Materials Design based on Quantum-Mechanical Simulations

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Good Design!

What would you like to design?
Computational materials design (CMD)
Theoretical developments of CMD

- Design of the framework of computational science

1st stage: Observation of Nature
2nd stage: Deduction of Mechanism by Empirical Model
3rd stage: Prediction of Materials Solution in a Design
4th stage: Quantum Simulation By the first-principles calc.
5th stage: Certification of Basic Mechanism & Deduction of Deeper understandings In Materials Solution
6th stage: Refinement of Materials Solution & Refinement of The Hamiltonian
7th stage: Quantum Simulation By a future 1st-principles calc.
Materials synthesis in the simulation

- If we solve the Schrödinger equation describing real materials, we can understand nature of the materials to design functional devices and systems.

  \[ i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \]

  The Schrödinger equation

- A bit hard to solve the equation!?
  → Let us ask the computer to do it.

Simulation: A virtual world mimicking the real world.
Let's make it!

Press it!

Heat it!
Designs of solids and/or molecules are given by knowledge of the condensed matter physics.
Examples of CMD (including ongoing projects):

- NEA of nano-BN: with Mr. K. Shiraishi & Prof. N. Suzuki
- Magnetic nano-carbon: with Prof. M. Fujita, Dr. K. Wakabayashi, Dr. K. Nakada, Dr. M. Igami, Mr. Y. Takagi, Mr. M. Maruyama, Mr. Y. Higuchi, Prof. S. Tsuneyuki, Dr. K. Akagi, Dr. Y. Yoshimoto & Dr. J. Yamauchi and Prof. T. Enoki, Prof. K. Fukui, Prof. Y. Kaburagi & Dr. Y. Kobayashi.
- Superconductivity of CaSi$_2$: with Mr. A. Nakanishi, Mr. T. Ishikawa and Dr. H. Nagara.
- Field effect doping of nanotube: with Mr. Y. Minamigawa, Dr. M. Otani & Prof. O. Sugino.
- Graphene device: with Mr. S. Sogo.
- Three-way catalyst: with Mr. Y. Ikuno & Mr. K. Harada.

Information is given at http://www.suzukilab.mp.es.osaka-u.ac.jp/
Negative electron affinity

- Let a place far separated from a surface of a material but within a length scale of it be an infinity. Let the scalar potential for electrons be $\phi(\infty)=0$. The workfunction of the surface is defined as the difference between $\phi(\infty)$ and $E_F$.
- Then, the workfunction depends on the atomic-scale details of the surface, e.g.
  - Direction of the surface,
  - Atomic structure of the surface.

- It is possible to estimate it qualitatively and quantitatively using the first-principles electronic structure calculation.
- For a wide-gap semiconductor, for a prepared surface, the negative electron affinity could appear.

Application for the electron beam source is expected!
Design of a functional nano-material: nano-BN

- A lot of functional nitrides are known. (GaN, etc.)

- An important observation is that, when polycrystals of hexagonal BN is suspended on surfaces of GaN or Si, the negative electron affinity appears.

- The experimentalists know that Hydrogenation of BN surfaces enhances the opportunity to have NEA.

Let us model the hexagonal BN in the nano-meter scale and confirm appearance of NEA in a simulation.
Interpolation of \( E_F \) is taken by changing the width of the vacuum layer of a slab model.

Calculation conditions
- Plane-wave expansion method with the ultra-soft pseudo-potential for B and N
- Exchange correlation energy functional: LDA of PW91
- Energy cutoff: 25Ry for w.f., 150Ry for charge density
- Sampling mesh of k-points: 10 x 10 x 1
- Structural optimization with fixed unit cell. Lattice constants in the directions perpendicular to the z-axis is assumed to be the same as values of the bulk.
Structures of nano-h-BN

Hydrogenated arm-chair edged BN films. (structure 1)

Non-Hydrogenated arm-chair edged BN films. (structure 3)

Hydrogenated arm-chair edged BN nano structure 2.

