

第3回レア・イベントの理論科学ワークショップ（CMSI 共催）のお知らせ

第一原理計算でラジカル解離反応を研究している Barcelona 大学の Jordi Ribas-Arino 博士が来日される機に、標記のワークショップを企画しました。藤崎弘士准教授（日本医大）、八木清博士（理研）とともに、物質科学分野における計算科学的研究の成果をお話いただく予定です。皆様のご来聴をお待ちしております。なお、講演は英語で行われます。

日時：平成 26 年 1 月 29 日（水）13 時 00 分 - 18 時 00 分

会場：東京大学本郷キャンパス浅野地区工学部 9 号館 1 階大会議室（101 号室）

アクセスの詳細はこちら：

http://www.u-tokyo.ac.jp/campusmap/cam01_04_17_j.html

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プログラム

- 13:00~13:05 Dr. Motoyuki Shiga (JAEA)
“Opening remarks”
- 13:05~14:50 Dr. Jordi Ribas-Arino (University of Barcelona)
“The key role of thermal fluctuations in dithiazoryl-based bistable magnetic materials”
- 14:50~15:10 Break
- 15:10~16:25 Dr. Kiyoshi Yagi (RIKEN)
“Variationally optimized coordinates for anharmonic vibrational structure calculations”
- 16:25~16:45 Break
- 16:45~18:00 Prof. Hiroshi Fujisaki (Nippon Medical School)
“Path search and path sampling methods for rare events”
- 18:30~ Free discussion

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The Key Role of Thermal Fluctuations in Dithiazolyl-based Bistable Magnetic Materials

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Recent years have witnessed a growing interest in the use of organic radicals as building blocks for bistable materials (i.e. materials that exist in two interchangeable phases under identical conditions).[1] The family of 1,3,2-dithiazolyl (DTA) radicals has furnished spectacular examples of materials that undergo spin transitions between a low temperature (LT) diamagnetic phase and a high temperature (HT) paramagnetic phase.[2] The neutral radical 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA) is the most prominent DTA-based compound, not least because its spin transition occurs with a wide thermal hysteresis loop that encompasses room temperature.[3] The LT phase of TTTA presents distorted π -stacks that comprise slipped pairs of nearly eclipsed radicals. The HT phase in turn present regular π -stacks, where each radical exhibits a slipped overlap with its two nearest neighbors along the stacking direction.

In this talk, it will be shown that the regular π -stacking motif of the HT polymorph of TTTA does not correspond to a minimum in the potential energy surface of the system. Ab initio molecular dynamics simulations reveal that the regular stacking motif of the HT polymorph is the result of a fast intra-stack pair exchange dynamics, whereby TTTA radicals continually exchange the adjacent TTTA neighbor (upper or lower) with which they form an eclipsed dimer. Such unique dynamics, observed in HT within the temperature range of the hysteresis loop, is the origin of a significant vibrational entropic gain in the LT - HT transition and thereby it plays a key role in driving the phase transition. It will be also shown that the magnetic properties of HT cannot be quantitatively understood without considering the large thermal fluctuations undergone by the radicals.

[1] R. Hicks. *Nature Chem.* 2011, 3, 189.

[2] J.M. Rawson et al. *J. Mater. Chem.* 2006, 16, 2560.

[3] a) W. Fujita, K. Awaga. *Science*, 1999, 286, 261; b) W. Fujita, K. Awaga, H. Matsuzaki, H. Okamoto. *Phys. Rev. B* 2002, 65, 064434.

Path search and path sampling methods for rare events

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The concept of rare events is important in physics, chemistry, and other branches of science because it can describe “state” change such as chemical reactions, conformational change, and phase change, which is a fundamental step to understand dynamical aspects of complex systems. However, there are diverse time and length scales embedded in such complex systems, making it difficult to characterize rare events. This is because the rare event is hard to sample (this is why it is called rare events!) and/or it takes much longer time duration than that easily accessible by conventional methods such as molecular dynamics simulations. Here we discuss our recent attempts to overcome these difficulties in molecular systems using the algorithms called path search and path sampling methods. One such method is the string method developed by Vanden-Eijnden and coworkers, which tries to search a minimum (free) energy path in a complex energy landscape. We apply the string method to the conformational change of an enzyme (adenylate kinase) [1] and extend it to a quantum regime by using the concept of centroid variables [2]. For sampling dynamic paths, we utilize the Onsager-Machlup action formalism, where a path has an intrinsic weight according to the action. For efficient path sampling, we combine the OM formalism with the replica exchange methods, which is a well known technique to accelerate configurational sampling [3,4]. Finally we discuss the further implications and future applications of the path search and path sampling methods.

[1] Y. Matsunaga, et al, PLoS Comput. Biol. 8, e1002555 (2012).

[2] M. Shiga and H. Fujisaki, J. Chem. Phys. 136, 184103 (2012).

[3] H. Fujisaki, et al, J. Chem. Phys. 132, 134101 (2010).

[4] H. Fujisaki, et al, J. Chem. Phys. 139, 054117 (2013).

Variationally optimized coordinates for anharmonic vibrational structure theories

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The selection of coordinates is of great importance for efficient computation of the molecular vibrational states. Local, internal coordinates (such as bond lengths, bond angles, and torsion angles) have been known to provide a compact representation of the vibrational Hamiltonian, and thus are advantageous to deal with the vibrational Schrödinger equation, e.g., for the highly excited states of X-H stretching modes ($X = \text{C}, \text{N}, \text{O}$) [1]. However, their applications have been rather limited because (1) complex coupling terms arise in the kinetic energy operator due to the curvature of the coordinates, (2) the definition of local coordinates is not unique, and above all (3) the advantage of the local representation is not theoretically granted in general. Thus, most of the vibrational structure calculations to date have been based on the normal coordinates, which are uniquely defined for any molecular system and provide the kinetic energy operator in a simple form. Nonetheless, the potential energy term in terms of normal coordinates is often coupled up to a very high order (four-mode coupling or beyond), which makes the vibrational structure calculation highly demanding.

We have recently developed a general procedure to determine optimal vibrational coordinates [2], which are defined as the unitary transform of the normal coordinates that minimizes the energy of the vibrational self-consistent-field (VSCF) method for the ground state. It is found that the optimized coordinates are neither entirely localized nor entirely delocalized (or normal) in any of the molecules examined. Rather, high-frequency stretching modes tend to be localized, whereas low-frequency skeletal vibrations remain normal. On the basis of these coordinates, we have introduced a series of new vibrational structure methods: optimized-coordinate vibrational configuration interaction (oc-VCI) [2], optimized-coordinate vibrational quasi-degenerate perturbation theory (oc-VQDPT) [3], and optimized-coordinate vibrational coupled cluster (oc-VCC) [4].

In this talk, I will outline the procedure of coordinate optimization based on VSCF, following some pilot applications using oc-VCI, oc-VQDPT, and oc-VCC. It is shown that the degree of coupling in the potential is effectively reduced by the transformation from normal to optimized coordinates, which enhances the accuracy of the vibrational structure calculations with low-rank excitations.

[1] B. Henry, *Acc. Chem. Res.* 10, 207 (1977); M. S. Child and L. Halonen, *Adv. Chem. Phys.* 57, 1 (1984).

[2] K. Yagi, M. Keçeli, and S. Hirata, *J. Chem. Phys.* 137, 204118 (2012).

[3] B. Thomsen, K. Yagi, and O. Christiansen, submitted.

[4] K. Yagi and H. Otaki, submitted.