

Development of Transferable Materials Information and Knowledge Base for Computational Materials Science

Project Representative

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The multi-industry CAMP program on the Earth Simulator (ES) is focused on dealing with various kinds of nanostructure materials using two kinds of simulation codes for non-periodic and periodic systems, of which calculated results are to be used as integrated information of comprehensive skills and knowledge base on computational materials science. We have calculated the metal-hydrogen systems using the LCAO-PS code which was tuned for the ES last year. We have been developing the CAMP-Atami code which can deal with periodic systems by solving the time-dependent Schrödinger equation. By analyzing the dynamic quantities to obtain dielectric functions, we can utilize physical quantities to design optical properties of molecules and semiconductor crystals in industrial products.

Keywords: nanostructure materials, metal-hydrogen system, TDDFT, optical properties

1. Overview of the Project

The goal of our project is to create the integrated knowledge base by exploiting calculated nanostructure material databases; transferable atoms and molecules picked up from calculated output-data are useful enough to use as the input data for other calculations. We plan to develop two type codes in the ES during FY2003-2005. One is for the non-periodic nanostructure system of molecules and clusters by the standard linear combination of atomic orbitals method using the norm-conserving pseudopotential (LCAO-PS). The non-periodic LCAO-PS code has been tuned for the ES in FY2003, a new chemical material synthesise code; the parallelization ratio is 99.95% and the parallelization efficiency is 64% evaluated from elapse time using 176 CPUs and 1080

CPUs for Pt₁₃₅ by the hybrid type parallelization. The other one is for the periodic system, CAMP-Atami, which focuses on the electronic structures for not only ground states but excited ones by solving the time-dependent Schrödinger equation based on the standard density functional theory (TDDFT). The characteristic feature of CAMP-Atami is that the Schrödinger equation is solved on the regular mesh in a real space of which initial input charge density for molecules is provided by the LCAO-PS output charge density. In FY2004, we have developed an interface between LCAO-PS and CAMP-Atami code.

In order to build up databases, we have also calculated nano-metal clusters, especially metal-hydrogen systems, using the LCAO-PS code. We have also been trying an effi-

cient parallelization for the CAMP-Atami. We can confirm that physical quantities obtained by our treatment are useful enough to design optical properties of industrial products.

2. Nano-metal Systems

There are a lot of varieties in nanostructure metal clusters because of free parameters of particle numbers and their shapes. As had being demonstrated by a characteristic electronic structure difference between of Pt_{135} and Au_{135} last year, the LCAO-PS code is designed to be effective in dealing with very narrow energy gap between the highest and lowest molecular orbitals like nano-metal systems. We have focused on metal-hydrogen (M-H) systems in FY2004. M-H systems are getting more and more important in a nanostructure materials science associated with energy and environmental problems in terms of the hydrogen storage. It has

been recognized that a vacancy plays a key role in hydrogen distribution in M-H alloys; the interaction between a vacancy and hydrogens in metal is strong enough to reduce the formation energy of a vacancy-hydrogen (Vac-H) cluster. Hydrogen atoms trapped by a vacancy are more stable than those in the interstitial sites, which causes the increase of the concentration of Vac-H clusters in the M-H system. Experimental data shows that the superabundant vacancy (SAV) formation is one of the most basic properties of the M-H system [1]. We have calculated various M-H systems utilizing the efficient ES system. Fig. 1-1 shows the geometrical structures and hydrogen binding energy curves for three types of clusters. There exist characteristic two stable positions at the vacancy site of the cluster center not in the smallest cluster of $Nb_{14}H_6$ but in both $Nb_{26}H_6$ and $Nb_{50}H_6$. Fig. 1-2 shows hydrogen binding energy curves in various atomic ele-