Vacuum layer
Dependence of $E_F$ on the width of the vacuum layer

Considering the gap reduction due to the usage of LDA, Str.1 should show NEA.

Table: Extrapolated values of energy ($\phi(\infty)=0$).

<table>
<thead>
<tr>
<th>Structure</th>
<th>VBT [eV]</th>
<th>CBB [eV]</th>
<th>KS gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Str. 1 (Hydro)</td>
<td>-5.643</td>
<td>-1.257</td>
<td>4.386</td>
</tr>
<tr>
<td>Str. 2 (Hydro)</td>
<td>-3.742</td>
<td>-1.121</td>
<td>2.621</td>
</tr>
<tr>
<td>Str. 3 (non-H)</td>
<td>-6.971</td>
<td>-2.921</td>
<td>4.050</td>
</tr>
</tbody>
</table>
Nano-ribbon structure: Enhancement of the gap
Large inter-plane distance (isolated nano-ribbons): Further enhancement of the gap
Hydrogenation: The position of $E_F$ becomes closer to the vacuum level than the case of non-hydrogenated edges.

Due to these facts, we conclude that NEA is obtained by making nano-BN ribbons with hydrogenated arm-chair edges in the nano-meter scale.

Careful theoretical analysis leads us to a deep understanding of phenomena and then we can achieve better design of nano-materials.
Nano-carbon systems

1. The Carbon Nanotubes
   • It is essentially a closed structure.
   • Two ends (edges of a tube) does not give an essential effect on the physical nature of nanotubes, if the tube is enough long.

2. The nano-graphene ribbon
   • It is essentially an open structure.
   • Two edges of a ribbon do give an essential effect on the physical nature of nanographite. If the ribbon has a finite size, all the boundaries are important.

Fabrication of various FETs have been done.

Fabrication on a surface may be easy!
The Marshall-Lieb-Mattis theorem

- A design given by anti-ferromagnetic Heisenberg model
- Alternant hydro-carbon “=” A bipartite graph

\[ H = \sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j \]

\( J_{ij} > 0 \) only if \( i \in A \) and \( j \in B \), or if \( i \in B \) and \( j \in A \). : Bipartite
All spins are connected by a path of interaction bonds, \( J_{ij} > 0 \).

\( N_A : \) # of red objects \hspace{1cm} \( N_B : \) # of blue objects

- A theorem: The ground state of the \( S=1/2 \) Heisenberg model on a bipartite connected graph is unique except for the trivial spin degeneracy and has the total spin of \( S=|N_A-N_B|/2 \).
Design of magnetic molecules

The Ovchinnikov rule

- The Longuet-Higgins rule & the Ovchinnikov rule are unified by the Lieb theorem for the Hubbard model.
- Shen, Qiu & Tian showed existence of the ferrimagnetic long-range order in the Hubbard model on the bipartite lattice with $|N_A - N_B| > 0$. 

\[ S = \frac{|N_A - N_B|}{2} = 1 \]
\[ S = \frac{|N_A - N_B|}{2} = 0 \]

MQDM
Clar predicted a hydrocarbon molecule with two unpaired electrons due to the non-Kekulé structure in 1941.

A pure benzenoid with the non-Kekulé structure was synthesized in 2001.


The methods of synthesis are often invented in the organic chemistry. In principle, theoretical design of the synthesis method is possible.
2,6,10-Tri-\textit{t}ert-\textit{Bu}tyltriangulene

1. \(R^1=R^2=H\)
2. \(R^1=R^2=Br\)
3. \(R^1=H, R^2=CHO\)
4. \(R^1=OH, R^2=OMe\)
5. \(R^1=H, R^2=OMe\)
6. \(R^1=H, R^2=OH\)
7. \(R=t-Bu\)
The nano-graphite

Nano-Graphite

Aromatic Molecule

Graphite

Flat bands caused by the edge states (non-bonding damping waves)

Tight-binding band structure ($\pi$-electrons, only)
Existence of the edge state at the zigzag edge & non-existence of the state at the armchair edge are thus confirmed.

