Computer Center

VIII-HH Computer Simulation of Quantum Systems in Condensed Phase

VIII-HH-1 An Analysis of Molecular Origin of Vibrational Energy Transfer from Solute to Solvent Based upon Path Integral Influence Functional Theory

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Molecular process of vibrational energy relaxation of CN^- ion in the aqueous solution has been investigated based upon path integral influence functional theory. In order to obtain a molecular-based picture, bath normal coordinates were retransformed to Cartesian coordinate, Eulerian coordinate, and intramolecular vibrational coordinate of the solvent molecule. Then, based upon this retransformation matrix, coupling of the solute with the normal modes may be assigned to the couplings with the solvent molecules. Further, with respect to two-phonon process which is dominant in the relaxation of the present system, the relaxation may be divided into single- and dual-molecular processes. We show that the single-molecular relaxation is dominant in the relaxation. Further, water molecules in the first hydration shell play an essential role in the relaxation, whereas the solvent molecules outside the first hydration shell make little contribution. The solvent molecules located in the direction of CN^- bond axis were found to make great contribution to the relaxation.

VIII-HH-2 Mixed Quantum-Classical Molecular Dynamics Study of Vibrational Relaxation of CN^- Ion in Water: An Analysis of Coupling as a Function of Time

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Mixed quantum-classical molecular dynamics method has been applied to vibrational relaxation of CN^- in water. The calculated relaxation time was in good agreement with that based upon Fermi's golden rule with classical interaction. Flexible water model adopted here enhanced the relaxation rate by a factor of about 5 compared with the rigid rotor model. This supports our previous result of path integral influence functional theory that intramolecular bending of water plays an essential role in the relaxation. Time-dependent interaction between the solute vibrational degree of freedom and the solvent water shows random-noise-like behavior, no collisional or stationary coupling observed in gas or solid, respectively, being found in the liquid. The interaction has been analyzed in detail defining the effective coupling for the relaxation. The relaxation mechanism in the liquid may be described by a variety of effective couplings, *i.e.*, relaxing and exciting as well as strong and weak, which arise successively as a function of time.

VIII-II Molecular Dynamics Study of Classical Complex Systems

VIII-II-1 A Molecular Dynamics Study of Single Molecular Manipulation by AFM Cantilever—Mechanical Extension of Polyalanine—

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Potential of mean force of polyalanine in water has been calculated as a function of molecular length by molecular dynamics calculations simulating mechanical extension of the molecule by AFM cantilever. When the molecule keeps alpha helix structure, it behaves like a spring following Hooke's law. After the helix is broken, the force becomes large with increasing extension. Hydrophobic interaction and conformational entropy must play an important role for this force-extension curve. At the extension of about 100%, the force curve rises sharply, showing the increase of molecular bending energy of all trans conformation.

VIII-JJ Development of Simulation Algorithms for Quantum Many-Body Systems

VIII-JJ-1 Path Integral Hybrid Monte Carlo Algorithm for Correlated Bose Fluids

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Path integral hybrid Monte Carlo (PIHMC) algorithm for strongly correlated Bose fluids has been developed. This is an extended version of our previous method applied to a model system consisting of non-interacting bosons. Our PIHMC method for the correlated Bose fluids is constituted of two trial moves to sample path-variables describing system coordinates along imaginary time and a permutation of particle labels giving a boundary condition with respect to imaginary time. The path-variables for a given permutation are generated by a hybrid Monte Carlo method based on path integral molecular dynamics techniques. Equations of motion for the path-variables are formulated on the basis of a collective coordinate representation of the path, staging variables, to enhance the sampling efficiency. The permutation sampling to satisfy Bose-Einstein statistics is performed using the multilevel Metropolis method developed by Ceperley and Pollock. Our PIHMC method has successfully been applied to liquid helium-4 at a state point where the system is in a superfluid phase. Parameters determining the sampling efficiency are optimized in such a way that correlation among successive PIHMC steps is minimized.