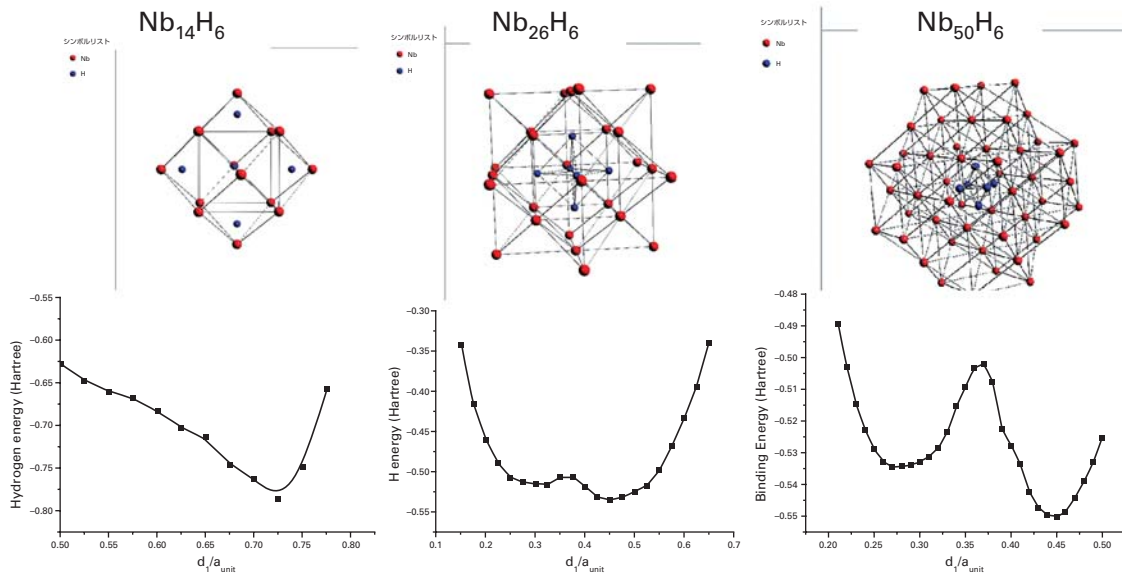


Fig. 1-1 Hydrogen stable positions in $Nb_{14}H_6$, $Nb_{26}H_6$, and $Nb_{50}H_6$. Red and blue spheres indicate metal and hydrogen atoms, respectively. d_1 is the hydrogen position from the vacancy at the cluster center. a_{unit} is the lattice constant. $d_1/a_{unit} = 0.5$ indicates the nearest square center in the bcc metal.

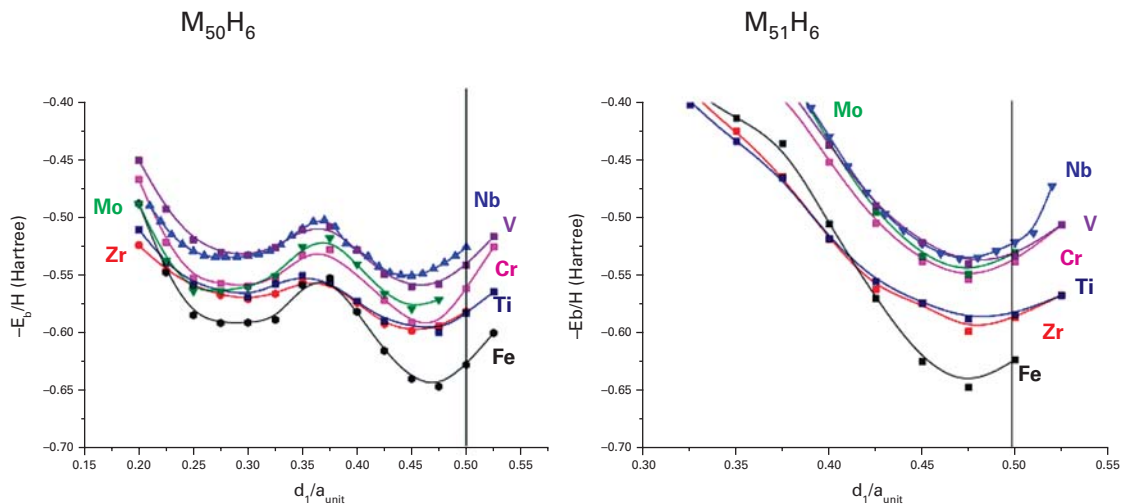


Fig. 1-2 Hydrogen binding energies for $M_{50}H_6$, the Vac-H model, and $M_{51}H_6$, the bulk like model. d_1 and a_{unit} are the same as Figure 1-1.

