the perfect crystal configuration. According to this outcome, a significant increase of $n_0$ in our simulations might be identified to the appearance of superfluidity in the system.

In order to ensure that the significant raise of $n_0$ observed in our simulations is not due to partial melting of H$_2$, we have calculated the corresponding radial pair distribution function at the density 0.056 Å$^{-2}$.
of both systems, like the total and kinetic energy per particle, radial pair distribution function, and Lindemann's ratio and quoted so isotopic quantum effects in hydrogen. Our results show that no stable liquid phase exists and therefore reducing one dimension with respect to bulk it is not enough to get the so-longly searched superfluid phase of H$_2$.

Interestingly, Wiechert et al. have reported very recently on an experiment on molecular ortho-deuterium coadsorbed on graphite preplated by a layer of Kr, up to temperatures of $\sim$ 1.5 K. The authors of this work claim evidence for the existence of a reentrant D$_2$ liquid at very low temperatures, based on their heat capacity and neutron diffraction measurements. The system explored by Wiechert et al. can be fairly modeled by a monolayer. However, on account of our results for H$_2$, the possibility of pure two-dimensional liquid deuterium at zero temperature must be ruled out. On the expectance of new and more explanatory experiments, we may point that, assuming that thermal effects are practically negligible, the role of the interactions between the deuterium molecules and the atoms of the substrate are the ones of relevance. Certainly, Turnbull and Boninsegni have already addressed recent work on this direction by means of the Path Integral Monte Carlo (PIMC) method and simple interaction models. Further improvement on the modeling of coadsorbed systems, putting especial emphasis on the description of the interactions and the effect of corrugation with the substrate, may open new and challenging venues for the realization of superfluidity in p-H$_2$ and o-D$_2$ systems.

At the variational level, we have analyzed the quality of three different symmetrized trial wave functions based on the Nosanow-Jastrow model in describing 2D solid molecular hydrogen. We have shown that the recently proposed symmetrized wave function used to describe the supersolid also characterizes hydrogen satisfactorily. By using that wave function, we have studied the behavior of the one-body density matrix of solid p-H$_2$ with density and predicted that the system could become superfluid at very dilute densities (where $P \leq 0$). Further work is being carried out to estimate the superfluid density in the negative pressure region trying to confirm the signature observed in the one-body density matrix.

VI. DISCUSSION AND CONCLUSIONS

To summarize, in this work we have studied two-dimensional p-H$_2$ and o-D$_2$ at zero-temperature and low pressures, with the diffusion Monte Carlo method and the Silvera-Goldman semi-empirical pair interaction. We have assessed several energetic and structural properties of both systems, like the total and kinetic energy per particle, radial pair distribution function, and Lindemann’s

Fig. 9 (Top), we report $g(r)$ for hydrogen and compare it with the one obtained for two-dimensional $^4$He above its freezing point. Clearly, a typical solid pattern emerges for H$_2$. Moreover, in the same figure (Bottom) we also plot the structure factor $S(k)$ for molecular hydrogen at the equilibrium density $\rho_0 = 0.067$ Å$^{-2}$ and $\rho = 0.056$ Å$^{-2}$; in both cases marked peaks emerge at the reciprocal lattice vectors. Therefore, the significant variation of $n_0$ that we observe when the density decreases is not caused by possible structural instabilities affecting the solid.

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