Study of distortion effects and clustering of isotopic impurities in solid molecular para-hydrogen by Shadow Wave Functions

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We employed a fully optimized Shadow Wave Function (SWF) in combination with Variational Monte Carlo techniques to investigate the properties of HD molecules and molecular ortho-deuterium (o-D\textsubscript{2}) in bulk solid para-hydrogen (p-H\textsubscript{2}). Calculations were performed for different concentrations of impurities ranging from about 1% to 25% at the equilibrium density for the para-hydrogen crystal. By computing the excess energy both for clustered and isolated impurities we tried to determine a limit for the solubility of HD and o-D\textsubscript{2} in p-H\textsubscript{2}.

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Isotopic impurities in quantum crystals are often used as a marker for testing the occurrence of quantum mechanical particle–particle exchange by means of the NMR experiments\textsuperscript{1,2}. In particular, in the case of \( J = 0 \) impurities, like HD or (o-D\textsubscript{2}) molecules, embedded in a \( J = 0 \) para-hydrogen (p-H\textsubscript{2}) matrix with small concentrations of ortho-hydrogen (less than 3%), the observed longer time relaxation can only be attributed to particle–particle tunneling, because the so-called "resonant conversion" is not allowed (see Ref. \textsuperscript{2} and its inner references). Concentrations of HD molecules in these experiments are about 1-2\%\textsuperscript{1}. It is safe to assume that the interaction among different hydrogen isotopes are very similar. Only the mass difference should distinguish the behavior of p-H\textsubscript{2} and HD. This is the main reason for relating the motion of HD impurities to the motion of the molecules in the matrix. However, in a quantum mechanical solid, the mass difference among the constituents can act in quite subtle way. In fact, heavier particles tend to be more localized, with a net gain in energy, while their nearest neighbors might find convenient to lower their kinetic energy by relaxing towards the impurity, in a very delicate balance between the gain in kinetic energy and the loss in potential energy. This is the case of HD and o-D\textsubscript{2}impurities in H\textsubscript{2}. The presence of impurities of lower mass (like \textsuperscript{3}He in \textsuperscript{4}He) should instead have a less dramatic effect, due to steric hindrance which prevents the impurity from relaxing too much against the rest of the crystal. Change of force constants and lattice distortion in the proximity of a isotopic impurity were studied in relation to their influence on the thermal conductivity of solid p-H\textsubscript{2} at low temperatures\textsuperscript{3}. More recently, Raman spectroscopy experiments\textsuperscript{4} clearly showed an effect on both rotational and vibrational spectra which can be attributed to local relaxation of the lattice around the impurity. The balance among kinetic and potential energy might also lead to clustering phenomena when the concentration of impurities exceeds a certain limit. Finally, HD impurities might play a role in the determining the results on measurements of non classical torsional inerti recently performed to investigate the existence of a supersolid phase in p-H\textsubscript{2}\textsuperscript{5}.

In this letter we report the results of Variational Monte Carlo (VMC) simulations performed with a modified Shadow Wave Function\textsuperscript{6, 7} (SWF) to study the properties of HD and o-D\textsubscript{2} molecules in a pure p-H\textsubscript{2} matrix. The main property of SWF is the capability of describing both the crystalline and the disordered phase of a quantum system with the same functional form, with is always translationally invariant. Unlike in the standard Jastrow–Nosanow trial wave function, using SWF no a priori equilibrium are imposed to describe the crystalline phase. This property allows SWF to provide a realistic description of a variety of inhomogeneous system, like liquid–solid phase coexistence in \textsuperscript{4}He\textsuperscript{8}, as well as finite system as, for instance, \textsuperscript{4}He clusters with and without impurities\textsuperscript{9}. Recently a SWF has been employed also for p-H\textsubscript{2}, in order to describe the homogeneous liquid and solid phase\textsuperscript{10, 11}, as well as to investigate energetic and structural properties of defective crystals\textsuperscript{11}.

We model the system of \( N_{H} \) molecules of p-H\textsubscript{2} and \( N_{I} \) isotopic impurities as a set of \( N = N_{H} + N_{I} \) point particles described by the following Hamiltonian:

\[
\mathcal{H} = -\frac{\hbar^2}{2m_{H}} \sum_{i=1}^{N_{H}} \nabla_{i}^2 - \frac{\hbar^2}{2m_{J}} \sum_{i=1}^{N_{J}} \nabla_{i}^2 + \sum_{i<j} v(r_{ij}),
\]

