Quantum localization of hydrogen atoms in solids

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Abstract
Quantum distributions of hydrogen-like atoms in solids were investigated theoretically by the first-principles path-integral molecular dynamics (FP-PIMD) method, in which interatomic forces are calculated precisely based on the density functional theory. Some distributions are qualitatively different from those obtained by conventional simulations with classical treatment of protons. Interestingly, quantum fluctuations sometimes cause localization of the nuclei. The mechanism of this ‘quantum localization’ is intuitively explained by considering characteristic potential energy surfaces.

Keywords: Quantum localization; Hydrogen atoms; Solids

1. Introduction
The zero-point energy of hydrogen atoms in solids, such as hydrogen-bonded materials, molecular crystals, metal hydrides and hydrogen impurities in semiconductors, is of the order of 0.1 eV. It is, therefore, not negligible in comparison with the thermal energy or activation energy for various reactions. As is easily anticipated from the fact, remarkable isotope effects (quantum effects) arise in the physical quantities related with the dynamics of hydrogen atoms.

In metallorganic crystals, it is well known that deuteration of the organic molecules gives rise to so-called chemical pressure, resulting in interesting electronic transitions. This is perhaps because the differences in the quantum-mechanical distributions of hydrogen isotopes affect the lattice constant of the crystals.

The ferroelectric or antiferroelectric transition temperature of hydrogen-bonded materials is strongly dependent on the hydrogen mass. In some cases it is almost doubled by deuteration. The isotope effect is usually explained by the difference in tunneling frequency between hydrogen and deuterium, although it is sometimes attributed to the overall geometrical difference caused by the quantum motion of the isotopes, since the tunneling motion is not observed in experiments. In fact, structural transformations of hydrogen-bonded materials generally accompany a drastic deformation of the lattice of heavier atoms, and we suspect that deuterization causes a large difference in the tunneling motion of such deformations. Thus, we believe that a non-empirical and quantitative simulation of the quantum distribution in hydrogen is needed to clarify what occurs in these materials.

In this context, we have investigated hydrogen isotope effects from first principles, treating electrons by the density functional theory. The method, which is called the first-principles path-integral molecular dynamics (FP-PIMD) method, was recently proposed by D. Marx and M. Parrinello [1]. They have applied the method to demonstrate quantum-mechanical delocalization of hydrogen in clusters [2,3], solids [4] and liquids [5]. The method is, to our knowledge, the most reliable way to see quantum distribution of hydrogen at low, but finite, temperature. In this article we briefly review two of our recent works on the quantum-mechanical distribution of hydrogen atoms in solids: hydrogen-like impurities in crystalline silicon [*6,7] and solid molecular hydrogen under ultra-high pressure [**8,9]. An important message here is that the quantum effect of nuclei sometimes causes the localization of hydrogen atoms, in contrast to our initial expectation.

For our other investigations on the isotope effects of hydrogen, see the original papers (antiferroelectric transition of KHS (K₂H(SO₄)₂) [10] and proton diffusion on metal surfaces [11]).

2. Method
The FP-PIMD method is based on the path-integral (PI)
formulation to simulate the quantum distribution of nuclei at finite temperature. It utilizes the molecular dynamics (MD) method to sample many-body configurations efficiently, and also first-principles (FP) electronic structure calculations based on the density functional theory (DFT) at each MD step to obtain reliable interatomic potentials.

The advantages of this method are: (i) all atoms are treated on the same footing, and so we can go beyond the static treatment of lattice relaxation; and (ii) the interatomic potential is calculated by the first-principles method without resorting to empirical potentials, the reliability of which, for wide configuration space, is, by construction, unclear. Quantum and thermal fluctuations of atoms are represented by a multi-integral in the imaginary-time path integral formulation with each Feynman path discretized into $P$ points. The partition function, $Z$, is expressed as

$$Z = \lim_{\beta \to \infty} \prod_{i=1}^{N} \left( \frac{P m_i}{2 \pi \beta \hbar^2} \right)^{3P/2} \int \prod_{j=1}^{P} \prod_{i=1}^{N} dr_i(j) \times \exp \left( -\sum_{j=1}^{P} \sum_{i=1}^{N} \frac{P m_i}{2 \beta \hbar^2} (r_i(j) - r_i(j+1))^2 \right) \times \frac{1}{P} \sum_{j=1}^{P} V(r_i(j), \ldots, r_n(j)), \quad (1)$$

