Semiquantum Molecular Dynamics Simulation of Liquid Water -Microscopic, Mesoscopic, and Macroscopic Dynamic Properties-

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We have developed the new semiquantum water (SQW) molecular dynamics (MD) simulation method. Here, the wave packet (WP) approach was for the first time applied to study condensed bulk water structure and dynamics. In order to account for nuclear quantum effects such as the zero point energy and WP delocalization, we described each hydrogen atom as a three-dimensional Gaussian WP basis function. Our SQW MD simulation requires only the additional equations of motion for the WP width and its momenta, and the computational cost is much cheaper than other semiquantum approaches. Nevertheless, our SWQ simulation successfully reproduced the major properties of centroid MD and ring polymer MD, namely that quantized water is less structured, that the diffusion coefficient is larger than is seen in classical simulations, and that the IR spectrum of the OH stretching mode is red-shifted. Furthermore, we found a new peak above the OH stretching peak set which could be a direct observation of the hydrogen WP dynamics in the liquid water.

Our SQW MD simulation made it possible to directly view the WP dynamics in the liquid water, and demonstrated that WP dynamics play an important role in the the hydrogen-bond network (HBN) dynamics; *e.g.* the WP dynamics accelerates the memory loss of the HBN. We also found significant correlations between the WP dynamics and mesoscopic rearrangements of water molecules such as a cage breakout in liquid water.