Electronic structure theory and magnetism

Olle Eriksson
Uppsala University
and
WISE-Wallenberg Initiative Materials Science

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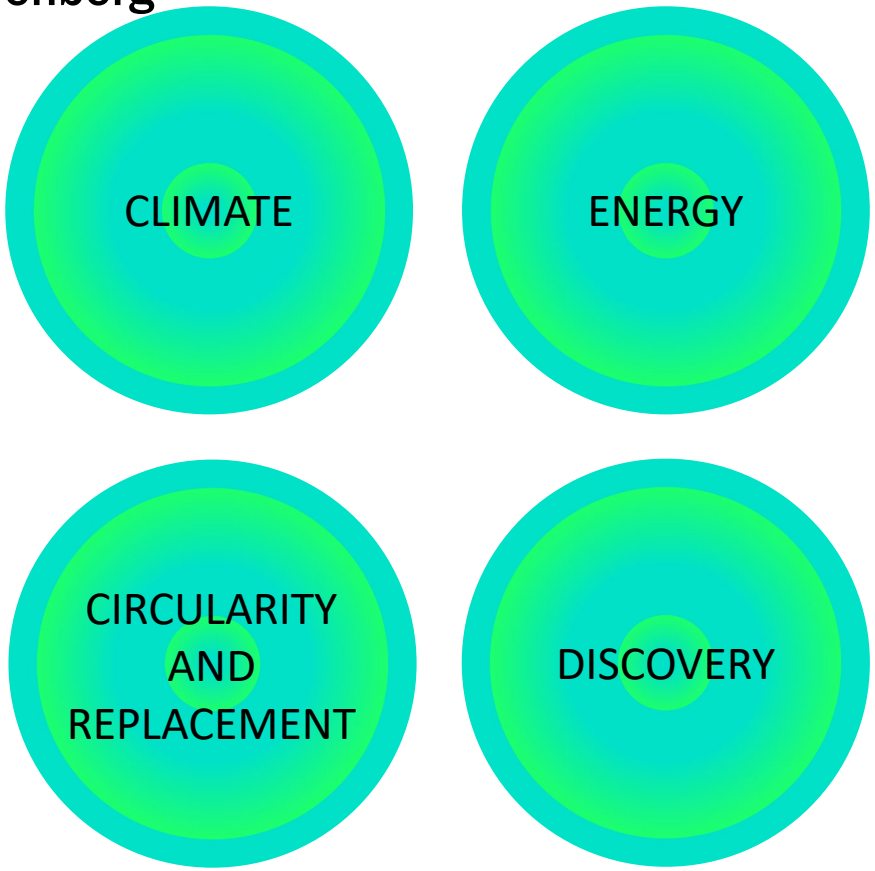
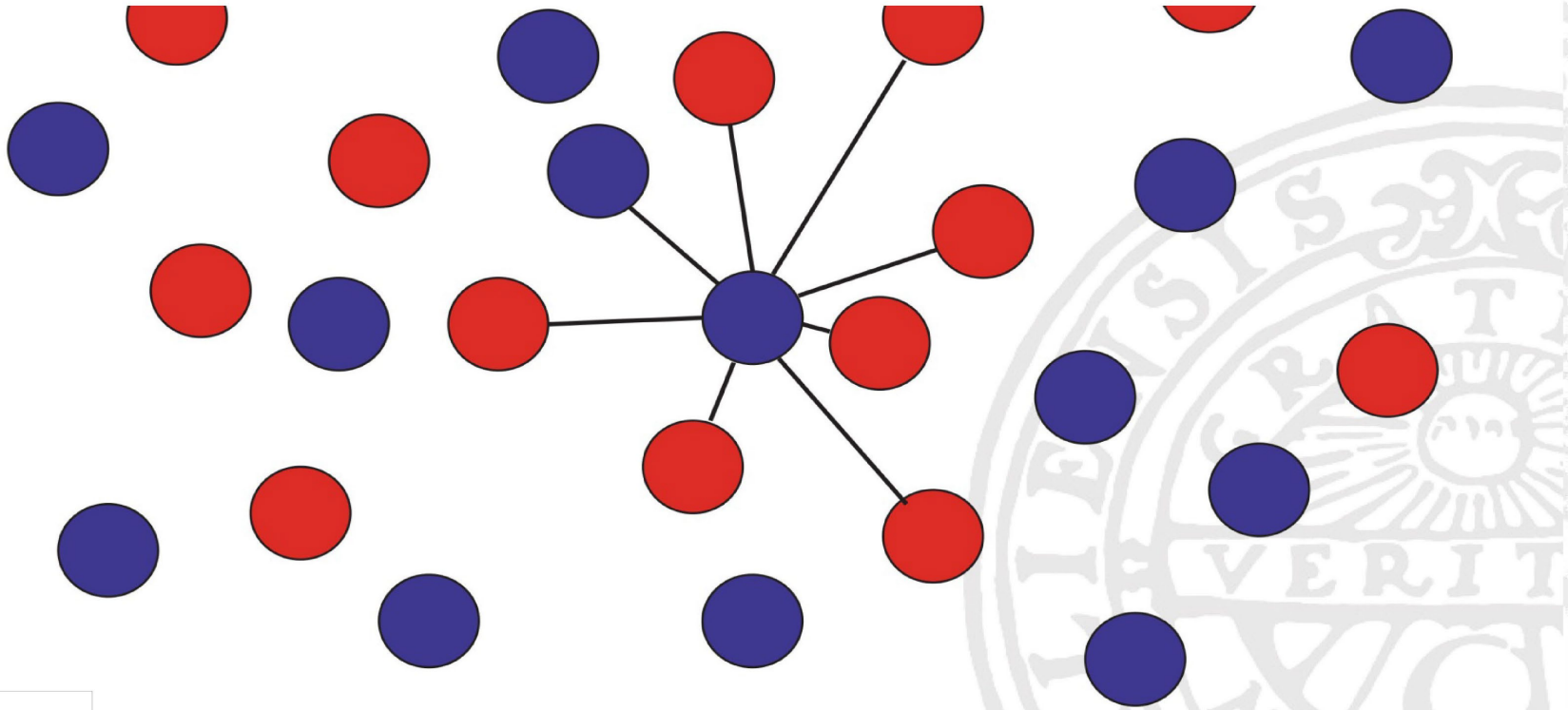
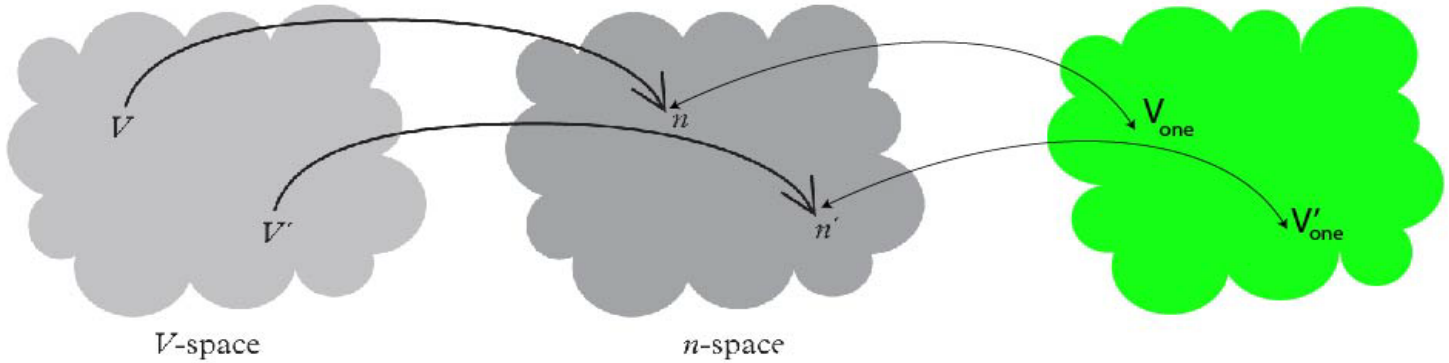