where \( v(r) \) is the well–known Silvera–Goldman (SG) potential\textsuperscript{12}. This model interaction includes a term \( \propto 1/r^3 \) which effectively accounts for triple dipole interactions in the system. This approximation is supported by the fact that both the p-H\textsubscript{2} molecule and the isotopic impurities considered in this paper, HD and o-D\textsubscript{2} are in the rotational ground state (\( J = 0 \)), and therefore the average interaction must be spherically symmetric. Higher terms in a multipolar expansion, due to the non–spherical nature of the molecules, may be safely considered as second order. The limit of validity of the SG potential and the influence of explicit many–body terms in the potential on the equation of state have been recently tested.
both for solid p-H$_2$\cite{13} and o-D$_2$\cite{14}. In the latter case, the SG potential has been found to give a rather good description of the equation of state, while in the case of solid p-H$_2$ the same interaction leads to a slightly more inaccurate result on the energies due to stronger many-body effects. However, the explicit angular dependence of the potential seems not to have sizeable effects on the structural properties, such as the pair distribution function. The many-body quantum mechanical problem is solved at temperature T=0 by means of a trial solution for the ground-state of the Hamiltonian in Eq. (1) in the form of a modified Shadow Wave Function:

$$\Psi_T(R) = \phi_v(R) \int K(R, S) \phi_s(S) dS,$$

where $R = \{r_1, \ldots, r_N\}$ are the coordinates of the molecules and $S = \{s_1, \ldots, s_N\}$ are 3N auxiliary degrees of freedom named shadows. Both functions $\phi_v$ and $\phi_s$ have been expressed as Jastrow products of pair functions:

$$\phi_v(X) = \exp \left[ \frac{1}{2} \sum_{i<j} u_{HH}(x_{ij}) \right] \exp \left[ \frac{1}{2} \sum_{i<j} u_{II}(x_{ij}) \right] \times$$

$$\times \exp \left[ \frac{1}{2} \sum_{i=1}^{N_H} \sum_{j=1}^{N_I} u_{IH}(x_{ij}) \right],$$

while the kernel $K(R, S)$ is written as a product of Gaussians connecting the real and auxiliary degrees of freedom:

$$K(R, S) = \prod_{i=1}^{N_H} \exp \left[ -C_H(r_i - s_i)^2 \right] \prod_{i=1}^{N_I} \exp \left[ -C_I(r_i - s_i)^2 \right].$$

The pair pseudopotentials between molecules have been expanded in term of suitable basis functions:

$$u_{xy}(r) = \left( \frac{b_{xy}}{r} \right)^5 + \sum_m a_{xy}^m \chi_m(r),$$

where both $x$ and $y$ indicate generically one of the two label "H" or "I". The basis functions $\chi_m$ (about 40) are the same used in Ref.\cite{13} and\cite{14} for DMC calculations in solid p-H$_2$ and o-D$_2$.

$$\chi_m(r) = \begin{cases} \{1 - \cos \left[ \frac{2\pi m}{L/2-r_c} (r - L/2) \right]\} r^{-5} & r > r_c, \\ 0 & r \leq r_c, \end{cases}$$

where $L$ is the side of the simulation box. The cutoff radius $r_c$ allows to remove divergences for $r \to 0$ in order to avoid numerical instabilities in the optimization procedure. If such cutoff is small enough, it does not influence the value of the energy. In our calculations it has been taken equal to 1Å. The pseudopotential between auxiliary degrees of freedom is indeed just the rescaled Silvera–Goldman interaction:

$$u_{xx}(s) = \delta_{xx}(v_{xx}s).$$

The parameters $\{b_{xy}\}, \{a_{xy}^m\}, \{C_x\}, \{\alpha_{xy}\}, \{\delta_{xy}\}$ have been optimized following the reweighting scheme, which alternate between VMC simulations and minimization of a combination of the variance on the expectation value of the Hamiltonian, and of the expectation value itself estimated on a subset of the sampled configurations. We performed simulations for a face centered cubic (fcc) lattice at densities $\rho = 0.02609\,\AA^{-3}$, very close to the bulk equilibrium density of pure p-H$_2$\cite{13}. The simulation cell was set to accommodate $3 \times 3 \times 3$ elementary cubic cells for fcc, with a total of $N=108$ lattice sites. All the intermolecular interactions are truncated at the edge of a sphere of radius equal to $L/2$, where $L$ is the length of the side of the cell. The contribution from the potential energy outside the sphere is estimated by integrating the potential in the $(L/2, +\infty)$ interval, assuming therefore all the pair correlation functions of molecules and impurities to be constant beyond $L/2$. Calculations were performed for different number of impurities, from 1 to 27, corresponding to concentrations ranging from about 1% to 25%. For each value of concentration, we repeated the optimization of the trial wave function both with all the impurities initially localized around next-neighbours site, as close to each other as possible, and with far impurities, i.e., separated by at least a shell of p-H$_2$. The excess energy per impurity $\epsilon_{imp}$ is defined as follow:

$$\epsilon_{imp} = \frac{1}{N_I} [E(N_H, N_I) - E(N, 0)],$$

where $E(N_H, N_I)$ is the total energy of the system of $N_H$ molecules of p-H$_2$ and $N_I = N - N_H$ impurities. It can be noticed that the excess energy per impurity remains almost constant in the range of concentrations considered. A rough estimate of the excess energy of a single
isotopic impurity in the p-H2 crystal might be obtained considering as a perturbation term in the Hamiltonian the difference in kinetic energy $\Delta E_{\text{kin}}$ due to the mass difference of the two isotopes.

