

Isotopic Effects in Solid LiH and LiD at Very Low Temperature

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The ground state of the ionic solids LiD and LiH is theoretically studied using the Variational Monte Carlo (VMC) method. Our main focus has been the calculation of relevant properties of the H^- and D^- ions using a fully quantum approach. In particular, we report results on their kinetic energies, mean-squared displacements, Einstein frequencies, radial distribution functions, and density profiles around the sites. The microscopic results obtained for both isotopes show corrections beyond trivial isotopic effects due to their quantum behavior. Finally, the VMC results are compared with predictions from self consistent average phonon (SCAP) theory at $T = 0$ K.

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1. INTRODUCTION

Lithium hydride and deuteride¹ are ionic crystals with a simple electronic structure, four electrons per unit cell, both fairly well-described structurally (neutron diffraction),^{2,3} and dynamically (second-order Raman spectroscopy),⁴ and through *ab initio* electronic structure simulations.⁵ Among other arguments, LiH and LiD are very interesting systems due to their extremely simple electronic structure and to the large isotopic effects when the hydrogen ions are replaced by the deuterium ones. On the other hand, the light mass of the ions, specially H and D, makes that these solids have to be considered like quantum crystals, and consequently, described theoretically by quantum theory.

In the present work, we present microscopic results for the ground state of H^- and D^- ions in the solid by using the variational Monte Carlo (VMC) method.⁶ VMC is a fully quantum approach which relies on the variational principle and it has been extensively applied in the past in the calculation

of quantum crystals, mainly ^4He and ^3He . Recently, we have carried out a VMC calculation of properties such as the kinetic energy and the mean-squared displacement in LiH and the results compare fairly well with data from incoherent inelastic neutron scattering.³ With this agreement in mind, we have extended the calculation to LiD trying to elucidate the relevance of isotopic substitution and the quantitative correction to the classical estimation induced by the quantum character of the solid. Quasiharmonic and harmonic solids such as Ne, Kr, and Xe have been studied in the past using the self-consistent average phonon (SCAP) formalism,^{7,8} and the results obtained are in good agreement with experimental data.⁸ We study the validity of this approach in LiH and LiD by comparing its predictions with the VMC results. The present application of SCAP theory consists in calculating the Einstein frequency, Ω_0 and, from it, the other magnitudes which in SCAP theory are analytical functions of Ω_0 . The SCAP results obtained are not far from the VMC data but the differences are nevertheless significant.

2. THEORETICAL MODEL

The crystalline structure of LiD (LiH) is a fcc lattice with a two-atom basis, Li^+ in $(0, 0, 0)$ and D^- (H^-) shifted by $(a/2)(\mathbf{i} + \mathbf{j} + \mathbf{k})$, where a is the lattice parameter equal to 4.044 (4.058) Å.¹ The Coulomb interaction between the ions is the responsible for the cohesion of the solid, while short-range interactions are globally repulsive and smaller in magnitude. The overlap repulsion potential takes the form of the Born–Mayer interaction and includes the usual van der Waals attractive term. In particular, we have adopted the Sangster and Atwood⁹ interatomic potential which additionally incorporates a term for the dipole–quadrupole attraction,

$$V_{\text{SA}}^{\alpha,\beta}(r) = B_{\alpha,\beta} \exp\left[A_{\alpha,\beta}(E_{\alpha,\beta} + F_{\alpha,\beta} - r)\right] - \frac{C_{\alpha,\beta}}{r^6} - \frac{D_{\alpha,\beta}}{r^8}, \quad (1)$$

with $\{\alpha, \beta\} = \text{Li}, \text{D}(\text{H})$. The values of the parameters in (1), which are reported in Ref. 3, do not distinguish between H^- and D^- . VMC is a well-known approach to the quantum many-body problem which relies on the variational method of quantum mechanics.⁶ It provides microscopic information on the ground state of the system and therefore works at zero temperature. This limiting temperature is not a serious drawback if we are interested in the dynamics of H^- or D^- since the Debye temperature of both solids is greater than 1000 K.¹ A necessary input in VMC is a trial wave function Ψ which incorporates the essential physical features of the problem. In the study of quantum solids, the most used model for Ψ corresponds to the Nosanow–

Jastrow approach

$$\Psi = F \Phi. \quad (2)$$

The Jastrow factor F takes into account the correlations induced by the potential; at the two-body level it is given by

$$F = \prod_{i,j}^{N_{\text{Li}}, N_{\alpha}} f^{\text{Li}, \alpha}(r_{ij}) \prod_{i < j}^{N_{\alpha}} f^{\alpha, \alpha}(r_{ij}) \prod_{i < j}^{N_{\text{Li}}} f^{\text{Li}, \text{Li}}(r_{ij}). \quad (3)$$

Φ in (2) localizes each particle around the equilibrium lattice sites \mathbf{R}_i^{α} ,

$$\Phi = \prod_i^{N_{\text{Li}}} g^{\text{Li}}(|\mathbf{r}_i - \mathbf{R}_i^{\text{Li}}|) \prod_i^{N_{\alpha}} g^{\alpha}(|\mathbf{r}_i - \mathbf{R}_i^{\alpha}|), \quad (4)$$

with $\alpha = \text{H}$ or D .

