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Study of Electron Solvation in Polar Solvents Using Path Integral Calculations

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A path-integral Monte Carlo algorithm for the simulation of electrons solvated in polar liquids is briefly outlined, and results are presented for the electron solvated in liquid water.

KEY WORDS: Path-integral Monte Carlo; two-stage discretization; electron solvation; structure of water around a localized electron; complex time-correlation function.

The path-integral Monte Carlo method provides a convenient algorithm for the simulation of quantum particles at finite temperature. Also in the study of ground state systems the path-integral Monte Carlo proves very useful, when the quantum particle interacts with a complicated classical many-body system.

We have applied a recently developed path-integral sampling algorithm to study the solvation of an electron in liquid water and ammonia. In this so-called staging algorithm the polymer chain representing the imaginary time path of the electron is partitioned into two levels; an intermediate scale primary (A) chain with P_A vertices and small scale secondary (B) chains with P_B vertices. The A chain particles are moved by the Metropolis importance sampling procedure according to weights determined by direct sampling of a set of free secondary chain configurations having a pair of next nearest-neighbour A chain vertices as fixed end points. This procedure is able to sample the fluctuations at the intermediate (molecular) scale defined by the primary chain more efficiently while the total discretization $P_A P_B$ can be refined to a much smaller scale

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($P_AP_B = 1024$ and 2048 in the present work). A further advantage of the two-stage sampling is that the interaction with molecule at larger distances can be evaluated with the more coarse discretization P_A of the A chain, thus saving a considerable amount of computer time.

In this communication we report some results for the electron in water. (For the electron in ammonia we refer to a forthcoming paper,[1] where a more detailed discussion of the sampling procedure can also be found.) The solvent molecules are treated classically and interact with a rigid simple point charge (SPC) potential[2] with a Lennard–Jones potential centered at the oxygen site. Two elementary models for the interaction of the electron with the molecules were considered, a pure Coulomb interaction with the charges in the SPC model ($Q_O = -0.82e$ and $Q_H = 0.41e$) and a pseudo-potential where the interaction with the hydrogen is cut off at 1 Å. The bare Coulomb potentials are regularized using a convenient quantum effective potential borrowed from the literature on plasma simulations (for details, see Ref. 1). Periodic boundary conditions are applied to a cubic cell containing 250 molecules and the

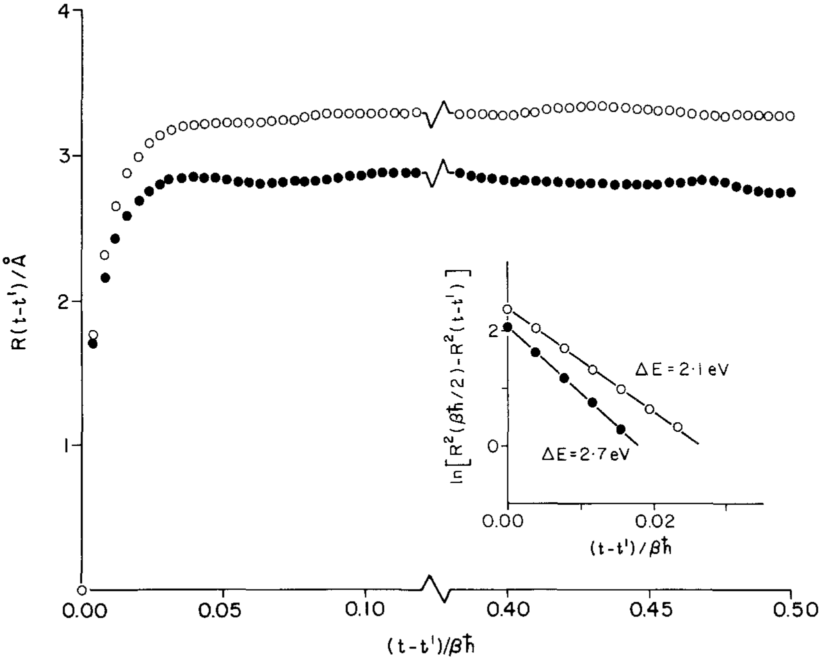

Fig. 1. Complex time displacement correlation function for the pure Coulomb potential (●) and pseudo-potential (○). Inset shows the estimated excitation energies and the initial part of the curves from which they are derived.

