Supplemental Material for “Nuclear quantum dynamics in dense hydrogen”

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I. IMPROVED CENTROID PATH-INTEGRAL MOLECULAR DYNAMICS

In the adiabatic centroid path-integral molecular dynamics (PIMD) formalism \[1\], the primitive path variables \( \{ \mathbf{R}_i \}^{(s)} \) \((s\) is the imaginary time.) is transformed to a set of normal mode variables \( \{ \mathbf{y}_i \}^{(s)} \), which diagonalize the harmonic bead coupling. The equations of motion of normal mode variables without thermostats are given by

\[
M_I^{(1)} \ddot{y}_I^{(1)} = -\frac{\partial}{\partial y_I^{(1)}} \frac{1}{P} \sum_{s=1}^{P} E^{(s)},
\]

\[
M_I^{(s)} \ddot{y}_I^{(s)} = -\frac{\partial}{\partial y_I^{(s)}} \frac{1}{P} \sum_{s'=1}^{P} E^{(s')} - M_I^{(s)} \omega_P^2 y_I^{(s)}, \quad s = 2, \ldots, P,
\]

where \( \omega_P = \sqrt{P} k_B T \), \( P \) is the number of beads in ring polymer, \( k_B \) is Boltzmann constant, \( T \) is the target temperature of the simulated system, \( E^{(s)} \) is the electronic energy functional in \textit{ab initio} calculations.

The centroid and non-centroid modes are mass-scale separated with adiabatic parameter \( \gamma \), i.e., the normal mode masses \( M_I^{(s)} \) are

\[
M_I^{(1)} = M_I, \quad M_I^{(s)} = \gamma M_I^{(s)}, s = 2, \ldots, P.
\]

where \( M_I \) is the physical nuclear mass. In this way, the centroids move in real-time in the centroid effective potential generated by all non-centroid modes.

Here we propose a new scheme for sampling of the force on the centroids during the molecular dynamics simulations within the framework of the adiabatic centroid PIMD, that is, for each ion \( \omega_P \) depend linearly on its instantaneous kinetic energy \( E(t) \) during simulations,

\[
\omega_P(t) = \frac{2N}{g} \sqrt{P} (aE(t) + bE_0).
\]

Now we obtain \( a \) and \( b \) as followed. When \( E(t) = 0 \), then \( \omega_P = CbE_0 \) (\( C \) is a constant), the radius of gyration of ring polymer reaches half of the de Broglie wavelength of the corresponding ion, i.e., \( R_g' = \lambda/2 \); When \( E(t) = E_0 \), then \( \omega_P'' = CE_0 \), the radius of gyration of ring polymer is equal to the value in traditional scheme, i.e., \( R_g'' = R_g \). Considering \( \omega_P \propto 1/R_g^2 \), we have

\[
\frac{\omega_P'}{\omega_P''} = \frac{R_g'}{R_g''}.
\]

Substituting \( \omega_P' \) and \( \omega_P'' \) with \( \omega_P' = CbE_0 \) and \( \omega_P'' = CE_0 \), we can obtain

\[
b = \left( \frac{2R_g}{\lambda} \right)^2.
\]
According to \( a + b = 1 \), \( a \) has the form

\[
a = 1 - \left( \frac{2R_g}{\lambda} \right)^2.
\]  

(7)

II. THE RESULTS OF ONE-DIMENSIONAL QUANTUM TUNNELING

The tunneling process of a hydrogen atom passing through a Gaussian potential barrier was simulated using the improved centroid path-integral molecular dynamics (PIMD) approach. Here, \( \gamma \) was set to 20. Polymer bead \( P \) is set to 32. Langevin thermostat was coupled to the non-centroid modes in order to conquer the ergodicity problem. We calculated the transmission probability with four different ratios of the half-height width of the potential barrier \( d \) to the de Broglie wavelength \( \lambda \) of hydrogen atom, i.e., \( d/\lambda = 1, 5, 10, 20 \). The Gaussian potential barrier has the form \( U(x) = U_0 \exp(-x^2/a^2) \). For each value of \( d/\lambda \) and \( E/U_0 \) (\( E \) is the incident energy of the hydrogen atom), we simulated the tunneling process 5000 times, then calculated the transmission probability statistically. From Fig. 1, it

![Figure 1](image-url)