The particular forms for the correlation functions are the following ones,

$$f = \exp \left[-\frac{1}{2} \left(\frac{b_{\alpha\beta}}{r} \right)^5 \right], \quad (5)$$

$$g = \exp \left[-\frac{1}{2} c_{\alpha} r^2 \right], \quad (6)$$

with a set of free parameters $b_{\alpha\beta}$ and c_{α} to be optimized. In the optimization search, we have looked for a minimum in the energy, where the interatomic potential is the short-range one (1), and in order to discern local minima of similar magnitude we have also considered Coulomb contributions considering the ions as point-like particles. The resulting values are, $b_{\text{LiD}} = 2.0 \text{ \AA}$, $b_{\text{DD}} = 1.5 \text{ \AA}$, $b_{\text{LiLi}} = 1.5 \text{ \AA}$, $c_{\text{D}} = 30 \text{ \AA}^{-2}$, and $c_{\text{Li}} = 150 \text{ \AA}^{-2}$. From the configurations generated according to the probability distribution function $|\Psi|^2$ one can obtain microscopic information of both structural and energetic character. Our attention in the present work has been the calculation of these properties for the H^{-} and D^{-} ions in the solids LiH and LiD, respectively. In particular, we have estimated the mean-squared displacement of the ions

$$\langle \mathbf{u}_{\alpha}^2 \rangle = \frac{1}{N_{\alpha}} \left\langle \sum_{i=1}^{N_{\alpha}} (\mathbf{r}_i - \mathbf{R}_i^{\alpha})^2 \right\rangle, \quad (7)$$

its mean kinetic energy

$$\langle T_{\alpha} \rangle = -\frac{\hbar^2}{2m_{\alpha} N_{\alpha}} \left\langle \sum_{i=1}^{N_{\alpha}} \frac{\nabla_i^2 \Psi}{\Psi} \right\rangle, \quad (8)$$

and finally, the Einstein frequency

$$\Omega_{0,\alpha}^2 = \frac{1}{3m_{\alpha} N_{\alpha}} \left\langle \sum_{i=1}^{N_{\alpha}} \nabla_i^2 V_{\alpha}(\mathbf{r}_i) \right\rangle, \quad (9)$$

where $V_{\alpha}(r)$ is the potential felt by the H^{-} or D^{-} ions.

3. RESULTS

In Table 1, we report VMC results obtained for the microscopic magnitudes under study, i.e, kinetic energy, mean squared displacement, Einstein frequency, and Lindemann ratio, for H^- and D^- in LiH and LiD, respectively.

Table 1. Kinetic energy per particle T_α , mean-squared displacement u_α^2 , Einstein frequency $\hbar\Omega_{0,\alpha}$, and Lindemann ratios γ_α for H^- and D^- ions in LiH and LiD. The figures in parenthesis are the statistical errors.

	T_α , meV	u_α^2 , \AA^2	$\hbar\Omega_{0,\alpha}$, meV	γ_α
H^-	84(1)	0.074(2)	110.3(5)	0.134
D^-	67(1)	0.043(2)	93.6(5)	0.102

In spite of the too simple model for the interatomic potentials, we have verified that the results obtained for LiH are in good agreement with recent neutron scattering data.³ Based on this fact, we expect similar accuracy for LiD. Comparing the results for H^- and D^- one can see that the larger mass of D^- translates into a lower kinetic energy and mean displacement; a comparison between the density profiles of both ions is shown in Fig. 1.

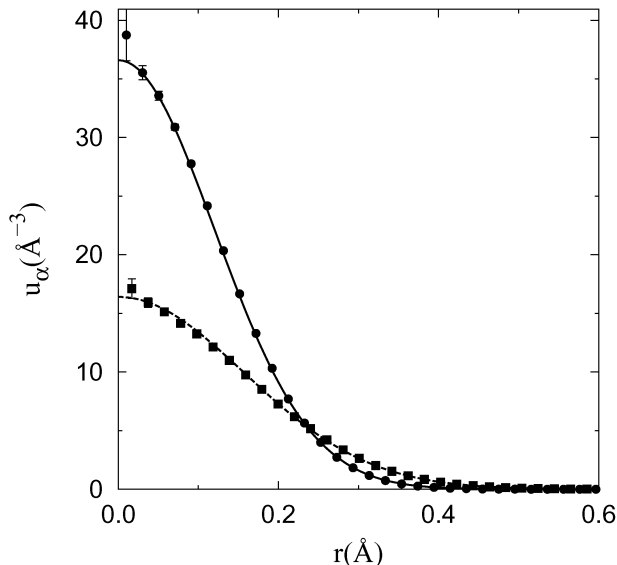


Fig. 1. H^- (circles) and D^- (squares) density profiles in LiH and LiD, respectively. The lines on top of the data correspond to Gaussians with the mean displacement reported in Table 1.