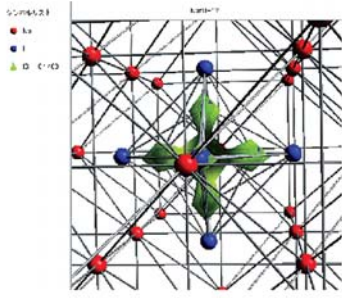


Fig. 2-1 Wave function of the lowest energy level, a_{1g} of the Vac- H_{12} . Blue (yellow) and red colors of the wave function contour map indicate negative and positive values, respectively.

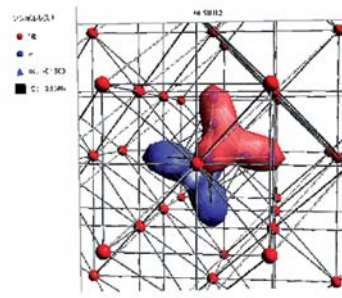


Fig. 2-2 Wave function of the next energy level, t_{1u} of the Vac- H_{12} . Blue and red colors of the wave function contour map indicate negative and positive values, respectively.

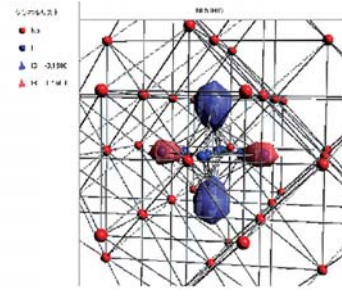


Fig. 2-3 Wave function of the third energy level, e_g of the Vac- H_{12} . Blue and red colors of the wave function contour map indicate negative and positive values, respectively.

ments of the bcc structure. The most striking feature is that stable hydrogen positions in the vacancy site are almost same in any atomic element. The binding energy differences, e_b , given by that of hydrogen of $M_{50}H_6$ (the Vac-H model) and $M_{31}H_6$ (the bulk model) are in good agreement with experiments; 0.42 eV per H (calculated) while 0.46 eV (experiment) in Nb, 0.81 eV (cal.) while 1.03 and 0.80 eV (exp.) in Mo, and 1.095 eV (cal.) while 0.89 and 0.73 eV (exp.) [1].

Since calculated result of e_b in Vac- H_{12} clusters in Mo and Nb are about 0.15 eV and 0.01 eV, respectively, they may form 12 hydrogens clusters at the vacancy sites. Typical hydrogen molecular orbitals, so called hydrogen induced states, are shown in Figs. 2-1, 2-2, and 2-3. These energy levels lie more than from 4 to 20 eV apart from the d-band bottom so that hydrogen induced states, which are s-, p-, and d-like states, comprises mainly hydrogen 1s states in both inner and outer equilibrium positions. Since there are 6 states in a_{1g} , t_{1u} , and e_g states, 12 hydrogen electrons form the closed shell state. Since vacancy formation energies are estimated experimentally as 2.6 to 3.07 eV, 3.2 eV, and 2.0 eV in Nb, Mo, and Cr, respectively [1], the Vac- H_6 in these bcc metals is likely to be stable in the M-H system with a very high concentration. It turns out to be very efficient to understand a general trend of the M-H system by calculated database for nano-metal clusters of almost all atomic elements using LCAO-PS code in the ES.