**FIG. 1.** Left: Schematic of the one-dimensional quantum tunneling. Right: Transmission probability of a hydrogen atom tunneling through a Gaussian potential barrier \( U(x) = U_0 \exp(-x^2/a^2) \). The height of barrier \( U_0 \) is 5000 K. From (a) to (d), the ratio of the half-height width of the potential barrier \( d = 2\sqrt{\ln 2}a \) to the de Broglie wavelength \( \lambda \) of hydrogen atoms is 1, 5, 10, 20, respectively. The result of classical treatment, WKB semi-classical approximation and solving the Schrödinger equation are presented for comparisons.
can be seen that as the value of $d/\lambda$ is increased, the results of our simulations are more and more consistent with the WKB semi-classical approximation [2] and the exact result through solving the Schrödinger equation. The applicability of the newly improved centroid PIMD method was also investigated. When the de Broglie wavelength of particles is equal to or larger than the half-height width of the potential barrier, the improvement proposed in this study can not describe the nuclear quantum dynamics properly, indicating the limitation of this approach. However, in this work, the chosen state points of warm dense hydrogen are within the valid region of this improved centroid path-integral molecular dynamics (PIMD) approach.

### III. MOVIE DETAILS

Two movies were produced to demonstrate the different diffusion behaviors of hydrogen atoms between the quantum and classical treatment for ions at 0.1 eV and 10 g/cm$^3$ by using simulated trajectories after thermalization. The supercell includes 250 atoms with bcc structure as initial structure in simulations. After thermalization, the solid bcc structure transforms into liquid phase with the inclusion of nuclear quantum effects (see “quantum.mpg”), whereas in the classical simulation, the structure remains bcc solid phase with large vibrational amplitudes (see “classical.mpg”).

### IV. COMPUTATIONAL DETAILS

The densities of hydrogen under consideration range from 10 g/cm$^3$ to 100 g/cm$^3$, corresponding to $0.3 \leq r_s \leq 0.65$ ($r_s$ denotes the Wigner-Seitz radius) with the temperature range of 0.1~1 eV. Simulations were performed for five state points along the 10 g/cm$^3$ isochore from 0.1 eV to 1 eV, and three state points along the 1 eV isotherm from 10 g/cm$^3$ to 100 g/cm$^3$. Figure 2 displays the comparisons between the average interparticle spacing and the thermal de Broglie wavelength of hydrogen atoms at a temperature range of 0.1-1 eV and densities from 10 g/cm$^3$ to 100 g/cm$^3$ for hydrogen. Results of two isotopes (i.e., D and T) are also presented. We can see that the properties of hydrogen at 10 g/cm$^3$ would be strongly affected by quantum character of nuclei at a low temperature of 0.1 eV. Up to 1 eV, $\lambda_H$ becomes less than one third of the interparticle spacing, implying weaker nuclear
spacial delocalization. When the density is increased to 100 g/cm$^3$, the interparticle spacing is close to $\lambda_H$ and nuclear quantum effects become significant again.

Within the framework of imaginary-time PIMD [3, 4], the quantum expectation value of a static physical quantity is given in terms of averaging over the canonical ensemble of the isomorphic classic system. Therefore, the radial distribution functions of hydrogen atoms are obtained by averaging over the PIMD time steps and imaginary time slices. The equation of state including energy and pressure is calculated by averaging of their corresponding estimators along the PIMD canonical ensemble.

In order to understand the different behavior of electrical conductivity between the \textit{ab initio} molecular dynamics (MD) and PIMD simulations, we calculated the electronic density of state (DOS) at three state points, i.e., 10 g/cm$^3$ and 0.1 eV (Fig. 3), 10 g/cm$^3$ and 0.3 eV (Fig. 4), 100 g/cm$^3$ and 1 eV (Fig. 5). A previous report [5] shows that the quantum zero-point motion of the carbon atoms could strongly affect the optical and electronic properties of diamond. Therefore, considering the lower mass, dense hydrogen is expected to exhibit pronounced quantum effects on electronic properties. Only the DOS near the Fermi energy are shown here since the electronic properties such as electrical conductivity are largely determined by the electronic distribution near the Fermi surface. As shown in Fig. 3, the two curves have an obvious cross near the Fermi energy because NQEs lower the melting point of hydrogen and phase transition from solid to liquid occurs at 0.1 eV with the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Comparisons between the average interparticle spacing and the thermal de Broglie wavelength of hydrogen atoms at different temperatures (a) and densities (b). $\lambda_H$, $\lambda_D$ and $\lambda_T$ denote the thermal de Broglie wavelength of H, D and T atoms, respectively. $r_s=0.3, 0.38, 0.45$ and 0.65 corresponds to 100, 50, 30 and 10 g/cm$^3$ for hydrogen.}
\end{figure}
FIG. 3. The electronic density of state (DOS) of hydrogen at 10 g/cm$^3$ and 0.1 eV. Results of randomly selected configurations along ionic trajectory in molecular dynamics simulations are shown in (a) and the averaged results are shown in (b). The vertical dashed line denotes the Fermi energy.