Possible models for magnetic materials

- The Heisenberg model
- The Pariser-Par-Pople model (The Hubbard model)

MQDM

Magnetic nanographite

Density functional theory (Kohn-Sham equation)

\[
\left\{ -\frac{\hbar^2}{2m} \Delta + \int \frac{e^2 \rho(r')}{|r-r'|} + \frac{\delta E_{xc}}{\delta \rho} + \nu_{ext} \right\} \phi_i(r) = \varepsilon_i \phi_i(r).
\]

Density & Spin density as order parameters
- Single-particle description
- A Mean-field theory (Self-consistent equation)

\[
H = - \sum_{\langle i,j \rangle} \sum_{\sigma} t_{i,j} (c_{i,\sigma}^\dagger c_{j,\sigma} + \text{H.c.}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}
\]

The Hubbard interaction as a correlation term
- Many-particle description
Design of magnetic nano-graphite

- **Idea:** Existence of flat-bands at $E_F$ suggests magnetic instability.
- **Strategy:** $\pi$-topology
- **Principle:**
  $$|N_A - N_B| > 0 \Rightarrow S > 0$$
- **Supporting facts:**
  - The Longuet-Higgins rule
  - The Ovchinnikov rule
  - The Lieb theorem for the Hubbard model
  - The Shen, Qiu & Tian theorem for the ferrimagnetic RLO for the Hubbard model

The basic design

Materials solution has to be figured out.
**Possible materials solutions**

Type I

Zigzag-edged graphene ribbon

Type II

Magnetic nano-graphite ribbons

sp³ carbon

Graphite-diamond hybrid structures


H₂ gives a \( \pi \) state.

Hydrogenated nano-graphite ribbons

A hydrogenated magnetic ribbon

LSDA calculation of the magnetic nanographite ribbon with mono- & di-hydrogenated zigzag edges (Isosurfaces represent spin density)

DOS of the magnetic graphene ribbon
The magnetic nano-graphene ribbon with a mono-hydrogenated edge and a di-hydrogenated edge is confirmed to have ferrimagnetic spin alignment in 0 temperature by,
- LSDA calculation, GGA calculation
- PP-PS calculation PAW calculation
- TAPP, VASP

A magnetic molecule, C14H13 (1,8,9-di-hydroanthracene) has $S=3/2$ confirmed by,
- LSDA calculation
- URHF calculation
The armchair edge is stable.
Removal of odd-numbers of carbon atoms would make magnetic moments.

Y. Kobayashi et al. (2005).
Defective armchair ribbons

A magnetic graphene ribbon may be created on the graphite surface.
Effects of Fe impurities

Fe impurity do not necessarily induce magnetic moments in graphene structure. But, the zigzag edge has moments.
Summary

- We have designed magnetic nano-graphite structures,
  - Magnetic nano-graphene including wires and molecules,
  - Magnetic nano-wire on a diamond surface.
- LSDA (or GGA) calculations conclude magnetic structures. The result is consistent with expectation obtained by consideration of the Hubbard model.
- All the available consideration using various electron models conclude existence of localized magnetism at the zigzag edges of graphene structures.
Introduction
– structure of CaSi$_2$ and its superconductivity –

S. Sanphilippo et al.

superconducting transition temperature $T_c$ [$K$]

$P = 0 \sim 10$ GPa
rhombohedral

$P = 10 \sim 15$ GPa
trigonal

$P = 15 \sim 20$ GPa
AlB$_2$-like
Introduction – structure of CaSi$_2$

Internal parameter $z$

Si(1): \[
\begin{pmatrix}
\frac{a}{2} \\
\frac{a}{2\sqrt{3}} \\
c \times z
\end{pmatrix}
\]

Si(2): \[
\begin{pmatrix}
0 \\
\frac{a}{\sqrt{3}} \\
c \times (1-z)
\end{pmatrix}
\]

P = 10~15 GPa

$z \approx 0.4$

P = 15~20 GPa

$z \approx 0.44$

The Si plane becomes flatter by increasing the pressure but it is not perfectly flat in the experiment.