3. Physical properties by TDDFT

The fundamental equation of time dependent density functional theory (TDDFT) is given by

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + \sum_a V_{ion}(\vec{r} - \vec{R}_a) + e^2 \int d\vec{r}' \frac{n(\vec{r}', t)}{|\vec{r} - \vec{r}'|} + V_{xc}[n(\vec{r})] + V_{ext}(\vec{r}, t) \right\} \psi_i(\vec{r}, t) = i\hbar \frac{\partial}{\partial t} \psi_i(\vec{r}, t) \quad (1)$$

where $n(\vec{r}, t) = \sum_i |\psi_i(\vec{r}, t)|^2$ is the electron density. In order to calculate the optical responses, first we have computed the optimized electron density for a given structure by the time

independent DFT where the real-space grid representation is used for the electron wave functions. In our TDDFT calculation, our exploitable databases are used as an initial data to maintain the self-consistent electronic structure in the sense of rapid convergence. We applied this TDDFT to study the optical responses of the conjugated polymer and to focus the dielectric response in semiconductor in the calculations; the real-time approach is employed, where we follow the linear responses of the systems under externally applied perturbations in the real time.

For the calculation, the desired physical observables are the dynamic polarizability $\alpha(\omega)$, which is equal to the Fourier transform of the time dependent dipole moment $\mu(t)$, and the polarization electric field $-dA(t)/dt$ which is correspond to a surface charge $\sigma(t) = dA(t)/4\pi dt$, respectively. The dielectric function is $\epsilon(\omega)$ the ratio of the Fourier components of the external and the total fields.

$$\frac{1}{\epsilon(\omega)} - 1 = \frac{1}{A_0} \int_0^\infty e^{i\omega t - \eta t} \frac{dA(t)}{dt} dt, \quad (2)$$

where is η a small quantity to establish the imaginary part of the response. The real time evolution is done by the time step $\Delta t = 0.001 \hbar/eV$ and up to the total length of time evolution $T = 10 \hbar/eV$.

Oligo-(9,9'-dialkyl-fluorene) has been well studied as a candidate for the blue emitting material in polymer light emitting diodes [2]. For this material, we have performed the calculations with $n = 2, 3$ and 4, and the obtained spectra are shown in Fig. 3-1. The peak wavelength are estimated at $\sim 370, 412,$ and 440 nm for $n = 2, 3,$ and 4, respectively. These values should be compared with the experimentally observed peaks at $\sim 329, 350,$ and 362 nm . The systematic overestimation of peak wavelength is due to the inherent problem in DFT as mention above. The red-shift of peak wavelength as a function of n is observed, which give us the insight to the n -dependence of the band gap in fluorine.

The dielectric response of a compound semiconductor $Al_xGa_{1-x}As$ is plotted as a function of the components of alu-

minimum in Fig. 3-2. The spurious plasmon has been excluded by using Kramers-Kronig relation to determine the real part of the dielectric function, integrating over the imaginary response from the value of the band gap. Since our calculation is done within the frame work of LDA, there is some difference in the higher energy. The calculated values in the lower energy, however, are in good agreement with experiments [3].

The static dielectric function $\epsilon(0)$ varies with the components of aluminum. In the imaginary part of the dielectric function, which corresponds to the absorption spectra, there are two peaks: the first peak E1 and the second peak E2 can be identified with the parallel bands along Λ and Δ , respectively. The dielectric function $\epsilon(0)$ is plotted as a function of components X in Fig. 3-3. It decreases monotonously according to the components. Near the point $x = 0.45$, the energy band separation between the conduction band minima and the top of the valence band changes from Γ to X. The static dielectric function $\epsilon(0)$ also shows this change.

