

Quantum Delocalization of Hydrogen in the Li_2NH Crystal

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By mapping out potential energy surfaces from density-functional theory (DFT) and solving a protonic Schrödinger equation, we find that the H atom in a unit cell of the Li_2NH crystal shows remarkably strong quantum behavior, leading to the delocalization of H over six octahedral sites around each N. This can be rationalized in terms of rapid coherent tunneling among these equivalent octahedral sites. Structural and dynamical consequences of our finding are discussed. Since the Li–N–H compounds are considered promising candidates for H-storage, understanding of these fundamental properties will be useful toward improving the performance of the material.

Owing to its light mass, hydrogen present in materials can exhibit significant quantum effects, such as tunneling.¹ There has been increasing interest in designing high-performance materials with hydrogen-storage capability; such effects can be of relevance in determining the basic properties of these systems, including, for example, the energetics and location of H absorption and also the diffusivity and transport. To a good approximation, it often suffices to include the minimum amount of quantum mechanics for the H by adding in the zero-point energy (ZPE) computed via a harmonic approximation. On the other hand, if the localizing potential is not sufficiently deep, the H atoms can tunnel between equivalent sites in the material, broadening localized vibrational states into bands and rendering a harmonic approximation invalid. In such cases, the H atom in its ground state is delocalized over several sites. Crystalline environments containing ordered absorption sites can ideally supply such a situation. However, such phenomena are quite rare. In body-centered cubic (bcc) metals, for example, quantum tunneling between equivalent interstitial sites is known.¹ In this letter, we report first-principles calculations on the Li_2NH crystal, in which the proton has been treated quantum mechanically by solving the Schrödinger equation for a proton in the potential energy surface (PES) derived from density-functional theory (DFT). What emerges from this study is that the proton in this material exhibits very strong quantum behavior, leading to the delocalization of the H atom in certain sites around the N atom.

Li_2NH is a newly emerged H-storage material.² Along with LiNH_2 , these materials exhibit promising features for H-storage: a H-storage capacity of 11.5 wt % was reported, which is well above the desired value for vehicular applications. The finding has stimulated much experimental research to enhance the H-storage efficiency.³ To design high-performance materials, an understanding of basic properties is of great importance. However, the atomic structure of Li_2NH appears to be controversial. Three models have been proposed in experiments, suggesting different H adsorption sites. In Figure 1a, the H atoms

are at the $4b$ sites in a face-centered cubic (fcc) structure with $Fm\bar{3}m$ symmetry,⁴ and in parts b and c of Figure 1, the H atoms are at the $48h$ ($Fm\bar{3}m$) and $16e$ ($F43m$) sites, respectively.⁵ In particular, in the latter two models, only one H position around a N is randomly occupied and thus the H must hop between H positions around the N to satisfy the crystallographic symmetry observed. These models immediately suggest probable H quantum motions in the crystal.

In this work, we adopt a first-principles approach developed to describe the quantum motion of H in periodic systems.^{6a,b} Here, the salient features of our method are briefly summarized as follows. We assume that the system host forms an external potential through which the H moves. We also assume the H to be adiabatically decoupled from the motion of the heavier N and Li, and the latter are treated as classical particles. We use DFT to generate the PES for the H and then solve the protonic Schrödinger equation in the periodic potential of the lattice. This approach gives the ground and excited protonic states, including anharmonicity and anisotropy. With this method, we have successfully predicted protonic eigenstates in some hydride systems.^{6b}

In practice, the PES for H in the system was calculated on a simple cubic grid with 32 points along each edge of the cubic unit cell, in which the N and Li are in the same positions as those suggested by experiments. The lattice constant was taken to be the experimental value. The PES on the 32^3 grid was interpolated into a finer grid 88^3 , to obtain converged eigenstates. Each point on the PES was the result of a wave function optimization using DFT. In the DFT calculations, exchange and correlation were treated within the Perdew–Burke–Ernzerhof generalized gradient approximation, and the ionic cores were described by ultrasoft pseudopotentials.⁷ The cutoff energy for the plane-wave expansion was set to be 330 eV, and the electronic Brillouin zone was sampled using a 12^3 Monkhorst–Pack k -point grid, which are sufficient to give well-converged total energies. The protonic wave function calculations were made at the Γ point, and the cutoff for the protonic wave

