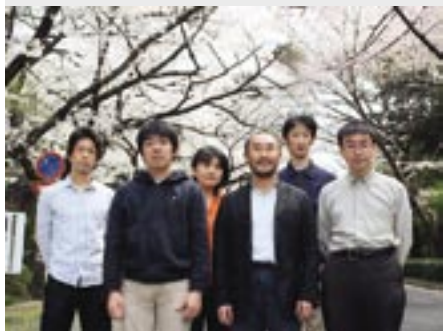


Electronic Structure and Electron-Nuclear Dynamics of Molecules in Contact with an Electron Reservoir

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Electronic structures and electron dynamics of molecules or nanostructured materials in contact with an electron reservoir play important roles in heterogeneous catalysis, surface photochemistry, and also electrochemistry. We have developed theoretical methods to calculate electronic structures of adsorbate-surface and electrochemical systems. We have also investigated exciton transfer dynamics in an array of quantum dot.

1. Open-Boundary Cluster Model for Calculation of Adsorbate-Surface Electronic States¹⁾

We have developed a simple embedded-cluster model approach to investigate adsorbate-surface systems. In our approach, the physically-relevant subsystem is described as an open-quantum system by considering a model cluster subject to an outgoing-wave boundary condition at the edge. This open-boundary cluster model (OCM) is free from artificial waves reflected at the cluster edge, and thus the adsorbate properties computed with the OCM are almost independent of the model cluster size. The exact continuous density of states (DOS) of a 1D periodic potential model is shown to be precisely reproduced with the OCM. The accurate DOS leads to an appropriate description of adsorbate-surface chemical bonding. Moreover, the open-boundary treatment of the OCM allows us to evaluate the electron-transfer rate from the adsorbate to the surface, whereas the conventional cluster model does not give any information about such a dynamical process.

2. Quasi-Adiabatic Decoupling of Born-Oppenheimer Potential Energy Curves for Adsorbate-Metal Surface Systems²⁾

We have applied the open-system treatment, recently developed by the authors, to a simple adsorbate-metal surface model potential. The open-system treatment is found to give a quasi-adiabatic representation where the adsorbate electronic states cross the metal ones in the manifold consisting of the Born-Oppenheimer potential energy curves of the whole system. On the obtained quasi-adiabatic curves, one can effectively follow time propagation of a nuclear wave packet. The computed propagation has revealed that the formation of a metastable adsorbate leads to the coherent vibrational motion of the neutral adsorbate as well as the desorption induced by electronic transitions.

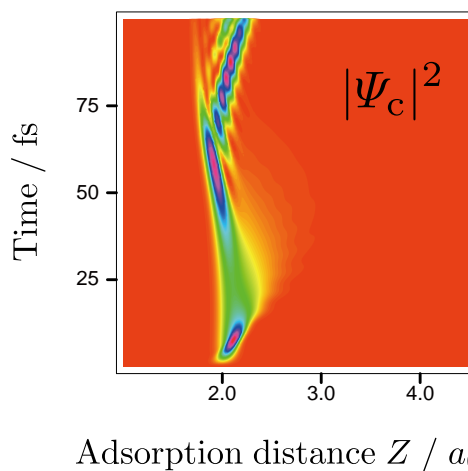


Figure 1. Nuclear wave-packet motion of the neutral adsorbate.

3. Exciton Transfer in Quantum Dot Arrays: Comparison of Eigenbasis and Site Basis Representations³⁾

We discuss differences between eigenbasis and site basis representations for models of exciton transfers in an array of quantum dots. The exciton relaxation processes are well described by the master equation in the eigenbasis representation. The site-basis evolution equation up to the second order of the interdot interaction is straightforwardly derived from the eigenbasis equation by using perturbation theory when the interaction is sufficiently small compared with the energy difference between the exciton states in each quantum dot. Although the higher order site basis equations can be derived similarly, the resultant equations are too complicated to use in the actual calculations. The master equation in the eigenbasis representation has several advantages over the site basis one: (i) the system described in terms of the eigenbasis representation can evolve into thermal equilibrium because the equation satisfies the detailed balance, (ii) the site basis equation does not reasonably describe the exciton state trapped in a local energy minimum at very low temperature, and (iii) it is computationally less demanding to carry out the eigenbasis evolution equation.

