Quantum-classical path integral simulation of ferrocene-ferrocenium charge transfer in liquid hexane

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SUPPORTING INFORMATION

1. Parameterization

Good parameters are the foundation of accurate MD (molecular dynamics) simulations. The CHARMM General Force Field (CGenFF)[1] is an extension of the CHARMM force field[2] to small non-biological molecules. Ferrocene and ferrocenium were parameterized in a manner consistent with this force field. Following the workflow described by Vanommeslaeghe et al.,[1] Gaussian09 [3] was used to optimize the geometries of both molecules at the MP2/6-31G(d) level. The Hessian matrix was also calculated for these geometries using the same level of theory. For each molecule, the output from these calculations was read into the VMD (Visual Molecular Dynamics[4]) plugin Paratool, which produced the initial topology, PDB and PSF files. Paratool was also used to generate the bonded parameters, extracting all the necessary information from the Hessian matrix. No additional optimizations or assignments were performed on the bonded parameters. The Lennard-Jones (LJ) parameters were also assigned at this time. The carbon and hydrogen LJ parameters were taken from the CHARMM 27[5,6] force field, while the LJ parameters for the iron were obtained from the Universal Force Field.[7] Unfortunately, the assignment of CGenFF partial charges is not supported by Paratool. However, it is supported by The Force Field Toolkit (ffTK),[8] a recently developed VMD plugin. ffTK generated the required Gaussian input files and analyzed the corresponding output files to produce the optimal partial charges. The obtained partial charges are shown in Table 1. The total charge on the cyclopentadienyl ring is -0.755 in ferrocene and -0.090 in ferrocenium.

Table 1. Atomic charges in ferrocene and ferrocenium

	ferrocene	ferrocenium
C	-0.213	-0.140
H	0.062	0.122
Fe	1.510	1.180

2. Solvation

The electron transfer complex was surrounded on all sides by a buffer of hexane molecules. Long-time, constant-temperature, constant-pressure MD simulations were performed using the donor charge configuration for several different solvent thicknesses. These simulations were used to construct an energy gap distribution function for each thickness. The energy gap distribution function and corresponding spectral density generated with a 13.0 Å thick solvation layer remained practically unchanged upon increasing the thickness of the surrounding solvent. A snapshot of the simulation cell (containing the transfer complex, the solvent and the periodic images) is shown in Figure SI1.

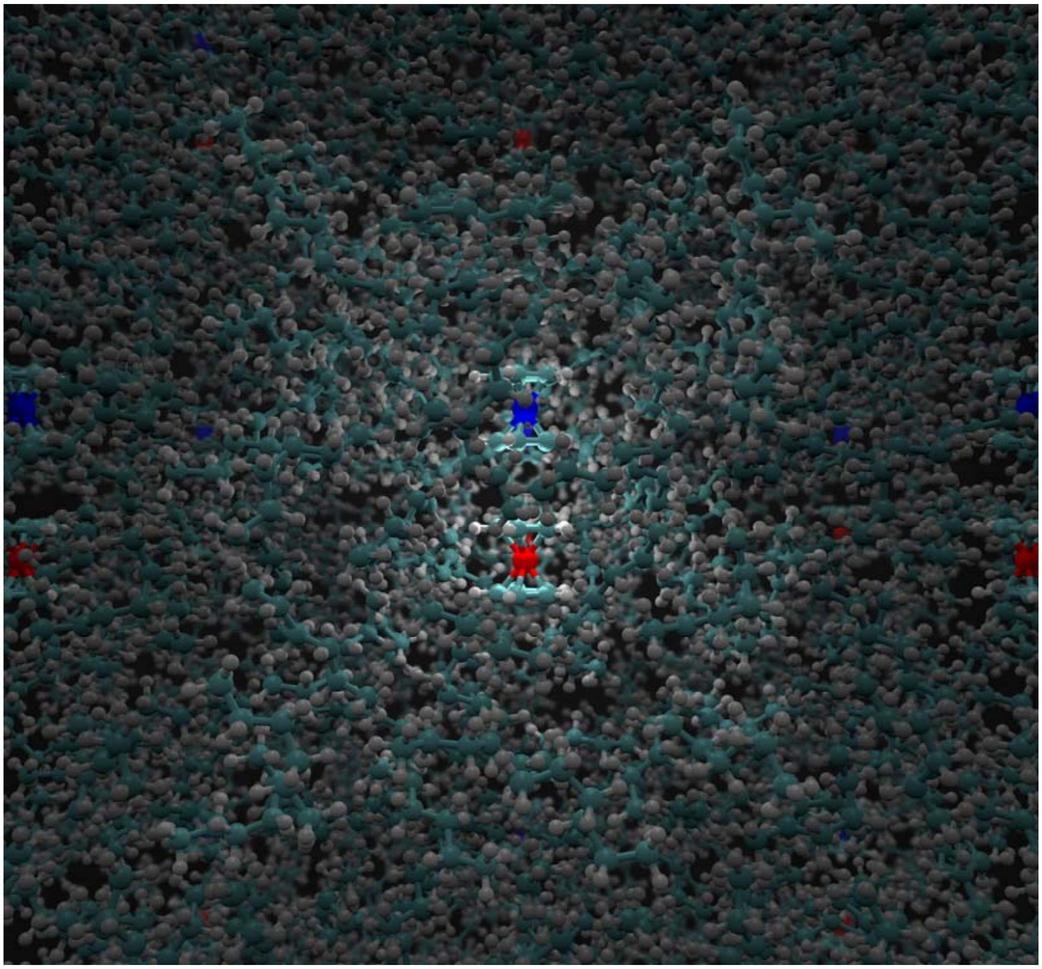

Fig. SI1. Snapshot of the simulation box. C and H atoms are shown in cyan and white. The Fe^{2+} and Fe^{3+} ions are shown in blue and red, respectively. The atoms in the periodic images are shaded darker.

3. Dynamically consistent state hopping (DCSH)

To accelerate the convergence with respect to memory length of the i-QCPI methodology,[9] we have developed[10] a stochastic DCSH procedure for selecting the single trajectory branch over the time preceding the active memory interval. In this, the solvent trajectories are launched and begin to evolve on the V_{D} surface. The value of the quantum influence function Q_{DD} at the end of each time $k\Delta t$ step serves to determine which of all solvent trajectories should be retained over the time step $[k\Delta t, (k+1)\Delta t]$ for use at times $(k+L)\Delta t$ or later. Specifically, when $0 \le Q_{\mathrm{DD}} \le 1$, the solvent trajectory propagated on V_{D} is selected with probability Q_{DD}. The trajectory associated with V_{D} is always chosen when $Q_{\mathrm{DD}} > 1$, and never chosen when $Q_{\mathrm{DD}} < 0$. The trajectory is then integrated for one time step subject to the force from the chosen charge state. The solvent trajectory determined this way also serves as the reference trajectory that is included in the system propagator.

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