where $\beta$ is the inverse temperature, $m_i$ is the mass of the $i$th atom, and $r_i(j)$ is the spatial coordinate of the $i$th atom at the $j$th imaginary-time slice. The interatomic interaction $V$ is the total energy of the conventional DFT calculation, which is calculated independently at each imaginary time and MD step. This formulation reduces an $N$-particle quantum system to an artificial classical system including $NP$ particles (see Fig. 1). As a result, the fluctuations are replaced by a thermal fluctuation that can be evaluated by the molecular dynamics (MD) method. We need computer resources at least $P$ times as large as for ordinary FP-MD (Car–Parrinello-type) simulations. We overcome this difficulty by parallelizing our original code for a massively parallel supercomputer in terms of beads and band indices.

In this method, we use the adiabatic approximation that electron charge density always follows the motion of atoms so that the electronic ground state is achieved at any time step. This is a reasonable approximation when the mass of the atom is large enough and the electronic temperature is negligible. We also neglect the exchange interaction of nuclei and assume that they are distinguishable. This approximation results in the significant problem that we cannot discuss differences between ortho-hydrogen and para-hydrogen. We will return to this point in Section 4.

3. Muonium in c-Si

We applied the FP-PIMD method to investigate the quantum distribution of muonium in crystalline silicon [1,2].

Muonium (Mu) is a bound state of a positive muon ($\mu^+$) and an electron. It is a light isotope of a hydrogen atom ($m_\mu \sim (1/9)m_\text{H}$) and is used as a substitute for an impurity hydrogen atom, since information on the location of Mu is obtained by $\mu$SR experiments, in contrast to a hydrogen atom, which cannot easily be detected in experiments.

Although $\mu$SR experiments suggest that muonium in c-Si distributes both at the Si–Si bond center (BC) site and at the center of the Si cage with tetrahedral symmetry (T site), previous first-principles calculations found that the T site is an unstable position of the potential energy surface [12–14]. We expected the quantum effect of the muon to be very important.

We performed FP-PIMD simulations of hydrogen and muonium in c-Si to investigate the quantum effect on the distribution of impurities. We also performed classical FP-MD simulations for comparison. The distributions of a classical particle, a proton and a muon are shown in Fig. 2a–c, respectively. Note that the potential energy surface (PES) for the nuclei is exactly the same for these three simulations, since it is calculated with the same accuracy by DFT.

The classical particle does not reside at the T site (indicated by a small sphere), but distributes around the potential energy minima. The quantum distribution of a hydrogen atom is somewhat different, but qualitatively it still distributes away from the T site. On the other hand, a muonium shows distinct behavior. It is localized at the T
center due to the quantum effect. This is the first theoretical explanation for the normal muonium consistent with μSR experiments.

The mechanism for this ‘quantum localization’ will be discussed in Section 4. An important point here is that the correlation in the motion of silicon and muonium is incorporated without assumption. We believe that this non-empirical feature of the method is especially important when dealing with unknown structures under extreme conditions.

4. Solid hydrogen under ultra-high pressure

For more than six decades, solid hydrogen has been studied theoretically using the current state-of-the-art techniques of their time. The central issue has been its metallization, while the unexpectedly rich phase diagrams obtained by the most advanced experiments have stimulated a variety of theoretical treatments of the material.

Recent low-temperature/high-pressure studies have revealed three relevant phases of solid molecular hydrogen: phase I (high-temperature, low-pressure phase), phase II (low-temperature phase), and phase III (high-pressure phase). Spectroscopic data suggest that symmetry breaking occurs on passing into phases II and III, which may be related to orientational ordering of the molecules, although the structures have not yet been determined [15].