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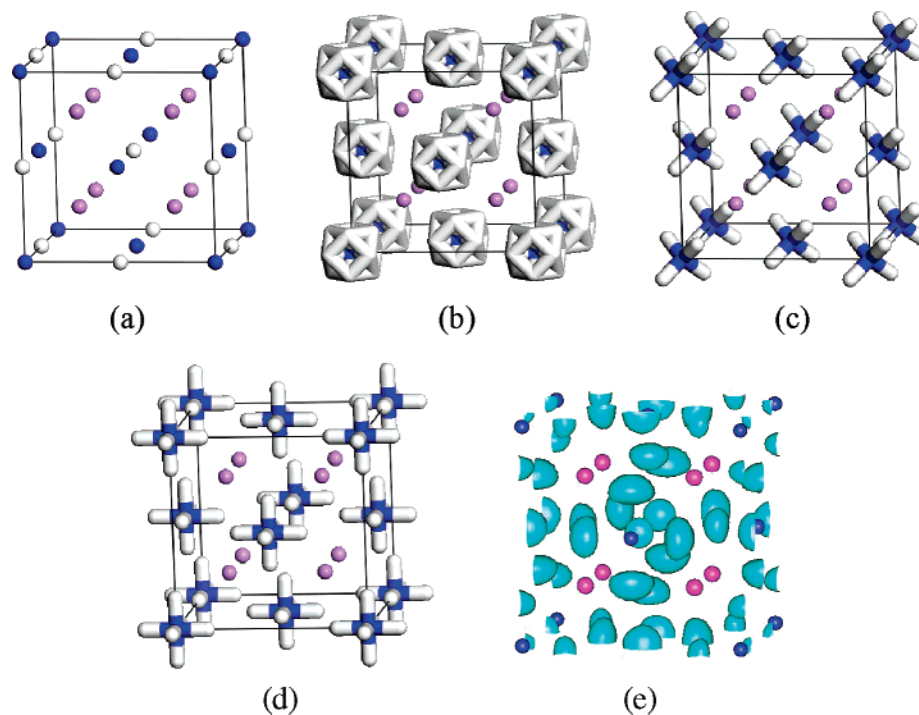


Figure 1. (a–c) Models suggested by experiments. (d) The structure found in this work. (e) A real-space plot of the protonic ground state wave function (green areas), which exhibits clearly 6-fold H positions around each N. In all cases, H is white, N is blue, and Li is purple.

function grids was set to be 1074 meV, which are also sufficient to give converged results.

We have chosen a range of lattice constants, and for each lattice constant, we have repeated the quantum treatment for H in the respective PES. From the minimum in the obtained ground state (GS) energies, the lattice constant predicted quantum mechanically is 5.007 Å, which is in very good agreement with experimental data. The most striking feature obtained from our calculations is the location of H positions: the H atoms reside neither in the $4b$ nor the $48h$ nor the $16e$ sites, as suggested in experiments, but rather in the $24e$ sites of the $Fm\bar{3}m$ space group (i.e., the H coordinate is $(x,0,0)$, $x = 0.210$), as shown in Figure 1d. This is clearly evidenced by the calculated GS wave functions, which show the probabilities of H distributions in the system. A real-space plot of the GS is shown in Figure 1e. As can be seen, the H clearly exhibits 6-fold positions around each N. It is worth mentioning that the new structure matches the crystallographic symmetry observed in the experiments. It is also interesting to note that the $24e$ site was mentioned in a recent X-ray study but ruled out due to a slightly unfavorable R -value in the Rietveld analysis.⁸ Clearly, further experimental study is required.