Full electron Hamiltonian

$$H = -\frac{1}{2}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|}$$



Walter Kohns ideas



Hamiltonian of real systems

Hamiltonian of one-electron system

i) A functional exists that couples total energy to ground state electron density
ii) Find best approximation of E[n(r)] and minimize w.r.t. n(r)→ Dirac eller Schrödinger eqn. for one-electron system

Density Functional Theory

$$\hat{H}\Psi_{gs} = E_{gs}\Psi_{gs}$$

$$n_{gs}(\mathbf{r}) = \sum_{i=1}^{N} \int d^3 r_i \mid \Psi_{gs}(\mathbf{r}_1, \mathbf{r}_2, \ldots . \mathbf{r}_N) \mid^2 \delta(\mathbf{r} - \mathbf{r}_i)$$ electron density

$$\hat{H}'\Psi'_{gs} = E'_{gs}\Psi'_{gs}$$

$$E_{gs} = \langle \Psi_{gs} \left| \hat{H} \right| \Psi_{gs} \rangle < \langle \Psi'_{gs} \left| \hat{H} \right| \Psi'_{gs} \rangle$$ variational principle

$$\langle \Psi'_{gs} \left| \hat{H} \right| \Psi'_{gs} \rangle = \langle \Psi'_{gs} \left| \hat{H} + V'_{ext} - V'_{ext} \right| \Psi'_{gs} \rangle = \langle \Psi'_{gs} \left| \hat{H}' + V_{ext} - V'_{ext} \right| \Psi'_{gs} \rangle$$

Density Functional Theory

$$\langle \Psi'_{\mathrm{gs}} \left| \hat{H} \right| \Psi'_{\mathrm{gs}} \rangle = E'_{\mathrm{gs}} + \int n'_{\mathrm{gs}} (V_{\mathrm{ext}} - V'_{\mathrm{ext}})\, d^3 r$$

$$E_{\mathrm{gs}} < E'_{\mathrm{gs}} + \int n'_{\mathrm{gs}} (V_{\mathrm{ext}} - V'_{\mathrm{ext}})\, d^3 r$$

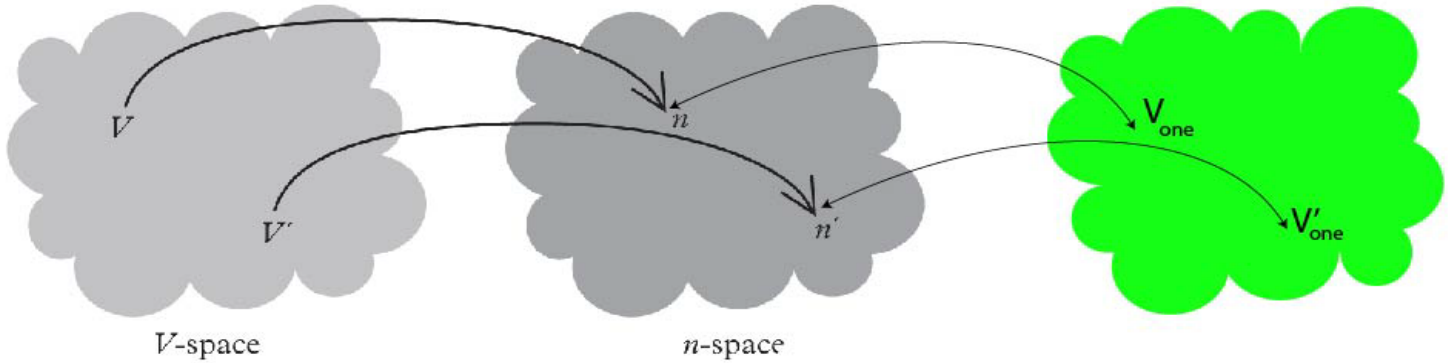
$$E'_{\mathrm{gs}} < E_{\mathrm{gs}} + \int n_{\mathrm{gs}} (V'_{\mathrm{ext}} - V_{\mathrm{ext}})\, d^3 r$$