FIG. 4. DOS of hydrogen at 10 g/cm$^3$ and 0.3 eV. Results of randomly selected configurations along ionic trajectory in molecular dynamics simulations are shown in (a) and the averaged results are shown in (b). The vertical dashed line denotes the Fermi energy.

inclusion of NQEs, while hydrogen remains solid phase in the MD simulation. This phase transition resulting from nuclear quantum tunneling leads to marked difference of electronic distribution near the Fermi energy and thus influence the electronic transport properties. When the temperature is increased to 0.3 eV, hydrogen exhibits liquid behavior from both the PIMD and MD simulations. The DOS obtained from the PIMD calculations is more broadened compared to the MD calculations, indicating that the quantum fluctuation has
FIG. 5. DOS of hydrogen at 100 g/cm$^3$ and 1 eV. Results of randomly selected configurations along ionic trajectory in molecular dynamics simulations are shown in (a) and the averaged results are shown in (b). The vertical dashed line denotes the Fermi energy.

stronger influence on electronic structure than thermal fluctuation. Also, we can see that a slight difference of DOS could lead to pronounced modification of electrical conductivity. The two curves of DOS at 100 g/cm$^3$ and 1 eV are close to each other, indicating relatively weaker NQEs, therefore the difference of the electrical conductivity is smaller than the other two state points.

The distribution of charge density and electron localization function (ELF) [6] are also calculated at two states, i.e., 10 g/cm$^3$ and 0.1 eV, 10 g/cm$^3$ and 0.3 eV. The electron localization function was introduced by Becke and Edgecombe. They associated the localization of an electron with the probability density for finding a second like-spin electron near the reference point. For small probability densities, $D(r)$ is also small and the electron is more localized,

$$D(r) = \sum_i |\nabla \Psi_i(r)|^2 - \frac{1}{4} \frac{|
abla \rho(r)|^2}{\rho(r)}, \quad (8)$$

The Pauli repulsion between two like-spin electrons, described by the size of $D(r)$, is taken as a measure of the electron localization. Using the corresponding factor found for a uniform electron gas, $D_h(r)$, Becke and Edgecombe, defined ELF as:

$$\eta(r) = \frac{1}{1 + \chi_{BE}^2(r)} \quad (9)$$

where $\chi_{BE}(r) = D(r)/D_h(r)$. Becke and Edgecombe attributed the ratio $\chi_{BE}(r)$ to a dimensionless localization index, calibrated with respect to the uniform electron gas. This
FIG. 6. The cut-plane of 3D distribution of charge density of hydrogen at 10 g/cm$^3$ with the temperature of 0.3 eV. (a)-(c) are obtained from the MD calculations with a randomly selected atomic configuration while (d)-(f) are obtained from the PIMD calculations with randomly selected imaginary-time slices in PIMD time steps.

reference was chosen arbitrarily, so ELF is a relative measure of the electron localization. High ELF values show that at the examined position the electrons are more localized than in a uniform electron gas of the same density. For example, when $\eta(r) = 1/2$ the effect of the Pauli repulsion is the same as in a uniform electron gas of the same density.

The results of charge density and ELF are shown in Fig. 6 and Fig. 7 are obtained with a randomly selected atomic configuration from both MD and PIMD simulations. We can clearly see from Fig. 6 that the maxima of charge density with the inclusion of NQEs are larger than that the MD results and the minima from PIMD calculations are smaller than the MD results, indicating that the electrons distribute more localized surround ions with quantum nuclei than classical particle treatment. It is also reflected by the reduced charge
FIG. 7. The cut-plane of 3D electron localization functions (ELFs) [6] of hydrogen at 10 g/cm$^3$ with the temperature of 0.3 eV. The results in left panel is obtained via the MD calculations and the right panel is from the PIMD calculations. The same configurations as employed in Fig 5 are used here. ELFs demonstrate that the electrons distribute more localized surround ions with quantum nuclei than classical treatment.

density in the interstitial space between ions. The ELFs of the same atomic configurations used in charge density calculations are shown in Fig. 7, which exhibits the similar behavior with the distribution of charge density and also indicates that NQEs introduce stronger electron localization.

