

First Principles Molecular Dynamics Simulation of Solution

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We summarize the preliminary results concerning the hydration structure of trivalent rare-earth ions and the charge localization process in DNA fibers obtained during this fiscal year using a first principles molecular dynamics approach. In the first case, we demonstrated that the free energy surface obtained using the metadynamics based on the Car-Parrinello molecular dynamics for the hydration of Y^{3+} and La^{3+} captures the characteristics of the hydration of the trivalent rare-earth ions belonging to the different groups. In the second project, instead, we have shown how a proton-coupled mechanism is able to enhance the charge localization on guanine (G) bases with respect to the localization induced by simple thermal fluctuations, providing support to experiments.

Keywords: first principles molecular dynamics, metadynamics, QM/MM method, hydration structure, rare-earth ions, DNA, charge transfer

1. Introduction

Although a considerable knowledge of both the physics and the chemistry of aqueous solutions has been accumulated during the years by using various experimental techniques, computer simulations have not yet reached an analogous satisfactory level. The main reason is that the phenomena typical of aqueous solutions take place on a time scale which is much longer than the one affordable with our present computational capabilities. A main goal of our joint project is the establishment of simulation techniques enabling us to explore slow processes such as chemical reactions in aqueous solutions with reasonable computational resources.

In this fiscal year, besides the development and tuning of the QM/MM hybrid code, we have applied our tuned full quantum CPMD code¹⁾ to two research topics of recent growing interest, i.e., the hydration structure of trivalent rare-earth ions and the DNA charge localization responsible for electron/proton transfer. In both cases, the applications of the metadynamics^{2,3)}, developed very recently and based on the Car-Parrinello molecular dynamics, was utilized to efficiently explore the free energy landscape and to simulate rare events. Our preliminary results obtained so far are summarized below.

2. Results

2.1. Hydration structure of trivalent rare-earth ions

Since mid 1960s a change of coordination number of trivalent lanthanide (Ln) ions in aqueous solutions from nine to eight around Sm ~Gd has been strongly supported from an extensive set of measurements of partial molar volumes, heat capacities, molar entropies, viscosities, etc. This change of coordination number, so called gadolinium break, is believed to result from the lanthanide contraction; ionic radius is likely to be a determining factor of the coordination chemistry for the cation where its hydration is mostly governed by electrostatic interaction. Indeed, the structural chemistry of the heavier lanthanides is traditionally compared to that of yttrium(III); its ionic radius of 1.02 Å is very close to the one found for trivalent cations of the late lanthanides, e.g., 0.99 Å for Tm^{3+} , 1.00 Å for Er^{3+} , and 1.04 Å for Tb^{3+} . Although a number of physical quantities allow us to infer a change of coordination number as mentioned above, the detailed hydration structure of trivalent rare-earth ions is not completely uncovered due to the complexity inherent in the aqueous solutions.

In this work, we performed the metadynamics simulations of YCl_3 and $LaCl_3$ aqueous solutions to illustrate the detailed hydration structures of representative trivalent ions of yttrium (Y^{3+}) and cerium (La^{3+}) groups. The aim of the metadynamics that we performed in the present work is to explore

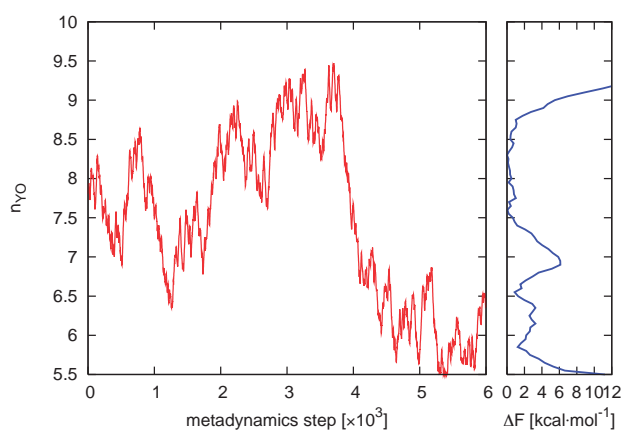


Fig. 1 Evolution of the yttrium-oxygen coordination number n_{YO} used as a collective variable of the metadynamics for hydration of Y^{3+} . The free energy difference ΔF is shown in right panel.