Assume densities are the same

$$E_{\mathrm{gs}} + E'_{\mathrm{gs}} < E'_{\mathrm{gs}} + E_{\mathrm{gs}} + \int n_{\mathrm{gs}} (V_{\mathrm{ext}} - V'_{\mathrm{ext}})\, d^3 r + \int n_{\mathrm{gs}} (V'_{\mathrm{ext}} - V_{\mathrm{ext}})\, d^3 r,$$

$$E_{\mathrm{gs}} + E'_{\mathrm{gs}} < E'_{\mathrm{gs}} + E_{\mathrm{gs}}$$

Walter Kohns ideas



Hamiltonian of real systems

Hamiltonian of one-electron system

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One-electron Hamiltonian

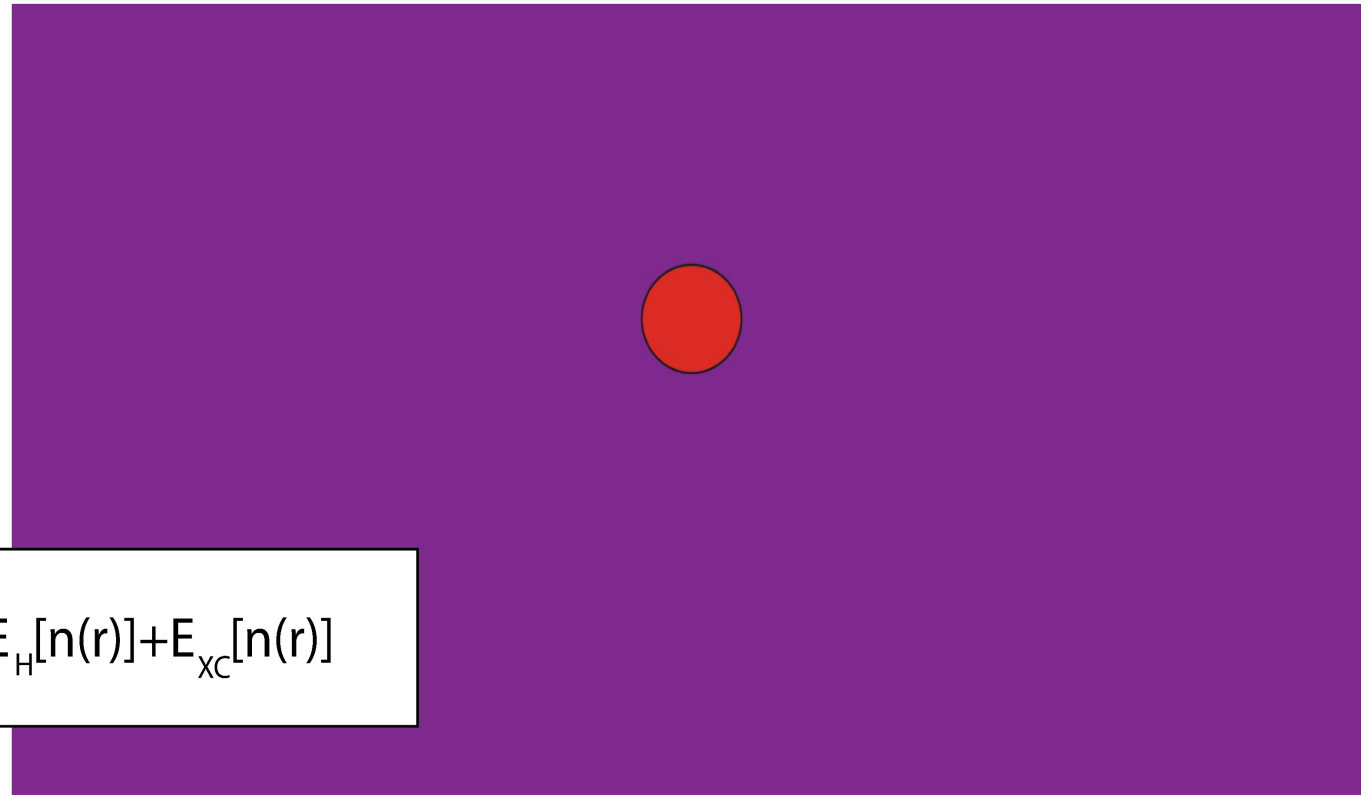
$$(-\frac{\nabla^2}{2} + V_{eff})\psi = \varepsilon\psi$$

$$V_{eff}(n(r))$$

$$n(r) = \sum|\psi(r)|^2$$

dE[n(r)]/dn=0

$$E[n(r)]=E_{kin}[n(r)]+E_{H}[n(r)]+E_{XC}[n(r)]$$



The density functional

$$E[n_{\mathrm{op}}(\mathbf{r})] = T_{\mathrm{op}}[n_{\mathrm{op}}(\mathbf{r})] + \int n_{\mathrm{op}}(\mathbf{r})\, V_{\mathrm{ext}}(\mathbf{r})\, d^3r + \iint \frac{n_{\mathrm{op}}(\mathbf{r}) \cdot n_{\mathrm{op}}(\mathbf{r}')}{\mathbf{r}-\mathbf{r}'}\, d^3r\, d^3r' + E_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})]$$

$$E_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})] = \int \epsilon_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})] n_{\mathrm{op}}(\mathbf{r})\, d^3r$$

$$V_{\mathrm{eff}}(\mathbf{r}) = V_{\mathrm{ext}}(\mathbf{r}) + \int \frac{n_{\mathrm{op}}(\mathbf{r}')}{|\,\mathbf{r}-\mathbf{r}'\,|}\, d^3r' + \mu_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})]$$

$$\mu_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})] = \frac{\partial\{\epsilon_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})] n_{\mathrm{op}}(\mathbf{r})\}}{\partial n_{\mathrm{op}}(\mathbf{r})} = \epsilon_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})] + n_{\mathrm{op}}(\mathbf{r}) \frac{\partial\{\epsilon_{\mathrm{xc}}[n_{\mathrm{op}}(\mathbf{r})]\}}{\partial n_{\mathrm{op}}(\mathbf{r})}$$