4. Development of Finite-Temperature Density Functional Approach to Electrochemical Reactions⁴⁾

We present a computational method to calculate the electronic states of a molecule in an electrochemical environment. The method is based on our recently developed finite-temperature density functional theory approach to calculate the electronic structures at a constant chemical potential. A solvent effect is treated at the level of the extended self-consistent reaction field model, which allows considering a nonequilibrium solvation effect. An exchange-correlation functional with a long-range correction is employed in this calculation, because the functional is adjusted so that the derivative discontinuity of energy with respect to a number of electrons could be satisfied. It has been found that the derivative discontinuity condition plays a crucial role in an electrochemical system. The computational results are presented for a reaction of $\text{NO}^+ + \text{e}^- \rightleftharpoons \text{NO}$ in chemical equilibrium. Owing to the improvement in the solvation effect and the exchange-correlation functional, the calculated activation free energy is in good agreement with experimental results.

5. Oligomeric Gold Clusters with Vertex-Sharing Bi- and Triicosahedral Structures⁵⁾

We present density functional studies of geometric and electronic structures of a gold cluster compound $[\text{Au}_{25}(\text{PH}_3)_{10}(\text{SCH}_3)_5\text{Cl}_2]^{2+}$ (**1**). The cluster has a unique geometric structure consisting of two icosahedral Au_{13} clusters bridged by methanethiolates sharing a vertex gold atom and terminated by chlorine atoms. This structure is very close to the biicosahedral gold cluster $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{SC}_2\text{H}_5)_5\text{Cl}_2]^{2+}$ reported in the recent experiment. We further demonstrate that a vertex-sharing triicosahedral gold cluster $[\text{Au}_{37}(\text{PH}_3)_{10}(\text{SCH}_3)_{10}\text{Cl}_2]^+$ is also achieved through bridging with the methanethiolates. A comparison between the absorption spectra of the bi- and triicosahedral clusters shows that the new electronic levels due to each oligomeric structure appear sequentially, whereas other electronic properties remain almost unchanged compared to the individual icosahedral Au_{13} cluster

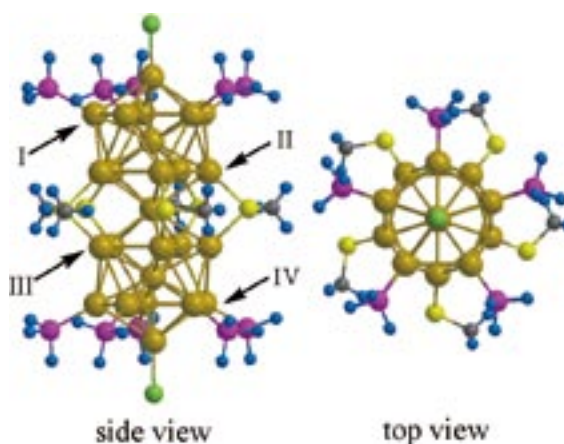


Figure 2. Side and top views of the optimized structure of **1**. The colored balls represent constituent atoms: Au (gold), S (yellow), C (gray), H (blue), P (magenta), Cl (green).

References

- 1) T. Yasuike and K. Nobusada, *Phys. Rev. B* **76**, 235401 (12 pages) (2007).
- 2) T. Yasuike and K. Nobusada, *Chem. Phys. Lett.* **457**, 241–245 (2008).
- 3) Y. Kubota and K. Nobusada, *J. Chem. Phys.* **129**, 094704 (7 pages) (2008).
- 4) K. Shiratori and K. Nobusada, *J. Phys. Chem. A* **112**, 10681–10688 (2008).
- 5) K. Nobusada and T. Iwasa, *J. Phys. Chem. C* **111**, 14279–14282 (2007).