$$e_{\text{imp}} \approx \left( \frac{m_H}{m_D} - 1 \right) \Delta E_{\text{kin}}$$  \hspace{1cm} (9)

The excess binding energy estimated in this way is about 35K for o-D2 and about 24K for HD. Both values are not far from the values of about 40K and 25K respectively, obtained from the VMC simulations. This fact suggests that the contribution of the mass difference to the excess energy of the impurity is dominant, in particular for HD impurities. We point out that in SWF simulations both relaxation and possible quantum diffusion effects are correctly taken into account. As shown in Figures 1 and 2 the excess energy computed with clustered or diluted impurities, is essentially coincident within errorbars for low concentrations. For concentrations up to 10% we are therefore lead to consider the o-D2 as not subject to clustering in the p-H2 crystal matrix. For higher concentrations, however, the excess energy per impurity for clustered molecules becomes lower than the energy for the diluted ones well outside errorbars. In the case of HD impurities, this threshold is higher, as it might be expected because of the lighter mass, and the VMC results are compatible with a limiting concentration for clustering of about 15%. In order to check if the estimate of the excess energy and of the clustering limits are affected either by finite–size effects or by the choice of the lattice fitted by the simulation box, we performed some simulations in a larger fcc lattice using $N = 256$ molecules arranged on $4 \times 4 \times 4$ elementary cubic cells and in the hcp lattice using $N = 180$ molecules filling $5 \times 3 \times 3$ elementary cells. In this case the simulation box is not cubic, but the ratio of the three sides is as close as possible to 1. The results for concentration of 25% of o-D2 molecules obtained with different lattices and different values of $N$ show that the values of the excess energy are largely independent from from the total number of particles, indicating the absence of substantial size–finite effects.

The energy differences between the system with clustered or diluted impurities, can be splitted into the mean kinetic and potential energy contributions for p-H2 molecules and impurities, as reported in Tables I and II. From this analysis it is possible to see how the lower energy of the system with clustered impurities is due to the drastic lowering of the expectation of the potential energy of the impurities themselves. As shown below, this result is related to the stronger localization of the impurities around equilibrium positions on a lattice with spacing reduced compared to that of p-H2 molecules. Although the average total energy of the p-H2 molecules becomes higher when the impurities are clustered, the net effect is lower total energy of the system. Some information about the distortions in the crystal induced by the impurities in the p-H2 matrix can be obtained by computing the pair correlation function

$$g_{\alpha\beta}(r) = \left\langle \sum_{i \neq j} \delta \left( |r_i^\alpha - r_j^\beta| - r \right) \right\rangle ,$$ \hspace{1cm} (10)

where $\alpha$ and $\beta$ indicate the species among which distances are computed and from the configurations of the system sampled in the MC simulations. When using the SWF it is also possible to define the same operator for the shadow degree of freedom

$$g_{\alpha\alpha,\beta}(s) = \left\langle \sum_{i \neq j} \delta \left( |s_i^\alpha - s_j^\beta| - s \right) \right\rangle .$$ \hspace{1cm} (11)

As discussed elsewhere[6, 10], the shadows in quantum crystals are more rigid degrees of freedom, which act
as heavier particles indicating a sort of “average” position for the real quantum particles. In Figures 3 and 4 we report the pair correlations functions both for p-H$_2$ molecules and for the impurities in the case of a concentration of 25% of clustered impurities embedded in a fcc p-H$_2$ matrix. The o-D$_2$ impurities tend to be more localized than the p-H$_2$ molecules, as expected due the higher mass. Moreover, the peaks of the pair correlation function of clustered o-D$_2$ impurities are clearly shifted inwards, with respect to the pair correlation of surrounding hydrogen molecules. The strong localization of the impurities around equilibrium positions closer to each other than ones of p-H$_2$ give probably rise to the drastic lowering of the potential energy of the o-D$_2$ molecules discussed above, making the clustering of impurities energetically favourite.

In conclusion, we used a Shadow Wave Function in connection with Variational Monte Carlo calculations to study the properties of o-D$_2$ and HD molecules in a p-H$_2$ crystal. In particular we computed the excess energy for clustered and isolated impurities at different concentrations, trying to determine a limit for the solubility of o-D$_2$ and HD in p-H$_2$.

For concentrations up to 10% and 15%, for o-D$_2$ and HD molecules respectively, the excess energy computed for clustered impurities becomes lower than that for diluted ones.

Calculations of the pair correlation function show that at large concentrations clustered impurities are localized around equilibrium positions closer than ones of p-H$_2$ molecule giving rise to a drastic lowering of the potential energy of the impurities themselves.

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