V. COMPARISONS BETWEEN THEORETICAL RESULTS

In order to compare our results with other theoretical results in the previous literature, we calculated the electrical and thermal conductivity of hydrogen at two state points (10
TABLE I. Comparisons of electrical conductivity $\sigma$ and thermal conductivity $\kappa$ of hydrogen at (10 g/cm$^3$, 1.25 eV) and (80 g/cm$^3$, 2 eV) between different theoretical methods. Ichimaru and Hubbard denote two theoretical models.

<table>
<thead>
<tr>
<th></th>
<th>MD</th>
<th>PIMD</th>
<th>Ichimaru$^{[11]}$</th>
<th>Hubbard$^{[12]}$</th>
<th>QMD</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 g/cm$^3$, 1.25 eV $\sigma$ (10$^7$Ω$^{-1}$m$^{-1}$)</td>
<td>2.70</td>
<td>2.61</td>
<td>2.58</td>
<td>3.38</td>
<td>3.09</td>
</tr>
<tr>
<td>$\kappa$ (10$^3$Wm$^{-1}$K$^{-1}$)</td>
<td>9.33</td>
<td>9.25</td>
<td>9.60</td>
<td>12.05</td>
<td>9.81</td>
</tr>
<tr>
<td>80 g/cm$^3$, 2 eV $\sigma$ (10$^8$Ω$^{-1}$m$^{-1}$)</td>
<td>2.31</td>
<td>2.22</td>
<td>2.18</td>
<td>3.03</td>
<td>2.42</td>
</tr>
<tr>
<td>$\kappa$ (10$^5$Wm$^{-1}$K$^{-1}$)</td>
<td>1.32</td>
<td>1.21</td>
<td>1.26</td>
<td>1.69</td>
<td>1.66$^{[13]}$ (0.80$^{[14]}$)</td>
</tr>
</tbody>
</table>

FIG. 8. Radial distribution functions of hydrogen atoms in the PIMD simulations at 10 g/cm$^3$ and 0.1 eV with 16 Trotter beads (solid line) and 32 Trotter beads (dashed line).

g/cm$^3$, 1.25 eV) and (80 g/cm$^3$, 2 eV) and the results are displayed in Table I. The Hubbard model, which assumes a complete Fermi degeneracy and the one component plasma model, is valid for a highly degenerate electron system. The Ichimaru model, which is widely used in astrophysics, is satisfactory in moderate ionic coupling and a wide regime for the electrons from a moderately degenerate fluid to a kinetic plasma. We note that the quantum molecular dynamics (QMD) results of thermal conductivity of hydrogen at 80 g/cm$^3$ and 2 eV in two papers $^{[13, 14]}$ are different. It is due to the fact that they used different atom number in simulations. Compared with the result at (80 g/cm$^3$, 2 eV) with 256-atom in Ref. 14, the thermal conductivity obtained with a 432-atom system in our simulation is closer to the other QMD result $^{[13]}$ and theoretical models, shown in Table I. Furthermore, according to the Wiedemann-Franz law, electric and thermal conductivity increases simultaneously. As
FIG. 9. Radial distribution functions of hydrogen atoms in the MD simulations at 10 g/cm$^3$ and 1 eV with systems consisting of 128 (solid line), 250 (dashed line) and 432 atoms (dot-dashed line). As shown in the convergence tests (next section), the differences of transport properties induced by NQEs can be clearly demonstrated using systems including 250-432 atoms.

VI. CONVERGENCE TESTS

To obtain the reliable results, we have performed extensive convergence tests including the size of simulation cell, the Trotter number in PIMD, the plane-wave cutoff and the k-points set. Both the PIMD and MD simulations were performed with a modified version of Quantum-ESPRESSO package [7]. Enough empty-band states are taken into account to

FIG. 10. Radial distribution functions of hydrogen atoms in the MD simulations at 100 g/cm$^3$ and 1 eV with systems consisting of 250 (solid line), 432 (dashed line) and 686 atoms (dot-dashed line).
FIG. 11. Mean square displacement (MSD) of hydrogen atoms in MD simulations at 10 g/cm$^3$ and 1 eV with systems consisting of 128 (solid line), 250 (dashed line) and 432 atoms (dot-dashed line).

make the maximum band energy higher than $10k_BT$. The plane-wave cutoffs of 200 Ry, 300 Ry and 400 Ry were adopted for 10 g/cm$^3$, 50 g/cm$^3$ and 100 g/cm$^3$, respectively, with 10 times large charge density cutoffs.

In the PIMD simulations, more Trotter number is needed at low temperatures. The comparisons of radial distribution functions of hydrogen atoms at 0.1 eV and 10 g/cm$^3$ indicates that the Trotter number of $P=16$ is sufficient in this work, as shown in Fig. 8.