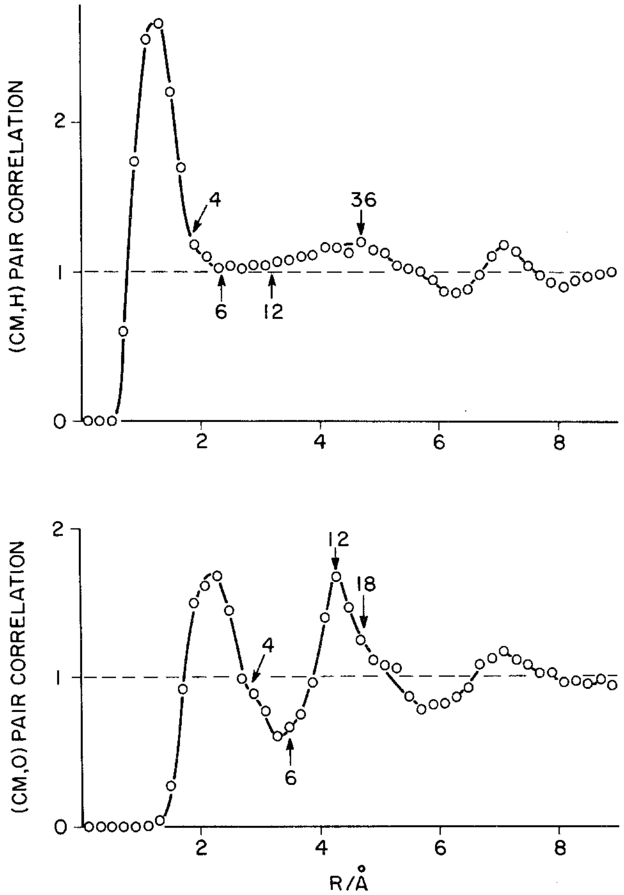

Fig. 2. Distribution of the hydrogen (top) and oxygen sites (bottom) around the center of mass of the classical isomorphic system for the bare Coulomb potential.

long-range interactions are calculated using a spherical truncation at the oxygen site with a radius of 9.8 Å.

In both models the electron is localized in a compact state of approximately the same shape and size. The complex time displacement correlation function defined as

$$\mathscr{R}^2(t-t') = \langle [\bar{r}(t) - \bar{r}(t')]^2 \rangle$$

exhibits the characteristic feature of ground state dominance as can be seen from Fig. 1. The value of $\mathscr{R}$ at half the chain length gives an average

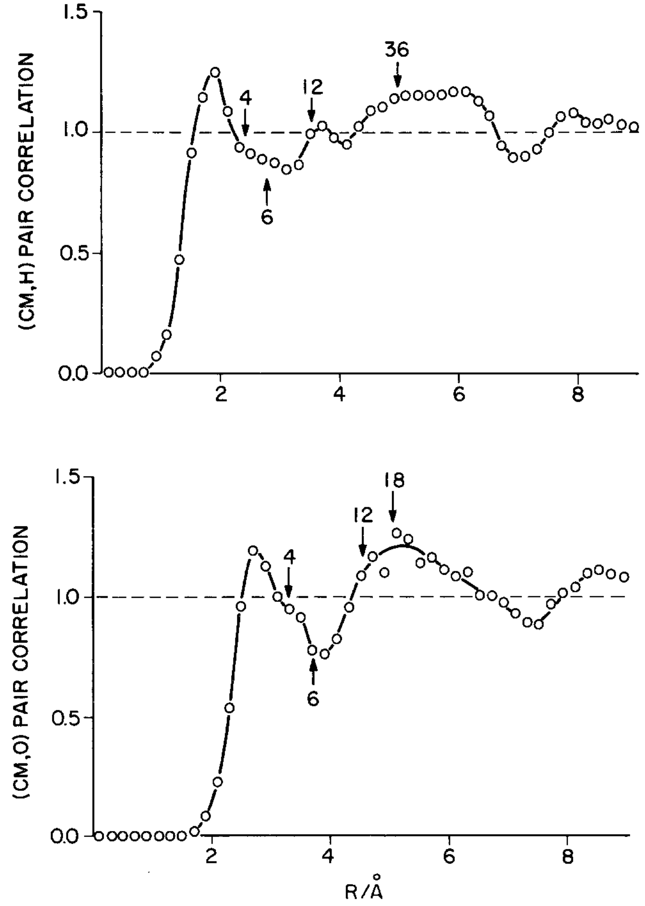

Fig. 3. As in Fig. 2 for the pseudo-potential.