To further support our findings, we examined the local structures of Li_2NH in experiments (i.e., the partially occupied models), in which only 1 among the 12 $48h$ sites (Figure 1b) or 4 $16e$ sites (Figure 1c) is occupied by a H atom. We found that H atoms in the $48h$ and $16e$ sites are 2.00 and 2.47 eV (per Li_2NH unit) less stable than those in the $24e$ site, respectively. We also optimized these local structures by using DFT methods and found that H in both cases moved to the $24e$ sites. These results can be understood as follows. First, in the two experimental models, the H–Li distances are short (1.62 and 1.38 Å) so that the Coulomb repulsion between the two species can be significant, making the configurations unfavorable. On the other hand, in the structure obtained in this work, the H resides in a position close to the center of the four nearest neighboring Li atoms, with each H–Li separation being 1.85 Å. Second, unlike those in the experimental models, the geometry of the Li_2 –

N–H unit in the crystal structure we found is planar, which is a favorable structure for the N sp^2 hybridization, and, indeed, the geometry of the monomer Li_2NH and LiNH_2 molecules.⁹ For the simpler model suggested by early experiments (Figure 1a), we found that it is in fact a metastable structure, with an energy 2.7 eV (per Li_2NH molecule) higher than the one we found. Finally, we calculated the formation enthalpy for the hydrogenation of Li_2NH to LiNH_2 with the structure we found, and the obtained result of 0.55 eV agrees well with the experimental data (0.47 eV).²

To understand the 6-fold H positions around each N in the structure in Figure 1d, we discuss now the mechanisms of the H motion. In Figure 2a, we plot the PES of the H within the (100) plane of the crystal, in which two minimum energy pathways can be seen. First, H moves from one H position to its neighbor around one N along an arc centered at the N (the solid curve). The energy barrier including ZPE was calculated to be 477 meV (per H). Each N has six such minima octahedrally disposed around it. Second, H moves between two H positions that are around different N atoms (the dashed curve). Due to the large separation between the two H positions, however, the barrier is very high (~ 2.9 eV). By applying the transition state (TS) theory, $r = (kT/h)(q_{\text{TS}}/q_0)e^{(-\Delta E/kT)}$, where q_{TS} and q_0 represent the vibrational partition function (including the ZPE energies) at the TS and the potential minimum, we evaluated the kinetic rate constant for the first path (i.e., $\Delta E = 477$ meV) to be $\sim 6.0 \times 10^{-8}$ ps⁻¹ at 300 K, implying a very slow classical hopping rate between the equivalent 6-fold sites.

On the other hand, the quantum tunneling of H (i.e., under-barrier process) is expected. To illustrate this, we show schematically the calculated protonic eigenspectrum in Figure 2b. As can be seen, relative to the potential minimum, the ground vibrational states ($|000\rangle$) are at ~ 275 meV. Per H atom, the ground state manifold contains six eigenstates, which correspond to the possible linear combinations of vibrational states localized in each well. The bandwidth (J) of this manifold is significant, ~ 4 meV, implying coherent tunneling motion between the different minima; the uncertainty principle implies

