Finite temperature magnetism in dilute magnetic semiconductors

Materials design for semiconductor spintronics

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Ab initio simulation at finite temperature

**Diffusion of Cu in Si**

- **Ab initio Molecular dynamics**
- **Electronic structure calculation + molecular dynamics simulation**
- **Atomic motion at finite temperature**
- Successfully applied to
  - Lattice relaxation
  - Phase transformation
  - Impurity diffusion
  - Chemical reaction

**Ab initio spin dynamics?**

Simulation for finite temperature magnetism

- Ab initio spin dynamics
- FCC Fe
  - Supercell (32 atoms)
  - 3k spin structure (a=3.59Å)
  - ↑↑↓↓ structure (a=3.73Å)
- Computationally demanding

Practical method
1. Disordered local moment (DLM) state by using coherent potential approximation (CPA)
2. Mapping on Heisenberg model

FIG. 1. The left column shows the evolution of spins in a 32-atom cell of fcc Fe with $a=3.59\,\text{Å}$. Top, the starting random configuration; middle, after 75 steps; bottom, after 200 steps. The last configuration is close to a 3k structure, the minimum-energy structure allowed by the simulation (no S5 allowed). The right column is similar, but for $a=3.73\,\text{Å}$. Spin configurations after 0, 20, 75, and 220 steps are shown, the last being close to the ↑↑↓↓ structure.
Coherent potential approximation

AB Alloy

Electronic structure of substitutional alloy

Taking configuration average by using multiple scattering technique
Example: Slater-Pauling curve

- Magnetic Alloys
- Average magnetic moment behaves regularly
- Theory reproduces experimental curves very well

H. Akai
Disordered local moment state

Electronic structure above $T_C$
- Fe: DLM solution exists ⇒ local moment picture ($\mu=1.9\mu_B$)
- Ni: No DLM solution ⇒ Stoner picture ($\mu=0$)

Energy difference between FM and DLM states ⇒ $T_C$
Mapping on Heisenberg model

- How to calculate $J_{ij}$
  - Finite rotation (Oguchi et al.)
  - Infinitesimal rotation (Liechtenstein et al.)
  - Frozen magnon approach (Sandratskii et al.)

Curie temperature

- Mean field approximation
- Random phase approximation
- Monte Carlo simulation (exact)

\[
H = - \sum_{i \neq j} J_{ij} e_i \cdot e_j
\]

$J_{ij}$: exchange interaction
$e_i$: direction of the moment

$t$: single site $t$-matrix
$\tau$: scattering path operator
$g$: KKR structure constant
$\vec{R}$: lattice vector

\[
J_{ij} = \frac{1}{4\pi} \text{Im} \int \frac{d\epsilon}{\epsilon_F} \text{Tr} \left[ \Delta_i(\epsilon) \tau_{ij}^\dagger(\epsilon) \Delta_j(\epsilon) \tau_{ij}^\dagger(\epsilon) \right]
\]

\[
\Delta_i(\epsilon) = t_{ij}^{-1}(\epsilon) - t_{ij}^{-1}(\epsilon)
\]

\[
\tau_{ij}(\epsilon) = \sum_k \left[ t^{-1}(\epsilon) - g(\vec{k}, \epsilon) \right]^{-1} \exp\left\{ i \vec{k} \cdot (\vec{R}_i - \vec{R}_j) \right\}
\]

Liechtenstein et al., JMMM 67 (1987) 65
Example: Typical ferromagnetic metals

- Fe, Co, Ni
- Exchange interactions
- Curie temperature
- Magnon-dispersion relation

Dilute magnetic semiconductors

- Dilute magnetic semiconductors $\rightarrow$ Spintronics
- $(\text{Ga, Mn})\text{As, (In, Mn)As: } T_C < \text{room temp.}$

**Ab initio technique for finite temperature magnetism**

- Origin of ferromagnetism in DMS
- Accurate $T_C$ calculations for DMS
- Effect of inhomogeneous impurity distribution in DMS
Electronic structure calculation

- Local spin density approximation (LSDA)
- Korringa-Kohn-Rostoker method (KKR)
- Coherent-potential-approximation (CPA)

⇒ MACHIKANEYAMA2002 by Akai

\[ \Delta E = TE(\text{DLM}) - TE(\text{FM}) \]

Stability of ferromagnetic state: \( \Delta E = TE(\text{DLM}) - TE(\text{FM}) \)
Coherent potential approximation

Dilute magnetic semiconductors

- Substitutional disorder + Magnetic disorder (paramagnetic state)