diameter of about 3 Å for the electronic state. The difference between the two models becomes evident when the distribution of charges around the center of mass of the polymer chain is investigated. The molecules around the electron are bond-ordered with a coordination number between 5 and 6, but the order is considerably stronger for the pure Coulomb case (Fig. 2) compared to the pseudo-potential (Fig. 3). This is confirmed by the radial distribution of charges with respect to the vertices in the chain. In the case of the Coulomb potential the protons of the coordinated molecules (Fig. 4) are bound more tightly together (cf. Fig. 5). The runs were initiated starting

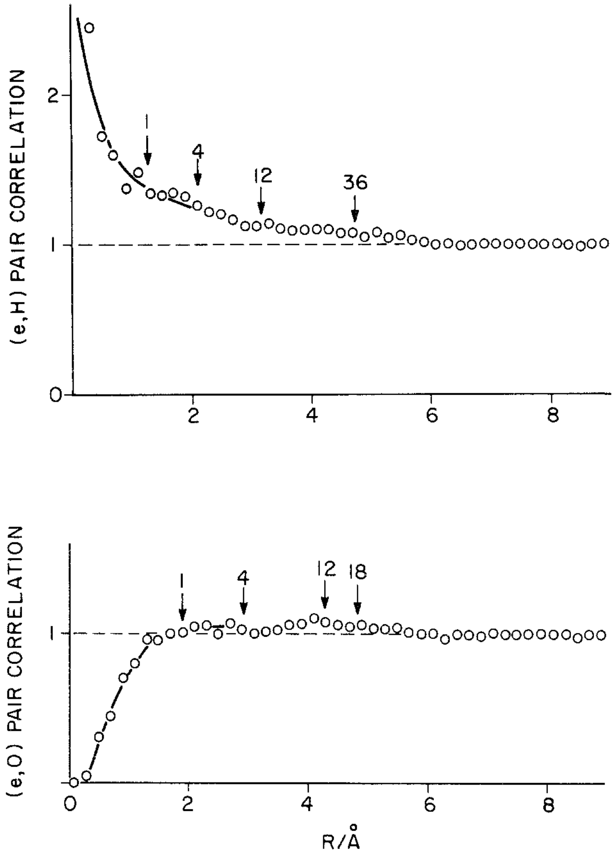

Fig. 4. Hydrogen–electron and oxygen–electron radial distribution function for the pure Coulomb potential.

from a delocalized state in an arbitrary configuration of the pure solvent. After an equilibration period of about 3×10^4 moves per water molecule, averages were collected over about 10^4 moves per molecule at a temperature of 280K. Within the statistical error, no difference in the simulation with $P = 1024$ and $P = 2048$ could be detected. The approximate excitation energies derived from the characteristic rise time of the correlation function $\mathscr{R}^2(t-t')$ are given in Fig. 1. The values should be compared to the 1.7 eV maximum in the experimental infrared absorption spectrum.(3)

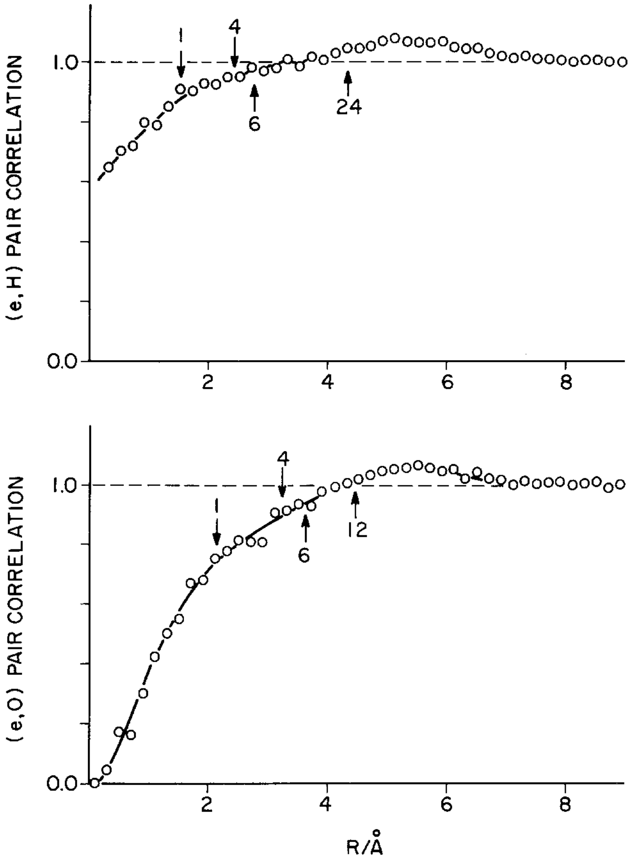

Fig. 5. As in Fig. 4 for the pseudo-potential.

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