For a crystalline material

$$H_{one} = \frac{-\nabla^2}{2} + V_{eff}$$

$$H_{one}\psi(\mathbf{r}) = \epsilon\psi(\mathbf{r})$$

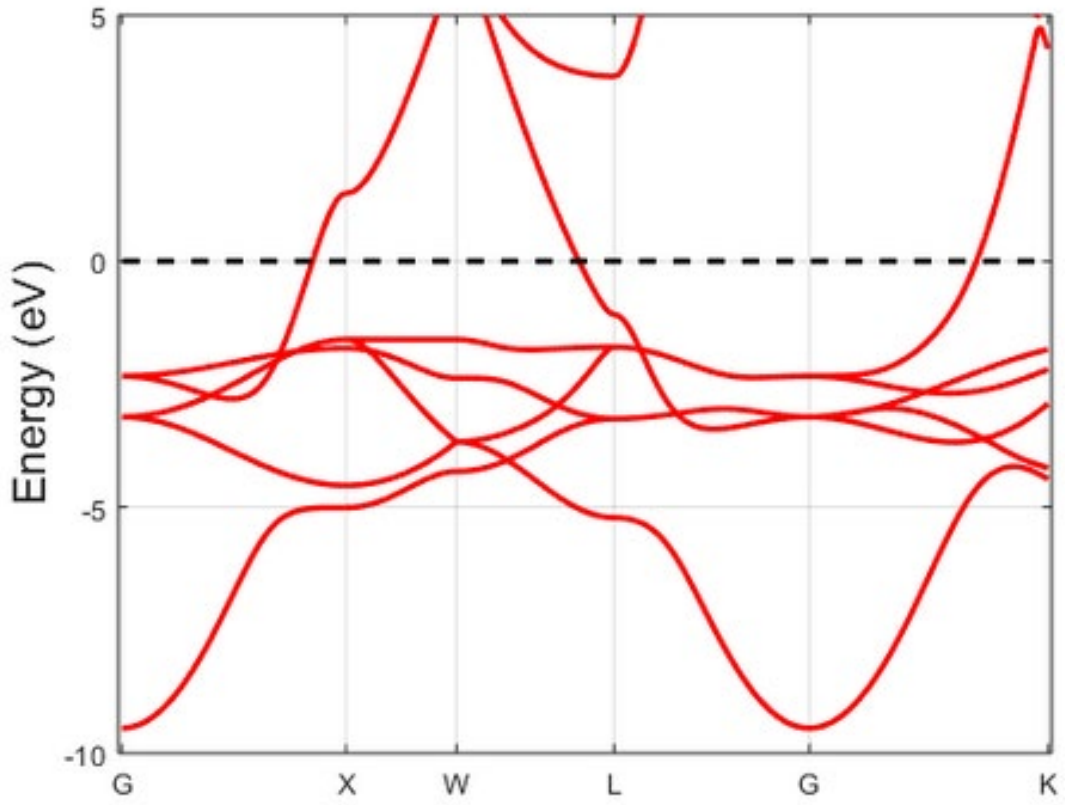
$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$$

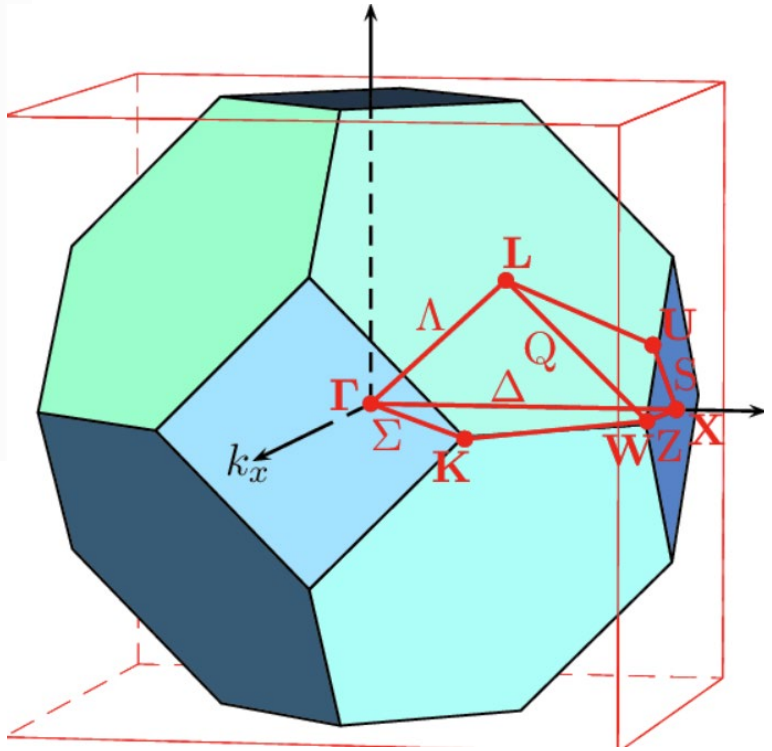
with $u(\mathbf{r})$ having the same periodicity as the lattice