Ferromagnetic DMS (total magnetization ≠ 0)

\[ \tau_{\text{cpa}} = c_A \tau_A + c_B \tau_B \]

\[ \tau_{\text{cpa}} = \sum_k \left[ t_{\text{cpa}}^{-1} - g(k) \right]^{-1} \]

\[ \tau = \left[ t_i^{-1} - t_{\text{cpa}}^{-1} - \tau \right]^{-1}, \quad i = A, B \]


Paramagnetic DMS (total magnetization = 0)

\[ \tau_{\text{cpa}} = \frac{c_A}{2} \tau_A + \frac{c_B}{2} \tau_B + \frac{c_B}{2} \tau_B^{\dagger} \]
$T_C$ in mean field approximation

Classical Heisenberg model

\[ \mathbf{H} = - \sum_{i\neq j} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j \]

- $J_{ij}$: exchange interaction
- $\mathbf{e}_i$: direction of local magnetic moment at site $i$

Mean Field Approximation (MFA)

A. Total energy difference

\[
\langle H \rangle_{FM} = - \sum_{i \neq j} J_{ij} \langle \mathbf{e}_i \rangle \cdot \langle \mathbf{e}_j \rangle = - c^2 N \sum_{i \neq 0} J_{i0}
\]

\[
\Delta E = \frac{- \langle H \rangle_{FM} + \langle H \rangle_{LMD}}{\mathcal{N}} = c^2 \sum_{i \neq 0} J_{i0}
\]

B. Curie temperature (Molecular field theory)

\[
k_B T_C^{MFA} = \frac{2}{3} c \sum_{i \neq 0} J_{i0} = \frac{2}{3} \frac{\Delta E}{c}
\]
$T_{c}^{MFA}$ of Mn-doped III-V DMS

Curie temperatures of Mn-doped III-V DMS:

- $(Ga, Mn)N$; $T_c \sim \sqrt{c}$
- $(Ga, Mn)P$
- $(Ga, Mn)As$
- $(Ga, Mn)Sb$; $T_c \sim c$

Electronic structure:

- Origin of the ferromagnetism:
  - double exchange
  - p-d exchange
Electronic structure of DMS

Impurity band in the gap $\rightarrow$ double exchange

Localized d-states below valence band $\rightarrow$ p-d exchange
Ferromagnetism in DMS

**Mechanism**

- **Double exchange mechanism**
  
  ![Diagram of double exchange mechanism](image)

  Band energy change in **impurity d-band**

  Band energy gain $\sim W \sim c^{1/2}$

  (if $E_F$ is in impurity band)

- **p-d exchange mechanism**
  
  ![Diagram of p-d exchange mechanism](image)

  **Hole mediated ferromagnetism**

  Band energy change in **valence band**

  **Half-metallic system**

  Valence band is polarized: $-1 \ \mu_B / Mn$

  Average polarization (mean field): $-c \ \mu_B$

  Interaction between Mn ions $\sim c$

---

Calculation for exchange interactions

\[ J_{ij} = \frac{1}{4\pi} \text{Im} \int d\varepsilon \text{Tr} \left[ \Delta_i(\varepsilon) \tau_{ij}(\varepsilon) \Delta_j(\varepsilon) \tau_{ji}(\varepsilon) \right] \]

\[ \Delta_i(\varepsilon) = t_{ij}^{-1}(\varepsilon) - t_{ij}^{-1}(\varepsilon) \]

\[ \tau_{ij}(\varepsilon) = \left[ t^{-1}(\varepsilon) - \tilde{t}^{-1}(\varepsilon) + \tilde{\tau}^{-1}(\varepsilon) \right]_{ij}^{-1} \]

\[ \tilde{\tau}_{ij}(\varepsilon) = \sum_k \left[ \tilde{t}^{-1}(\varepsilon) - g(k, \varepsilon) \right]^{-1} \exp \left\{ i \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j) \right\} \]

Mn random distribution

CPA medium

t: single site t-matrix
\( \tau \): scattering path operator
\( \tilde{t} \): cpa single site t-matrix
\( \tilde{\tau} \): cpa scattering path operator
\( \mathbf{R} \): lattice vector
\( g \): KKR structure constant
Exchange interactions in DMS

- Double exchange system (Ga, Mn)N → strong, but short-ranged interactions
- p-d exchange system (Ga, Mn)Sb → weak, but long-ranged interactions
Magnetic percolation problem

- 2D square lattice with nearest neighbor interaction.