The simulated system consists of 250∼432 atoms in a cubic supercell with periodic boundary conditions according to different densities (250 atoms for 10 g/cm$^3$; 432 atoms for 100 g/cm$^3$). Firstly, we check the size effects on the structural properties. Figure 9 and Figure 10 show the radial distribution functions of systems consisting of different atom numbers at 10 g/cm$^3$ and 100 g/cm$^3$, respectively. We can clearly see that a good convergence has been reached with 250 atoms for 10 g/cm$^3$ and 432 atoms for 100 g/cm$^3$.

The self-diffusion coefficients of hydrogen atoms were calculated from the slope of the mean square displacement obtained from $ab$ initio centroid PIMD simulations [1, 8]. We calculated the self-diffusion coefficient with systems consisting of 128, 250 and 432 atoms at 10 g/cm$^3$ and 1 eV. The results (see Fig. 11) show that the diffusion coefficient using the system including 250 atoms is in a satisfactory accuracy. The viscosity integral of the average stress autocorrelation function as a function of time was fit to the function form $A[1 - \exp(-t/\tau)]$, where $A$ and $\tau$ are free parameters with $A$ giving the resulting viscosity.
FIG. 12. Viscosity integral (circles) of the average stress autocorrelation function as a function of time for hydrogen at 10 g/cm$^3$ and 1 eV in MD simulation. The fit (line) was performed for a sample window of [0, 10\tau].

FIG. 13. The electrical conductivity of hydrogen in MD simulations at 10 g/cm$^3$ and 1 eV with systems consisting of 128 (solid line), 250 (dashed line) and 432 atoms (dot-dashed line). A k-point set of 6\times6\times6 is employed. The results are averaged from 10 atomic configurations along the MD trajectory.

[9]. The result is shown in Fig. 12. It should be noted that different from the self-diffusion coefficient, the viscosity is the property of the system as a whole, and no additional averaging over the particles is possible. Consequently the viscosity suffers from larger statistical error than self-diffusion coefficient and needs very long trajectories to improve statistical accuracy.
FIG. 14. The thermal conductivity of hydrogen in MD simulations at 10 g/cm$^3$ and 1 eV with systems consisting of 128 (solid line), 250 (dashed line) and 432 atoms (dot-dashed line). A k-point set of $6\times6\times6$ is employed. The results are averaged from 10 atomic configurations along the MD trajectory.

The error of viscosity in this work is $\sim 10\%$. According to the Kress’s reports [9], a total uncertainty of $\sim 20\%$ can be reached due to the finite procedure and extrapolation to infinite time.

The electrical and thermal conductivity and optical absorbtion coefficient were calculated with ABINIT package [10]. In order to achieve good convergence, we checked the size effects and k-points sampling in the Brillouin zone in MD calculations. Figure 13 and Figure 14 show the results of the electrical and thermal conductivity at 10 g/cm$^3$ and 1 eV with different simulation size. These results are averaged from 10 atomic configurations along the MD trajectory. We can see that the system with 250 atoms is satisfactory for conductivity calculations, although the thermal conductivity is more sensitive to the number of atoms than the electrical conductivity. For hydrogen at 100 g/cm$^3$, the error of the electrical conductivity of the system with 432 atoms is slightly larger than that at 10 g/cm$^3$, as shown in Fig. 15. Figure 16 and Figure 17 show the comparisons between the electrical conductivity with different k-points set. The k-points sets of $6\times6\times6$ and $8\times8\times8$ were adopted for 10 g/cm$^3$ and 100 g/cm$^3$, respectively.
FIG. 15. The electrical conductivity of hydrogen in MD simulations at 100 g/cm$^3$ and 1 eV with systems consisting of 250 (solid line), 432 (dashed line) and 686 atoms (dot-dashed line). A k-point set of 8×8×8 is employed. The results are averaged from 10 atomic configurations along the MD trajectory.

FIG. 16. The electrical conductivity with different k-points sets of 4×4×4, 6×6×6 and 8×8×8 in MD simulations at 10 g/cm$^3$ and 1 eV. The results are averaged from 10 atomic configurations along the MD trajectory.
FIG. 17. The electrical conductivity with different k-points sets of $4 \times 4 \times 4$, $6 \times 6 \times 6$ and $8 \times 8 \times 8$ in MD simulations at $100 \, \text{g/cm}^3$ and 1 eV. The results are averaged from 10 atomic configurations along the MD trajectory.