$$\psi(\mathbf{r}) \rightarrow \psi_{\mathbf{k}}(\mathbf{r})$$

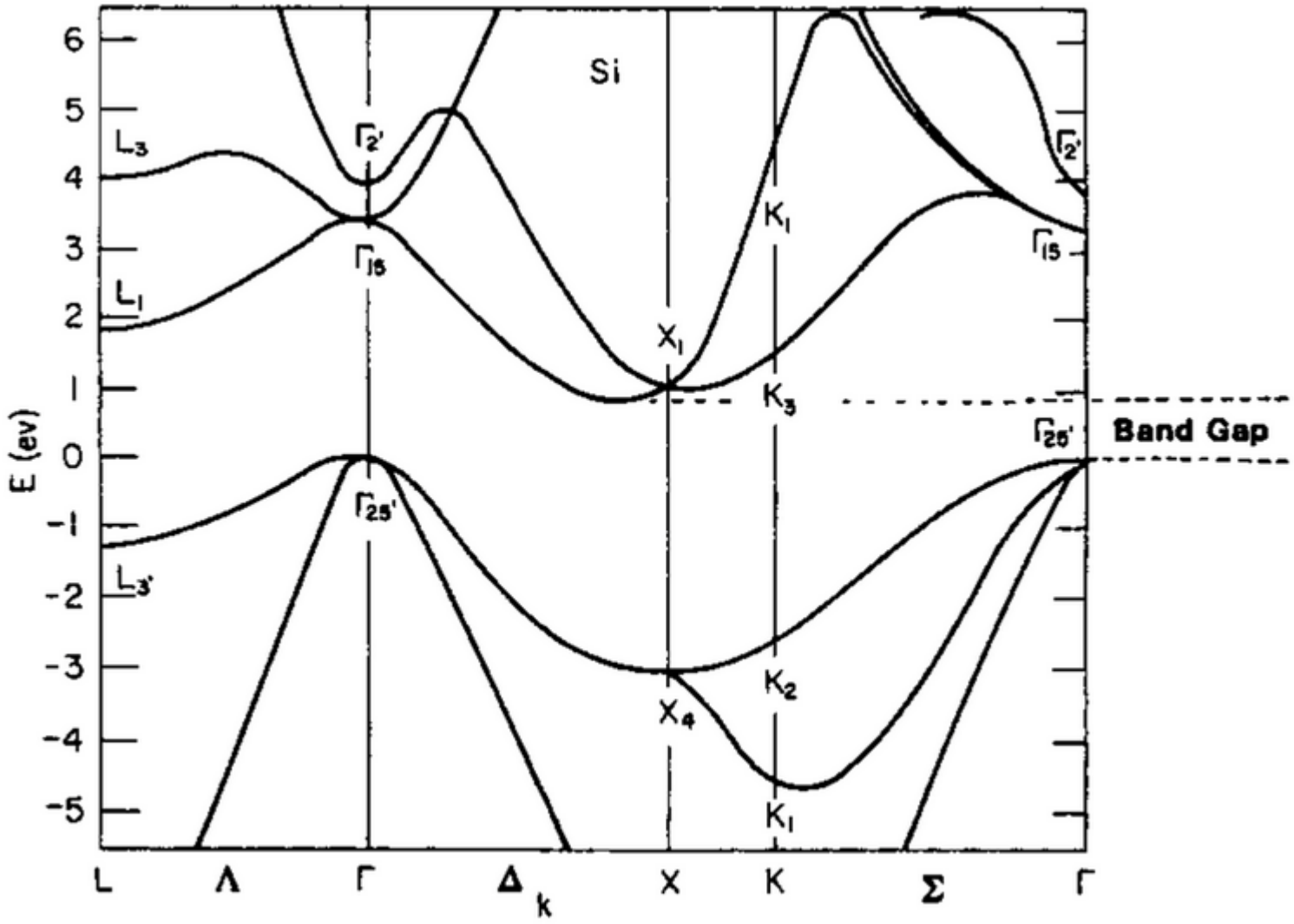
$$\epsilon \rightarrow \epsilon_{\mathbf{k}}$$