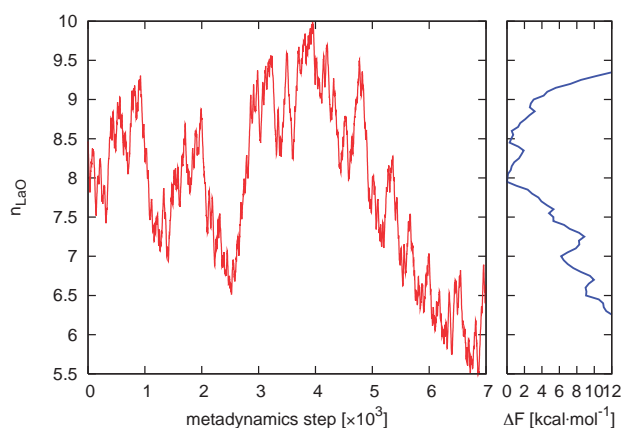


Fig. 2 Evolution of the lanthanum-oxygen coordination number n_{LaO} used as a collective variable of the metadynamics for hydration of La^{3+} . The free energy difference ΔF is shown in right panel.

the free energy surface in the coarse grained space of collective variables relevant to the problem. In the metadynamics method collective variables are treated as dynamical variables and the efficient exploration of the free energy surface is ensured by the presence of the additional history-dependent potential, which encourages the system to move from one minimum to the other via the lowest free-energy barrier. Figures 1 and 2 show the evolution of the metal (M)-oxygen(O) coordination number n_{MO} ($\text{M}=\text{Y}$ or La) used as a collective variable in our metadynamics run along with the reconstructed free energy curve ΔF for Y^{3+} and La^{3+} , respectively. We found that a variety of aqua and chloro-aqua complexes of Y^{3+} and La^{3+} are producible within the time scales of 10 ps by employing the metal-oxygen coordination number as a collective variable. This is in sharp contrast to the previous standard Car-Parrinello molecular dynamics for YCl_3 aqueous solution,⁴⁾ where we did not observe any changes of hydration structure of Y^{3+} within the same time

scales as the present metadynamics runs. The reconstructed free energy curves shown in Figs. 1 and 2 successfully capture the characteristic features of the hydration of both the ions. Thus, the present study demonstrated that the metadynamics based on the first principles molecular dynamics is a promising tool for exploring the free energy surface of complicated systems consisting of many degrees of freedom such as solutions.

2.2. DNA electron/proton transfer in solution

Charge transfer in DNA is currently the subject of intense theoretical and experimental investigation. This is due both to a possible use of DNA as a component in nanoelectronic and electrochemical devices and to the fundamental role of conductivity in the oxidative damage and mutations of DNA. By using the Car-Parrinello molecular dynamics,¹⁾ we have been able to study the mechanism of electron-hole localization in a laboratory realizable radical cation Z-DNA crystal.⁵⁻⁸⁾ We find that at room temperature structural deformation is not sufficient to provide an efficient localization mechanism (Fig. 3). Instead we find evidence for both an ion-gated and proton-coupled mechanism.⁵⁾ Namely, a hole h^+ can be localized by two mechanisms: (i) proton shift or (ii) fluctuations in the solvation shell. In the first case, a proton is supposed to move from a G base to the adjacent C base and this induces an increase in the spin density $\rho_s(x)$, representing an unpaired electron (negative charge), on G, accompanied by a decrease (hole) on C, where the proton (positive charge) is transferred (Fig. 4). Between the two proposed scenarios, this proton-coupled charge transfer mechanism seems to provide the best agreement and the key to interpret EPR and H/D substitution experiments. Due to the large size of the

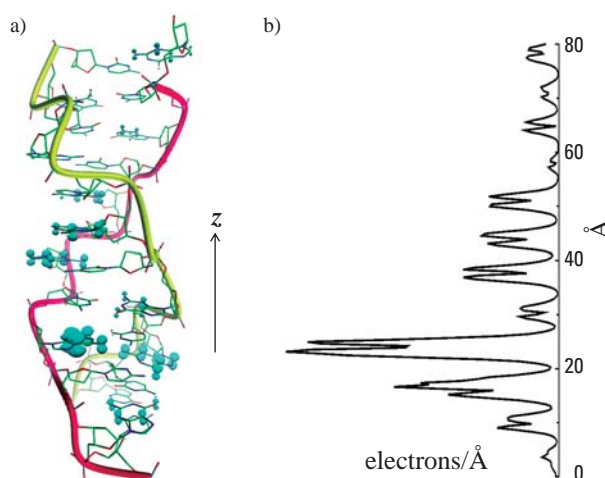


Fig. 3 Localization of the spin density $\rho_s = \rho_{\text{up}} - \rho_{\text{down}}$ (blue isosurfaces) due to the thermal motion that induces a tilt of the G base with respect to the DNA z -axis. Panel b) shows the spin density $\rho_s(z)$ projected along the z -axis.