We performed FP-PIMD simulations for three combinations of density and temperature corresponding to the three phases: phase I (120 GPa, 300 K), phase II (130 GPa, 80 K) and phase III (180 GPa, 100 K) [**8]. We found distinct distributions of protons for the three phases. In phase I, hydrogen molecules are almost freely rotating, while they are orientationally ordered in phases II and III. The space group of phase II was found to be Cmc2,1, and that of phase III Cmca. We also performed FP-MD simulations and found that ‘classical protons’ distribute differently in phases II and III. The resultant structures are summarized in Fig. 3. It should be noted that the molecules are still rotating in phase II in the classical simulation [**8,9].

The present result indicates that the proton distributions or crystal structures of solid molecular hydrogen at high pressure are significantly affected by the quantum property of the protons. Especially in phase II, the rotation of hydrogen molecules seems to be hindered in the quantum simulation. This might also be called quantum localization.
A different quantum effect is seen in phase III. The Cmca structure found in the quantum simulation is realized because the zero-point energy of the molecular vibration is much lower than that in the off-center Cmc2₁ structure obtained in the classical simulation.

5. Discussion

An intuitive explanation for ‘quantum localization’ is illustrated in Fig. 4a and b. Fig. 4a shows the localization in solid hydrogen, where the two degrees of freedom in the potential energy surface are the two angles determining the orientation of the molecules. Even when the classical system can move thermally (or rotate in this case) from one potential minimum to the other, it will be localized quantum mechanically if the transition state has a higher zero-point energy in the direction perpendicular to the rotation direction. We have confirmed the shape of the potential energy surface by static total energy calculations.

It is known that the diffusivity of hydrogen atoms adsorbed on some metal surfaces shows an inverse isotope effect, that is, the diffusion constants of hydrogen, deuterium and tritium increase in this order in a certain temperature range [11]. If the diffusion mechanism were classical, lighter particles should diffuse faster because of the trial frequency for their hopping motion. In the quantum limit at low temperature, we also expect lighter particles to tunnel with higher probability. The inverse isotope effect occurs in a modest temperature range. If the potential energy surface is like that in Fig. 4a, the inverse isotope effect is easily understood because the effective potential barrier for hopping is larger for lighter particles [16].

Fig. 4b shows another type of localization, which we found for the T-site distribution of muonium in silicon. In this case, the two (or rather three) degrees of freedom are the Cartesian coordinates of the impurity particle. The classical particle distributes thermally with the highest probability at the potential minima, while quantum-mechanical muonium is confined at the hilltop of the potential energy surface, since the zero-point energy is the lowest there. In fact, the T site is the most open space in the silicon framework, while the potential minimum is quite narrow, as we can see from the distribution of a classical particle in Fig. 2a.

With regard to Mu in c-Si, there is one more discrepancy between experiments and theoretical calculations: although a bistability between the T-site distribution and the BC-site distribution has been reported in experiments, the calculated potential barrier between the two site seems too small. We believe that the effective barrier height is much enhanced by the quantum nature of muonium. In this case, the mechanism is similar to the localization mechanism in Fig. 4a [16].

6. Concluding remarks

We have investigated the quantum distributions of hydrogen-like atoms with the first-principles method. We found that the quantum fluctuation of nuclei sometimes causes their localization, in contradiction to our naive expectation. The quantum localization is, however, intuitively understood if we consider the zero-point energy in

![Fig. 4. Schematic views of the potential energy surfaces for an explanation of ‘quantum localization’. See text for details.](image-url)
multi-dimensional potential energy surfaces of characteristic shape.

Finally, we would like to point out that the crystal structures of hydrogen obtained in the present simulations are not necessarily realistic, as they are the result of the unreliability of the DFT-GGA treatment of the electronic total energy. In fact, the Cmca structure obtained becomes metallic, although phase III is known to be an insulator experimentally. It is very likely that the zero-point vibron energy of the Cmca structure is lowered too much due to metallization. For a quantitative prediction of the ultra-high-pressure phase of solid hydrogen, we have to go beyond the DFT-GGA formalism (e.g. Ref. [17]). Quantum localization is a simple application of quantum mechanics and we expect such a phenomenon to be found not only in the present system. We should be very careful when investigating material properties, including hydrogen.

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References

Papers of particular interest, published within the annual period of review, have been highlighted as:
* of special interest;
** of outstanding interest.