Bands of fcc Cu

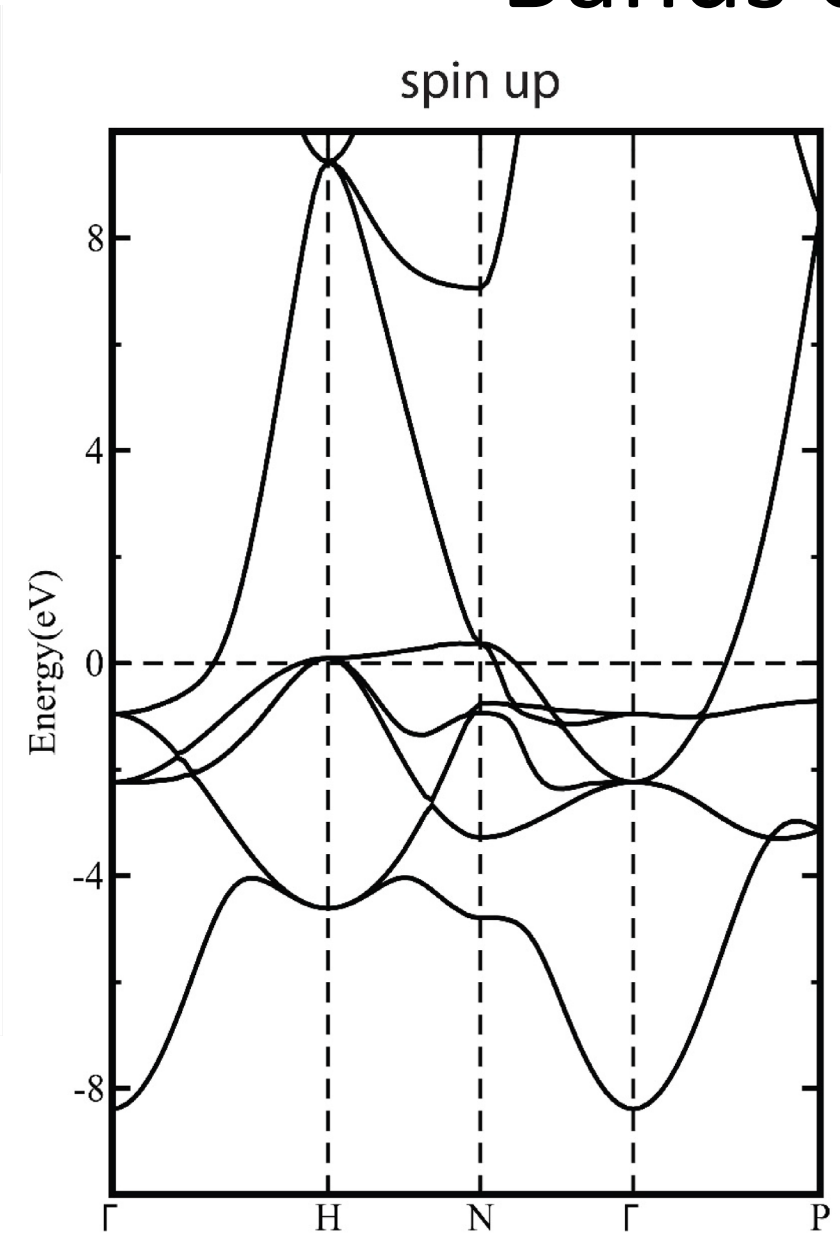


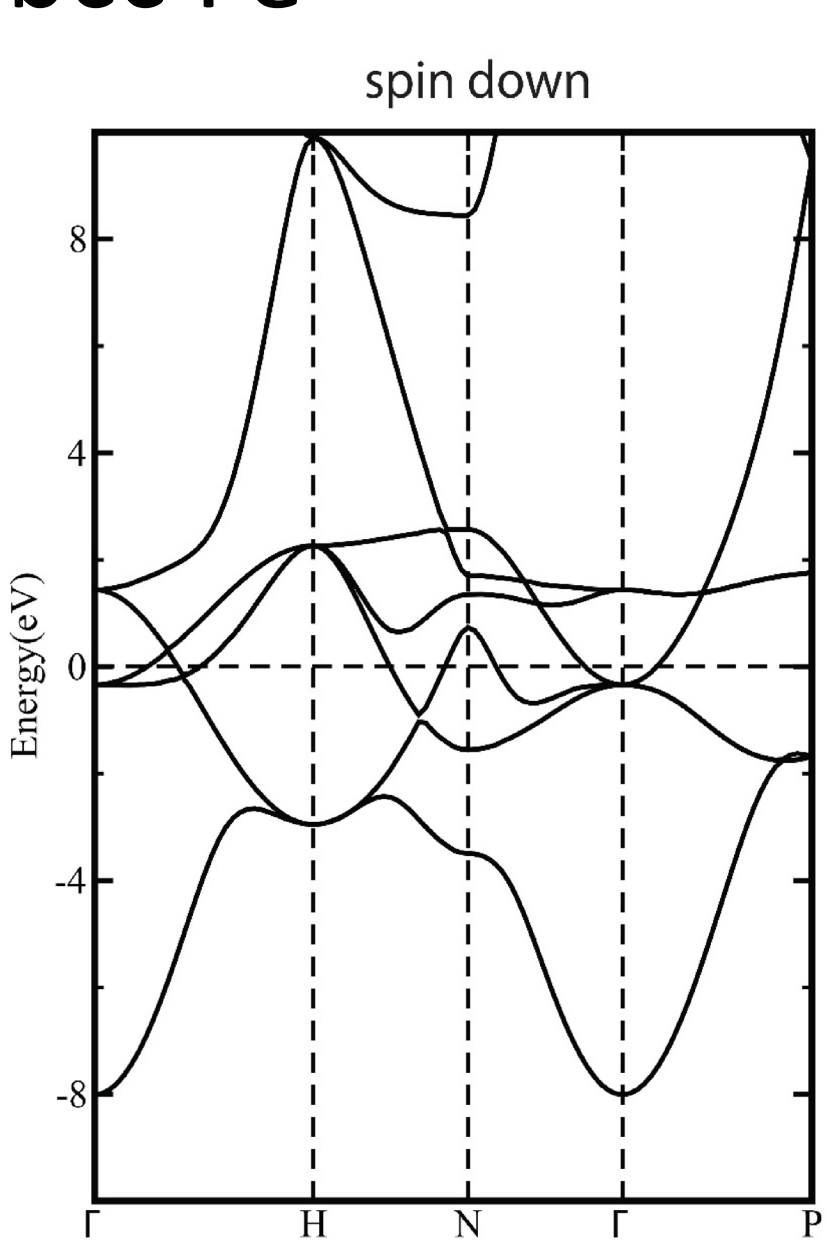


Bands of Si

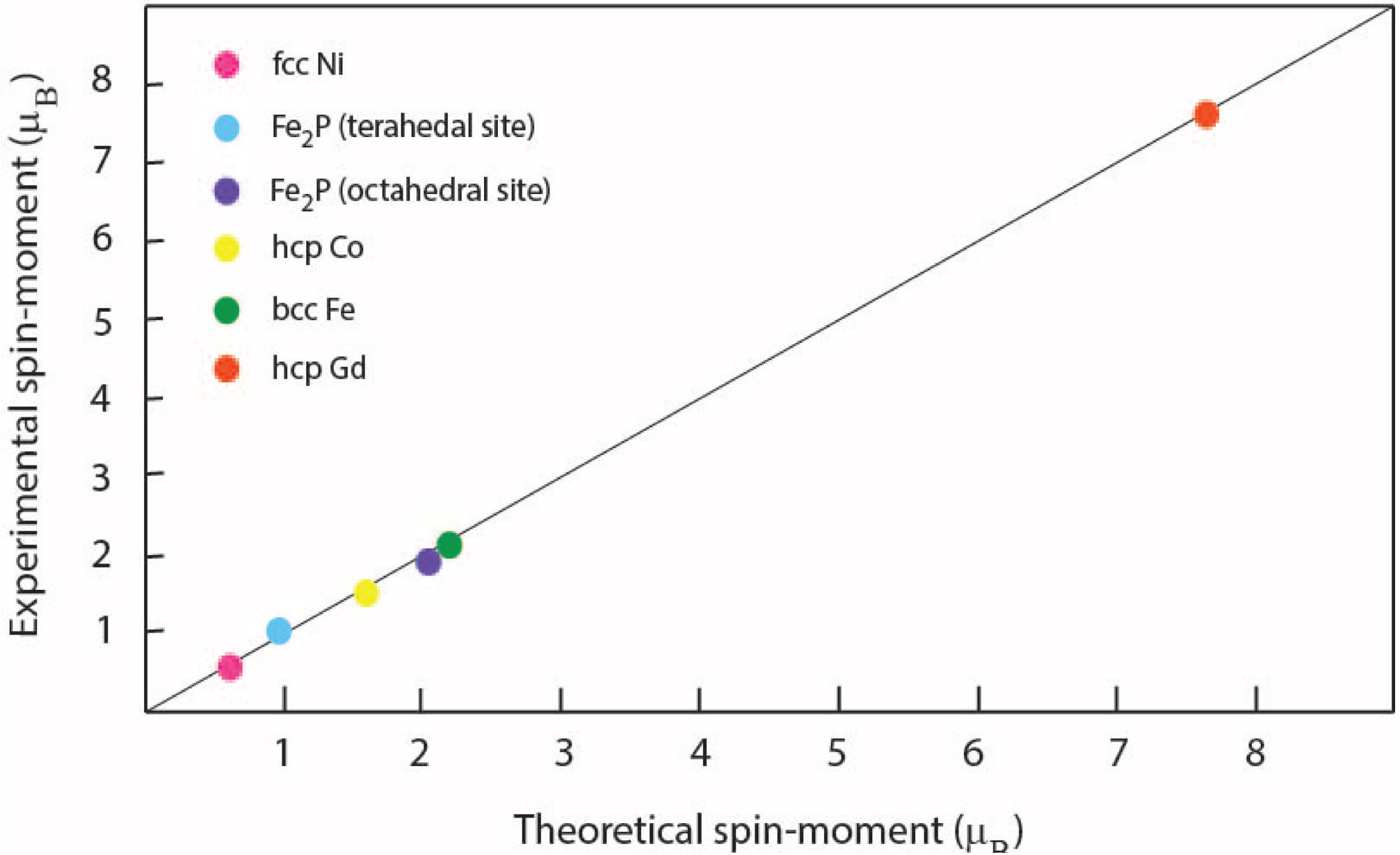

Si
E (ev)
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
L
Λ
Γ
Δ
k
X
K
Σ
Γ
L3
L1
L3'
Γ2'
Γ15
Γ25'
X1
X4
K1
K3
K2
K1
Γ2'
Γ15
Γ25'
Band Gap