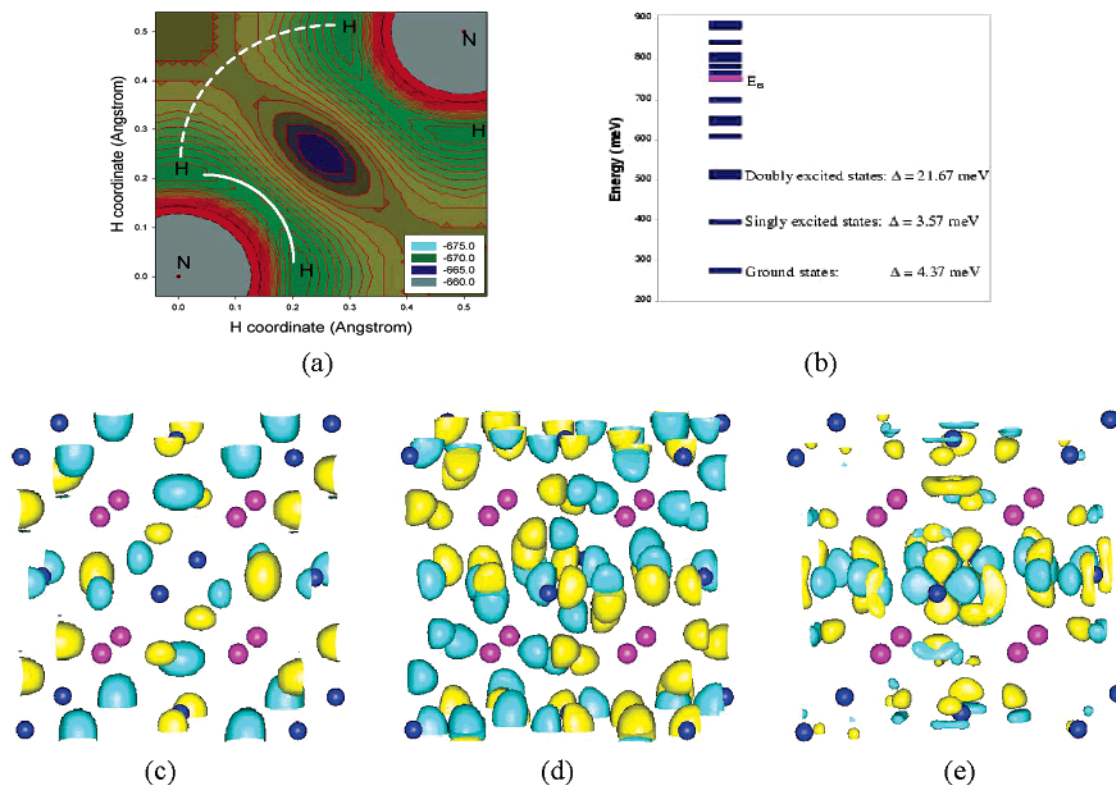


Figure 2. (a) PES of H within the (100) plane, in which two paths are indicated by solid and dashed curves. (b) Protonic eigenspectrum, in which coherent widths (Δ) are shown for the first three states. (c–e) Plots of wave functions (green and yellow areas) corresponding to the three states.

a tunneling rate of $\tau \approx (J/\hbar) \approx 1 \text{ ps}^{-1}$, many orders of magnitude larger than the classical hopping rate. In Figure 2b, we have also identified the manifold of singly ($|100\rangle$) and doubly ($|110\rangle + |200\rangle$) excited vibrational states, which are ~ 122 and ~ 233 meV above the ground states, respectively, and which also possess significant coherent bandwidths. Examples of wave functions from the three manifolds are shown in Figure 2c–e.¹⁰ As can be seen, the protonic states are also distributed around the $24e$ sites, implying that the $24e$ sites are the most stable sites even at finite temperatures.

It is noteworthy that H-storage materials require that the barriers to H diffusion through the material should be low, so that H can be easily absorbed or desorbed in the system. Properties such as the H diffusion coefficient and diffusion barrier are important parameters which characterize the transport properties. The strong quantum behavior has a direct bearing on these properties. To illustrate this, we compute the quantum diffusion coefficient using a Kubo–Green–Greenwood formalism, outlined in a recent paper,^{6b} and compare it with the classical result. We find that the H diffusion coefficient is indeed significant, being $\sim 10^{-8} \text{ cm}^2/\text{s}$ at 300 K. Fitting the diffusion coefficients over a temperature range (300–800 K) to an Arrhenius expression, $D(T) = D_0 \exp(-\beta E_a)$, we obtain an effective diffusion barrier (E_a). Remarkably, this barrier is 259 meV, which is considerably lower than the classical barrier (477 meV), indicating that the proper quantum diffusion rate is some 4 orders of magnitude higher at 300 K than that which classical theory would suggest. These results strongly suggest that the quantum description of H diffusion in the material is essential and the conventional treatment, even with the ZPE included, is not adequate.

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- (10) It is interesting to note that in both the singly and doubly excited states the excitation modes are in tangential rather than radial directions (in a virtual sphere centered at the N). This can be rationalized from the fact that the radial direction coincides with the axis of N–H and is therefore a bond stretch. In a harmonic approximation, we calculated the vibrational modes in tangential and radial directions and found the latter is 268 meV higher in energy than the former. Therefore, the excitation modes in radial direction only appear at higher energy levels.