Motivation

1. What relation is there between structure and $T_c$?

2. In the region $P > 20$ GPa, what structure appears and how is the $T_c$?
DFT simulations of the structure and estimation of electron-phonon coupling constant by the density-functional perturbation theory in the range of $P = 10 \sim 20$ GPa. The plane wave pseudo potential method is applied.

1. Structural optimization by Parrinello-Rahman dynamics
   USPP for Ca (valence: 3s,3p,4s) and Si (valence: 3s,3p)
   $E_{\text{cut}}^{\text{wf}} = 16$ Ry, $E_{\text{cut}}^{\text{c}} = 64$ Ry, k-points sampling $16 \times 16 \times 16$

2. Estimation of $T_c$ by the standard strong coupling theory

Program code employed - Espresso ver.3.2
A phase transition is detected in the calculation. (It could be due to inaccuracy of the simulation.)
Results – structure optimization

Internal parameter $z$  
$z = 0.5 \rightarrow$ Si network is flat

- In our simulation, CaSi$_2$ becomes the AlB$_2$ structure at high pressure (transition pressure may be underestimated).
- Experimentally the AlB$_2$ structure has not been found.
Results – structural stability

Phonon dispersion of the AlB$_2$ structure of CaSi$_2$

The AlB$_2$ structure can be stable.
Results – transition temperature $T_c$

In 10～15GPa, $T_c$ disagrees with experiment. (Possible reasons may be lacks of accuracy, multiband effect, anharmonicity of phonon, …)

$T_c$ increases when the structure transforms from trigonal to AlB$_2$ structure.
Results – origin of increase in $T_c$

McMillan formula

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right)$$

<table>
<thead>
<tr>
<th>$P$ [GPa]</th>
<th>$\lambda$</th>
<th>$\omega_{\log}$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.27</td>
<td>300</td>
</tr>
<tr>
<td>20</td>
<td>0.41</td>
<td>280</td>
</tr>
</tbody>
</table>

$\lambda$ electron-phonon interaction

$\omega_{\log}$ averaged phonon frequency

$\mu^*$ screened Coulomb interaction (assumed to be 0.1)

Increase in $T_c$ is caused by increase of $\lambda$
Results – contribution to $\lambda$

- The circle size represents contribution of each mode to $\lambda$.
- High frequency phonon increases contribution to $\lambda$.
- A soft mode optical is observed around the $\Gamma$ point.
Results – contribution to $\lambda_{\text{eff}}$

- $E_{2g}$ mode
- $B_{2g}$ mode

AlB$_2$ structure
A design of new superconducting structure

Press CaSi$_2$ over 20GPa

Superconducting AlB$_2$ phase will appear.
Summary and the results

- We theoretically studied high pressure structures of CaSi$_2$ and the superconducting transition temperature by the strong coupling theory.

- At high pressure above 16 [GPa], the AlB$_2$ structure can appear.

- Enhancement of $T_c$ through the structural transition is due to increase of electron-phonon interaction parameter $\lambda$.

- E$_{2g}$ phonon mode contributes most to $\lambda$. 
CNT-FET with the air gap

- **Air gap structure**: The channel and the gate are separated by the air or the vacuum.
- **Field effect doping**: Carriers are induced by the applied gate bias.

- Field induced charge creates the electric field.
- **Quantum confined Stark effect (QCSE)** was proposed.
  
  (T. Takenobu et al. 2005)

Takenobu et al.
Effective Screening Medium (ESM) Method

Using the ESM Method
- We can obtain electronic structure of nanotube modeling the channel of FET

\[
\begin{align*}
\text{permittivity} & \quad \varepsilon_2 = 0 \\
\text{(vacuum)} & \quad \\
\text{permittivity} & \quad \varepsilon_1 = \infty \\
\text{(metal gate)} & \\
\end{align*}
\]

Obtain the electronic state by the first principles calculation only in the central tube.