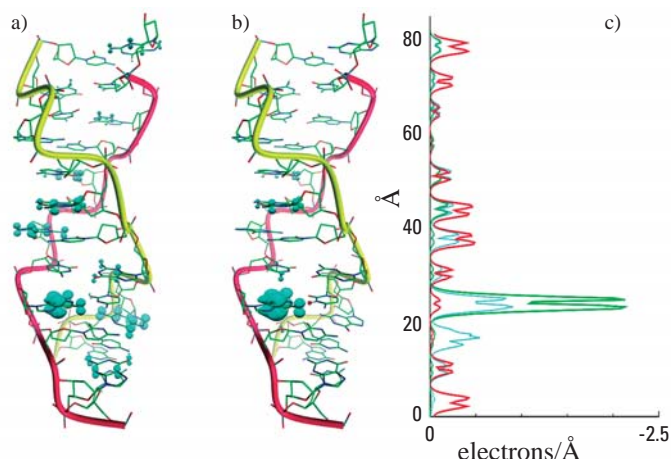


Fig. 4 Increase in the localization of the spin density $\rho_s(x)$ on the G base of the DNA (panel a) due to a proton transfer (small red ball) from the G base to the adjacent C base (panel b). In panel c) the blue curve shows $\rho_s(z)$ before the proton shift and the green curve after the shift. The red curve is the spin distribution at 0 K (higher DNA symmetry) in the absence of localization phenomena.

full quantum system, these calculations have been possible thanks to the Earth Simulator (ES) computer facility and will be published in a forthcoming paper⁹⁾ and presented as invited talk to the CSW2005 meeting.¹⁰⁾ This project is now continuing with the study of electron spin migration via a metadynamics^{2,3)} approach on a hybrid QM/MM system of the same Z-DNA fiber.

3. Summary

During this fiscal year, we studied the hydration structure of trivalent rare-earth ions and the DNA charge localization and proton coupling. In the first case, we demonstrated that the metadynamics based on the first principles molecular dynamics is a promising tool for exploring the free energy surface of complicated systems such as solutions. In the second project, instead, we have shown how a proton transfer (positive charge) from a G to a C base can induce a strong localization of the spin on the G bases and how a coupling of negative (electron) and positive (hole) charges provides the best agreement with the experimental outcome. Both the systems have been fully treated on quantum mechanics grounds. To reduce the computational cost and achieve further speed-up in the calculations of larger systems, a QM/MM hybrid code has been developed and tuned for the ES. Though the performance of our hybrid code is a little bit worse than the standard full quantum code, it already reaches a satisfactory level to use efficiently the ES.

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溶液の第一原理分子動力学シミュレーション

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本共同プロジェクトにおいて、平成16年度に実施した1)3価希土類イオンの水和構造と2)Z-DNA 2重螺旋鎖での電荷局在化に関するシミュレーションの結果をまとめる。どちらの課題も第一原理分子動力学に基づいた手法を用いて実施したものである。本年度は、計算コストを低減するためにQM/MM法を導入した。さらに、自由エネルギー面探査のためにLaioとParrinelloにより開発されたメタダイナミクスを導入し、上記課題に適用することにより、その有用性を確認した。

最初の課題では、3価希土類イオンの中で異なる族に属すイットリウムイオン(イットリウム族)とランタンイオン(セリウム族)の水和構造を比較することを目的に、Car-Parrinello分子動力学に基づいたメタダイナミクスシミュレーションを実行した。メタダイナミクス法の処方箋に従い、両イオンの水和に関する自由エネルギー差を求めたところ、実験から良く知られている両族に属す3価希土類イオンがとる配位数と良く対応した自由エネルギー曲線が得られた。このことより、メタダイナミクス法が水溶液などの複雑な系での反応を調べる方法として有望であることが分かった。

2番目の課題では、昨年度に引き続き、グアニン基とシトシン基からなるZ-DNA 2重螺旋鎖におけるグアニン基への正電荷(正孔)局在化のメカニズムを第一原理分子動力学法により調べた。熱揺らぎにより正孔がグアニン基に局在化する程度と比較することにより、プロトン移動とカップルして電荷移動が起きるproton-coupled charge transfer mechanismによって正孔がグアニン基により局在化する可能性が高いことが分かった。さらに電荷移動の詳細を解明するために、QM/MM法を導入しメタダイナミクスと組み合わせることにより、Z-DNA 2重螺旋鎖での電荷移動のシミュレーションを実行しているところである。

キーワード: 第一原理分子動力学, メタダイナミクス, QM/MM法, 水和構造, 希土類イオン, DNA, 電荷移動