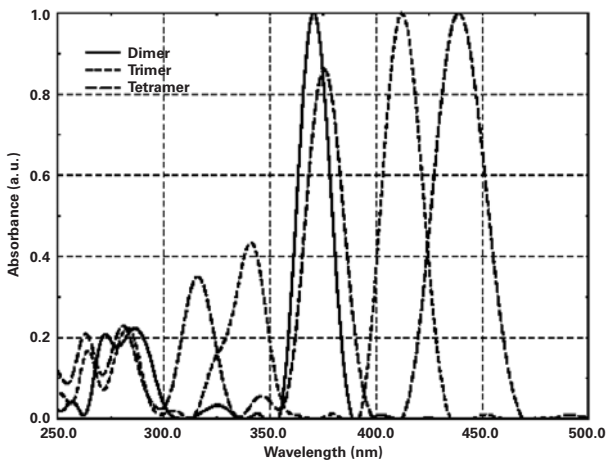


Fig. 3-1 Optical properties of the fluorene dimer ($n = 2$, solid line), trimer ($n = 3$, dashed line), and tetramer ($n = 4$, long dashed line).

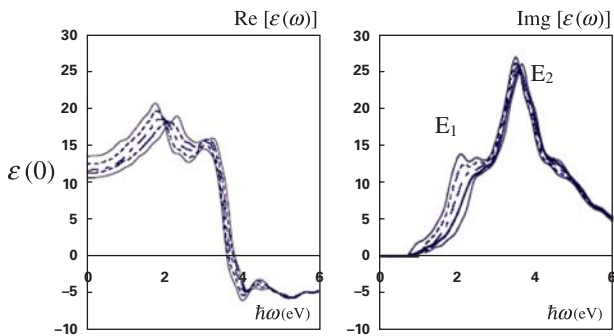


Fig. 3-2 The dielectric properties of AlGaAs. The solid lines represent those of GaAs and AlAs respectively. Dashed, dashed-dotted and dashed-tow-tdotted lines show those of $Al_{0.25}Ga_{0.75}$, $Al_{0.5}Ga_{0.5}$ and $Al_{0.75}Ga_{0.25}$, respectively.

4. Future Work

We have been developing a parallel code for the CAMP-Atami for the periodic system. Since both codes of the LCAO-PS for non-periodic and CAMP-Atami for periodic systems are basically designed to deal with all quantities at the real space, they will be tuned up to be more efficient parallelization in the ES by sharing transferable databases. We will focus on creating the knowledge base as a next stage. Since CAMP-Atami is useful enough to design optical properties of industrial products, we will develop the code as an industrial manufacturing system.

References:

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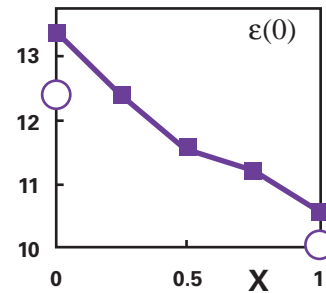


Fig. 3-3 Static dielectric constant in this calculation is plotted as the composition of aluminum by squares. The experimental value is shown by the circles.

計算材料科学のための物質情報構築法の開発

プロジェクト責任者

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2003年度から約3年計画で始まったCAMP-ES プロジェクトは、非周期系と周期系の2種類のシステムが取り扱える2つのプログラムの開発によって、データ共有と知識ベース化による計算の効率化向上を目的とした企業内研究者の共同研究プロジェクトである。昨年度は分子・クラスターなどの非周期系のためのLCAO-PSクラスターコードのESへのチューニングを終え高い並列化性能を達成し、本年度はそれを用いてナノクラスター系の計算とデータベース構築のため金属水素系の計算を行った。結晶系の計算コードCAMP-AtamiはESへの並列化のチューニングを進めた。周期系の計算は時間依存シュレディンガー方程式を解き、基底状態だけでなく電子励起状態計算をおこなうものである。計算結果から物理量の時系列解析から系の誘電率の計算を行うことにより現実の製品開発に役立つような物質系の光学的性質の予測を通して物質設計に有用であることを実証した。

キーワード: nanostructure materials, metal-hydrogen system, TDDFT, optical properties