Optimized structure

- Shift in the atom position due to the applied bias is about $10^{-5}$~$10^{-6}$ Å in the calculation

(8,0) Tube

Electric field (plane side)  
0.162V/Å  
($1.62 \times 10^9$V/m)

Direction of the field

(9,0) Tube

Electric field (plane side)  
0.078V/Å  
($7.8 \times 10^8$V/m)
Charge redistribution

The gate electrode is on the right side of the tube. Red: Electronic charge increases, Blue: It decreases

Accumulated charge distributes almost only out of the tube wall.

(8,0) tube

Gate voltage: 1.62V (0.162V/Å)  O. 012% increase

Gate voltage: -1.08V (0.108V/Å)  O. 012% decrease
Static potential changes and the electric field appears between the tube and the gate.

Potential curves on a plane including the tube axis averaged in the axis direction.

Potential shift in the tube is not so large.
Double layer of tubes: tube film

Second layer of (8,0) tube

Top layer of (9,0) tube

Electric field is almost screened by the first layer.
### Summary on the field effect doping

<table>
<thead>
<tr>
<th>Case</th>
<th>Induced electrons / Carbon • V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. (nanotube film)</td>
<td>$7.28 \times 10^{-4}$</td>
</tr>
<tr>
<td>Calc. (7,0) tubes with 10 Å spacing</td>
<td>$1.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>Calc. (7,0) tubes with 5.3 Å spacing</td>
<td>$8.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Calc. a tube film (double layer)</td>
<td>$3.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>Calc. a tube film (double layer)</td>
<td>$6.7 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

This result shows that feasibility of the simulation. The electric field is screened almost completely by a single layer of tubes. The field effect doping is done in the top layer of the tube film.
Electronic structure of graphene

Graphite structure is a stacking structure of graphene structures. # of layers >> 2.

- ABAB stacking: Bernal structure
- ABCABC stacking: Hexagonal-rhombohedral

The electronic structure surely depends on the stacking sequence.

If a single layer graphite, i.e. graphene is given, it has an interesting electronic structure with the two-dimensional Dirac Fermions.

Application of the graphene for the device physics is demanded.
For both models, the majority band has a slightly filled upper $\pi$ branch, and the minority band has a filled lower $\pi$ branch at K.

Calculation conditions

- The plane-wave expansion method with the ultra-soft pseudo-potentials for C & Ni.
- GGA by PBE96.
- 8x8x1 k-mesh for graphene/Ni(111) interface, 8x1x1 k-mesh for graphene with a Ni bar.
- The vacuum layer : 10 a.u. width.
- The Quantum-espresso ver 3.2.2 is utilized,
Band structure of graphene/Ni(111)

Minority band

Majority band

\[ \varepsilon \text{ [eV]} \]

Model B

Model B

\[ \varepsilon \text{ [eV]} \]

Model B

Model B
Band structure of graphene/Ni(111)

- The systems are spin polarized.
- For the model B and C, the $\pi$ band has a gap at the K point.
- The majority $\pi$ band has a small electron pocket at K. The minority $\pi$ band is embedded in Ni d bands.
- For the model B, the p-d mixed majorith branch is well above the Fermi level. But, it goes down to the Fermi level in the stable model C.
A graphene/Ni junction structure

Gapped graphene
(Gap at the K points)

Magnetic electrode

Metallic graphene

A MM/G/M/G/MM junction (M: metal, G: Gapped, MM: magnetic metal)

Theoretical clues to understand its nature:
1. The LDA band structure loses dispersion in the $y$ direction around $E_F$.
2. Gapped graphene is formed by potential due to the Ni substrate.
Two edge structures

- In a tight binding description, Ni atoms produce site-selective potential, which appears as a diagonal (flavor dependent) potential to the two-dimensional Dirac fields.
- We would have two different edge structures of interfaces, a zigzag and Klein’s edges, between graphene and Ni electrodes.
- Thus, we have a room to have a finite graphene ribbon in between two Ni electrodes.
These are non-magnetic solutions, although the starting magnetization is finite for this spin-GGA calculation.