Using SCAP theory,^{7,8} the mean-squared displacement and the kinetic energy are simple analytical functions of the Einstein frequency. Considering the values for $\hbar\Omega_{0,\alpha}$, reported in Table 1, the SCAP results are: $T_{\text{H}}^{(\text{SCAP})} = 82.7(4)$ meV, $T_{\text{D}}^{(\text{SCAP})} = 70.2(4)$ meV, $u_{\text{H}}^{2(\text{SCAP})} = 0.0564(3)$ Å², and $u_{\text{D}}^{2(\text{SCAP})} = 0.0332(3)$ Å². The SCAP results are not far from the VMC ones, with a better agreement in the prediction for the kinetic energies. The larger discrepancies in u_{α}^2 are mainly due to the simplification of the SCAP density of phonon states which corresponds to an Einstein solid (a delta function centered at $\Omega_{0,\alpha}$).

In a purely harmonic approach, and neglecting the slight differences in the lattice constants for LiH and LiD, the isotopic correction by substituting H by D would be in the Einstein frequency $\hbar\Omega_{0,\text{D}}^{\text{h}} = 1/\sqrt{2}\hbar\Omega_{0,\text{H}}^{\text{h}}$. Then, using SCAP, $T_{\text{D}}^{\text{h}} = 1/\sqrt{2}T_{\text{H}}$, and $u_{\text{D}}^{2,\text{h}} = 1/\sqrt{2}u_{\text{H}}^2$. These values are $\hbar\Omega_{0,\text{D}}^{\text{h}} = 78$ meV, $T_{\text{D}}^{\text{h}} = 59.4$ meV, and $u_{\text{D}}^{2,\text{h}} = 0.052$ Å². The significant differences between these results and the accurate ones of Table 1 shed light on the relevance of quantum effects in the ionic solids LiH and LiD.

Additional information on the spatial structure of the solid can be drawn from the two-body radial distribution functions $g^{(\alpha,\beta)}(r)$. In Fig. 2, results

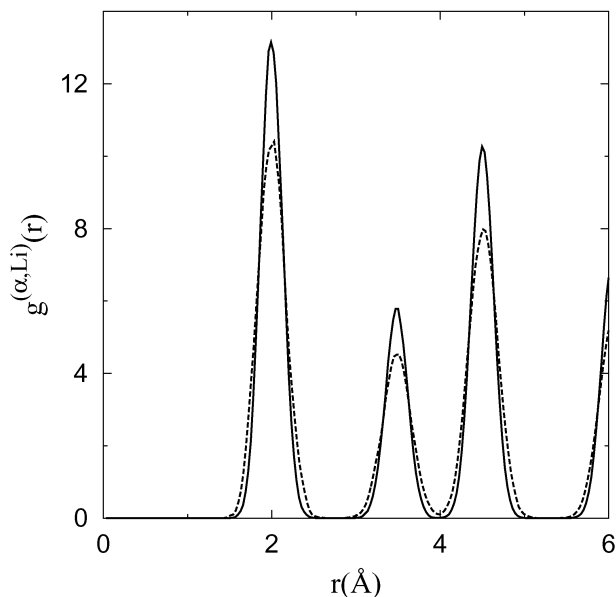


Fig. 2. Radial distribution functions between Li and H or D; $\text{Li}^+ - \text{H}^-$ (dotted line) and $\text{Li}^+ - \text{D}^-$ (solid line) pairs.

for the radial distribution functions corresponding to the pairs of ions Li^+-H^- and Li^+-D^- are plotted. The position of the peaks coincide in LiD and LiH because the lattice structure is practically the same, but the peaks in lithium deuteride are slightly narrower because the displacements of the D^- ions around the equilibrium positions are smaller due to their larger mass.

In conclusion, the application of the VMC method to the study of the ionic solids LiH and LiD has allowed for the estimation of relevant microscopic properties of the H^- and D^- ions, in spite of the relatively poor models for the interatomic potentials nowadays available. The fully quantum treatment of the system has shown that there are isotopic effects H-D sizable different from the corresponding ones expected from a merely harmonic estimation. New neutron scattering experiments, such as the recent ones reported in Ref. 3, would help enormously to check our theoretical predictions and to confirm once more the unavoidable quantum character of both LiD and LiH.

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