Percolation threshold (c=0.59)

- Magnetic ion
- MCS (Reality)
- perfect network
- only clusters
- percolated

\[c \approx 0; \text{ still ferromagnetic}\]

\[\text{dilution with concentration factor } c\]

Short ranged interaction
→ Ferromagnetism is suppressed below the percolation threshold

<table>
<thead>
<tr>
<th>lattice</th>
<th>percolation threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>square</td>
<td>0.59</td>
</tr>
<tr>
<td>triangle</td>
<td>0.50</td>
</tr>
<tr>
<td>diamond</td>
<td>0.43</td>
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<tr>
<td>sc</td>
<td>0.31</td>
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<tr>
<td>bcc</td>
<td>0.25</td>
</tr>
<tr>
<td>fcc</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Nearest neighbor Heisenberg model

- $c \approx 1$, MFA values are reasonable
- Ferromagnetism disappears below the percolation threshold
Monte Carlo simulation

Thermal average of physical observable $A$

$$< A > = \frac{1}{Z} \int dx \exp \left[ -H(x) / k_B T \right] A(x) = \frac{\sum_{i=1}^{M} \exp \left[ -H(x_i) / k_B T \right] A(x_i)}{\sum_{i=1}^{M} \exp \left[ -H(x_i) / k_B T \right]}$$

$Z$: partition function  
$k_B$: Boltzmann constant  
$H$: model Hamiltonian  
$T$: temperature

Metropolis algorithm  
...... efficient sampling technique in the phase space

1) Prepare a simulation box.

$$H = - \sum_{i,j} J_{ij} \vec{e}_i \cdot \vec{e}_j$$

2) Choose a site $i$, and calculate the energy change $\Delta E$ due to a random rotation of the magnetic moment.

3) Generate random number $r$ between 0 and 1.

4) If $r < \exp [-\Delta E / k_B T]$, rotate the moment.

5) Analyze the resulting configuration and store the property for the averaging.

Exact $T_C$ values taking disorder effect fully into account
$T_C$ by Monte Carlo Simulation

Reasonable agreement with experiments.
High-$T_C$ phases can not be explained.
Inhomogeneous impurity distribution in DMS

- MBE
- (Al, Cr)N, Cr 7%, Tc>900K
- (Ga, Cr)N, Cr 3%, Tc>900K

TEM, EELS

One-dimensional Cr-rich region:
Ferromagnetic

Spherical clusters:not FM

Gu et al., JMMM 290-291(2005)1395.

Singh et al., APL 86 (2005)12504
Generalized perturbation method

Ducastelle and Gautier: ‘Generalized perturbation method’

\[ H = - \sum_{i \neq j} V_{ij} \sigma_i \sigma_j \]

\[ V_{ij} = V^{AA}_{ij} + V^{BB}_{ij} - 2V^{AB}_{ij} \]

- \( V_{ij} \): Effective pair interaction between site i and j
- \( \sigma_i \): Occupation number
- \( \Delta_i (\varepsilon) = \chi_A^i (\varepsilon) - \chi_B^i (\varepsilon) \)
- \( \tau_{ij} (\varepsilon) = \sum_{\mathbf{k}} \left[ t^{-1}(\varepsilon) - g(\mathbf{k}, \varepsilon) \right]^{-1} \exp\{ i \mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j) \} \)


\( X \): single site scattering-matrix
\( \tau \): scattering path operator
\( \mathbf{R} \): lattice vector
\( g \): KKR structure constant
Effective pair interaction in DMS

Effective attractive interactions between nearest neighbors → tendency toward phase separation

M. van Schilfgaarde et al., PRB 63 (2001) 233205.
Generate inhomogeneous distribution

Simulation of spinodal decomposition

1) Prepare a simulation box.

\[ H = - \sum_{i \neq j} V_{ij} \vec{\sigma}_i \cdot \vec{\sigma}_j \]

2) Choose a site i, and try to move it to one of the nearest neighbor sites. Calculate the energy change \( \Delta E \) due to the transfer.

3) Generate random number \( r \) between 0 and 1.

4) If \( r < \exp \left( -\Delta E / k_B T \right) \), rotate the moment.

5) Store the resulting configuration and calculate magnetic properties.
Spinodal decomposition in (Ga, Mn)N

- Low concentration (5%)
  - Small clusters
  - No percolation
  - $T_C$ enhancement is expected.

- High concentration (20%)
  - Connecting random pattern
  - Magnetic network
  - $T_C$ enhancement

annealing of bulk sample
Effects of spinodal decomposition on $T_C$

- **Low concentration (5%)**
  - Small clusters
  - No percolation
  - No $T_C$ enhancement is expected.