Dispersion relation around the X point suggests that $\pi$ character remains in the electronic state.

To construct an effective theory for this structure, modeling of d orbital as well as $\pi$ orbital should be demanded.
Possible device structures

Graphene sheet

Comments:
1. To avoid undesired direct current flow from magnetic electrodes to graphene we may utilize SiC to induce alternating potential to make a gap in graphene.
2. The spin-orbit interaction may be enhanced in the $\pi$ electron system, if the single-layered graphene is placed under an non-symmetric environment, e.g. on a metallic substrate.
Valuable materials

- Gold  ¥2,887/g
- Platinum ¥4,922/g
- Palladium ¥1,312/g

Rhodium may be about 4 times more expensive than Platinum!

Rh: ~$6,000/oz, Pt ~$1,400/oz.

The Tokyo commodity exchange

We are using amount of Palladium, Platinum and Rhodium for 3-way catalyst of the automobile. If we can design non-noble-metal catalyst by CMD, a new catalyst with a low price would be given.
Automotive catalyst: its function

Catalyst components: noble metal, Pt, Pd, Rh etc.

Toxic substances in exhaust gas
- **HC**: hydrocarbon
- **CO**: carbon monoxide
- **NO\textsubscript{x}**: nitrogen oxides

Oxidation: $\rightarrow$
- **H\textsubscript{2}O + CO\textsubscript{2}**
- **CO\textsubscript{2}**

Reduction: $\leftarrow$
- **N\textsubscript{2} + O\textsubscript{2}**

Harmless exhaust gas
World transition of demand and prices of noble metals

Reduction in consumption of noble metals is required.
Intelligent catalyst: self-regenerative function of Pd, Rh & Pt

Intelligent catalyst

Precious metals

Atomic level complex
Segregated at 1-3 nanometers
Restored to atomic level

Self-regeneration!

Passage of time

Oxidative (initial condition) Reductive atmosphere Oxidative atmosphere

Precious metals

Conventional catalyst

Dispersed on conventional ceramic
Enlargement of precious metal
Further enlargement and deterioration

Possible reactions in the perovskite catalyst

In redox atmospheres, there are many possible reaction paths transforming structure and components of the perovskite catalyst:

1. \( \text{La(Fe,Pd)O}_3 \)
   \[ \leftrightarrow \alpha \text{LaFeO}_3 + \beta \text{Pd} + \gamma \text{La}_2\text{O}_3 + \delta \text{O}_2 \]

2. \( \text{La(Fe,Pd)O}_3 + z \text{O}_2 \)
   \[ \leftrightarrow \alpha' \text{LaFeO}_3 + \beta' \text{Pd} + \gamma' \text{La}_2\text{O}_3 + \delta' \text{O}_2 \]

3. \( \text{LaFeO}_3 + z \text{O}_2 \)
   \[ \leftrightarrow \alpha'' \text{LaFeO}_3 + \beta'' \text{Fe} + \gamma'' \text{La}_2\text{O}_3 + \delta'' \text{O}_2 \]

4. \( \text{La(Fe,Pd)O}_3 + \text{Pd} + x \text{CO} + y \text{NO} + z \text{O}_2 \)
   \[ \rightarrow \alpha''' \text{La(Fe,Pd)O}_3 + \beta''' \text{Pd} + \gamma''' \text{La}_2\text{O}_3 + \delta''' \text{O}_2 + \varepsilon \text{CO}_2 + \phi \text{N}_2 \]

Microscopic dynamics of the catalyst are expected to be understood by cooperation of high-resolution in-situ observation & CMD engine.

Design of non-noble-metal three-way catalyst