- **High concentration (20%)**
  - Connecting random pattern
  - Magnetic network
  - $T_C$ enhancement
Layer by layer growth condition

Spinodal decomposition in 2D

Island formation

Repeat N-times

Inter-layer diffusion is not allowed

One dimensional structure due to the spinodal decomposition under the layer by layer condition.
Layer by layer growth simulation

(Zn, Cr)Te, Cr 5%

![Images](a), (b)

- Spinodal decomposition in 3D
  - Small clusters
  - No percolation
  - No $T_C$ enhancement

(Ga, Mn)N, Mn 5%

![Images](c), (d)

- Layer by layer growth simulation
  - One dimensional fragments
  - Magnetic network
  - No $T_C$ enhancement
  - Strong anisotropy

Super paramagnetic blocking phenomena
Summary

- **Ab initio simulation of finite temperature magnetism**
  - Disordered local moment technique
  - Mapping on Heisenberg model + statistical method

- **Application to dilute magnetic semiconductors**
  - Mechanism and $T_C$ calculations
  - Impurity band in the gap
    - $\rightarrow$ double exchange $\rightarrow$ short ranged interaction
  - Localized moment
    - $\rightarrow$ p-d exchange $\rightarrow$ long ranged interaction
  - Low concentration, Low $T_C$ (Magnetic percolation problem)

- **Inhomogeneous distribution of impurities**
  - Phase separation *(spinodal decomposition)*
  - Layer-by-layer growth condition
    - Quasi one-dimensional structure
    - Superparmagnetic blocking phenomena
Magnetization curve

Monte Carlo Simulation for Hysteresis loop
Super exchange interaction

Anti-parallel configuration of two local magnetic moments

→ Band energy gain by the super-exchange interaction
Effects of spinodal decomposition on $T_C$ of (Ga, Mn)As

![Diagram showing the effects of spinodal decomposition on $T_C$ of (Ga, Mn)As. The graph plots Curie temperature (K) against Monte Carlo Step, with different percentages of Mn and Monte Carlo steps (10MCS, 20MCS, 50MCS, 100MCS) depicted.]
Systematic error of LDA

The LDA predicts occupied d-states at too high energy.

The ferromagnetism depends on the energetic position of d-states → LDA+U method

Okabayashi et al., PRB 59 (1999) R2486
LDA+ $U$ method

In the LDA+$U$, Coulomb repulsion between electrons in localized state is treated by the Hubbard like procedure.

$$E_{\text{LDA}+U}[n^\sigma(r), \{n^\sigma_m\}] = E_{\text{LDA}}[n^\sigma(r)] + E_U[\{n^\sigma_m\}] - E_{\text{dc}}[\{n^\sigma_m\}]$$

$$E_U[\{n^\sigma_m\}] = (U/2) \sum_\sigma \sum_m n^\sigma_m n^{-\sigma}_m + (U-J)/2 \sum_\sigma \sum_{m\neq m'} n^\sigma_m n^{-\sigma}_{m'},$$

$$E_{\text{dc}}[\{n^\sigma_m\}] = (U/2) N(N-1) - (J/2) \sum_\sigma N^\sigma(N^\sigma-1)$$

$$V_{\text{LDA}+U}(r) = V_{\text{LDA}}(r) - (U-J)(n^{-\sigma}_m 1/2)$$

$n^\sigma(r)$: electron density

$n^\sigma_m$: electron occupation

$\sigma$: spin

$m$: orbital

$$N^\sigma = \sum_m n^\sigma_m \quad N = \sum_\sigma N^\sigma$$

$U$: Effective Coulomb interaction

$J$: Effective exchange interaction

Mn-doped III-V, $U = 4$ eV, $J = 0.8$ eV


SIC calculation: ThM3.4C, M. Toyoda et al.
LDA+U calculations for (Ga, Mn)As

In LDA+U we find localized 3d states $\rightarrow$ p-d exchange

$T_C$ is approximately proportional to Mn concentration.

LDA+U with MCS gives reasonable $T_C$ values.
LDA+U calculations for (Ga, Mn)N

Around $E_F$, the LDA+U predicts very similar electronic structure to the LDA.

Unoccupied d-states are shifted to higher energy. → anti-ferromagnetic super-exchange interaction is suppressed.
Self-Interaction correction: (Ga, Mn)As

- M. Toyoda et al., 2006.

PES J. Okabatashi et al. (1999)

Zener's p-d exchange mechanism

LDA

SIC-LDA

Zener's p-d exchange mechanism
Self-Interaction correction: (Ga, Mn)N

M. Toyoda et al., 2006.

Zener’s double exchange mechanism

J. I. Hwang et al. (2005)

PES
Exchange interactions and $T_C$

- Double-exchange-like
- DOS at $E_F$ is smaller than in LDA.
- Exchange splitting is two times larger.
- $\rightarrow$ Suppresses antiferromagnetic super-exchange Int.
Exchange interactions and $T_C$

- *p-δ*-exchange-like
- DOS at $E_F$ is reduced.
- Long-range behavior of the exchange interactions.
  - Enhances $T_C$ in the diluted region (but not in MFA).
Self-Interaction correction: (Zn, Co)O

- *M. Toyoda et al., 2006.*

PES *M. Kobayashi et al. (2005)*

**Weak ferromagnetic super-exchange mechanism**