Bands of bcc Fe

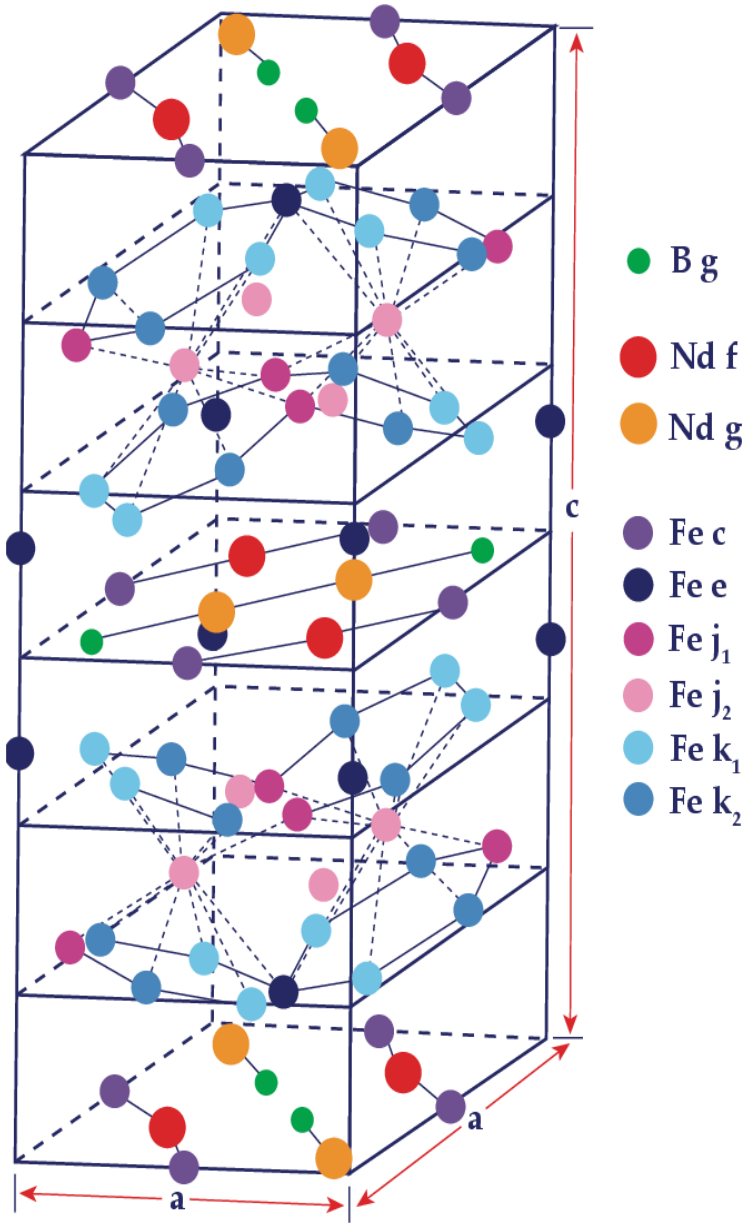




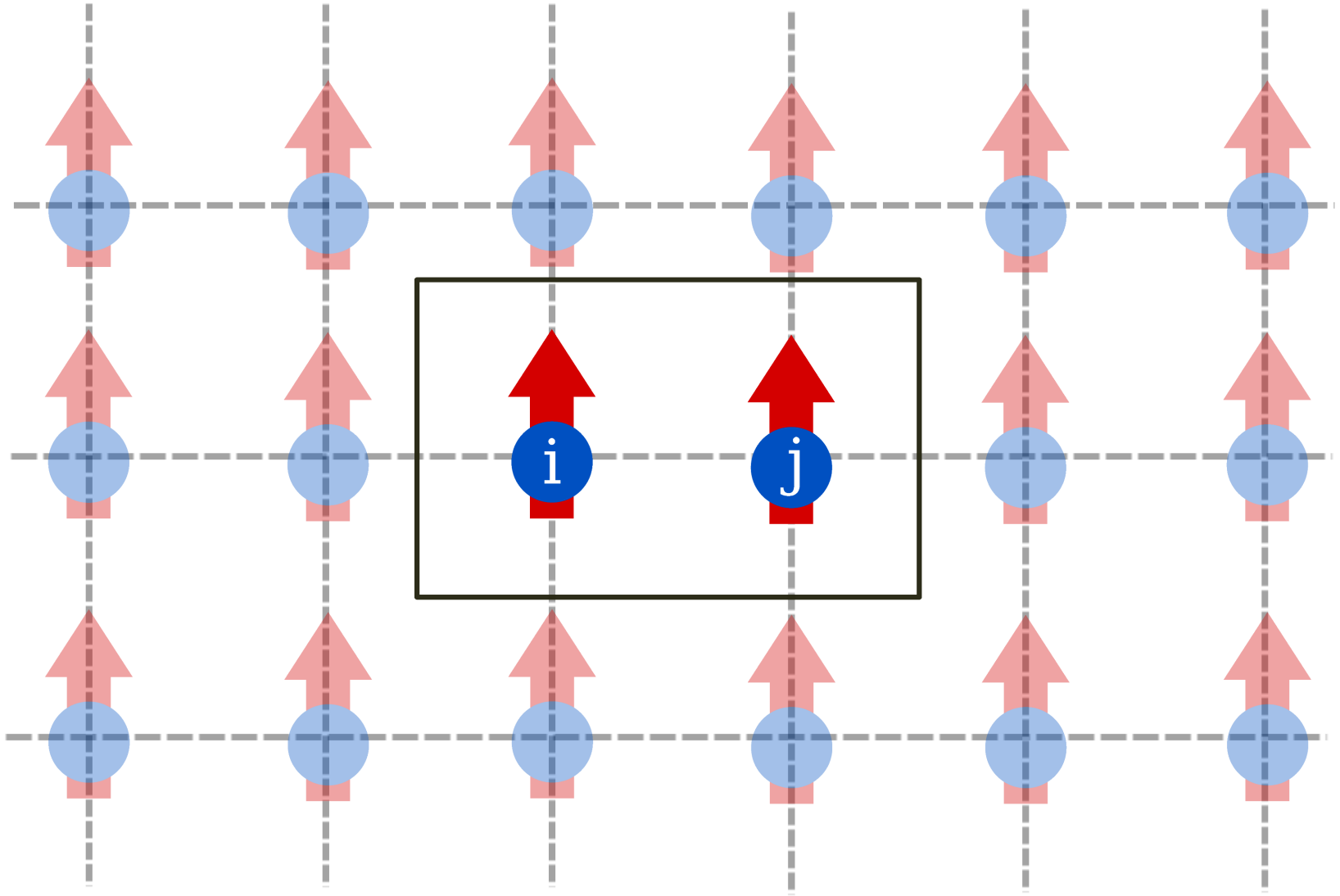
Calculations of magnetic moments



Permanent magnet applications



Inter-atomic exchange



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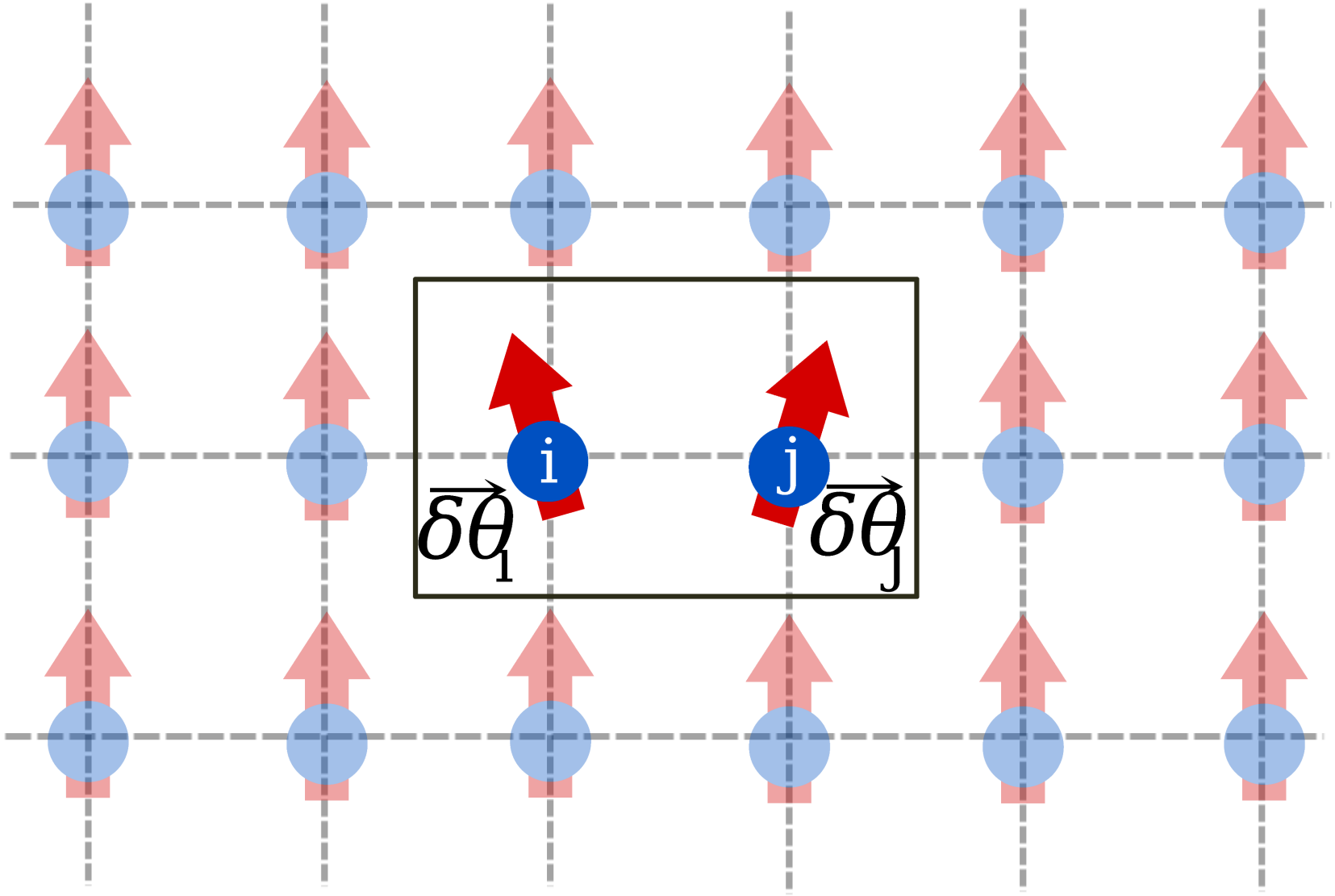


Heisenberg Hamiltonian

$$\Delta E = -J_{ij}\, \mathbf{m}_i\, \mathbf{m}_j$$

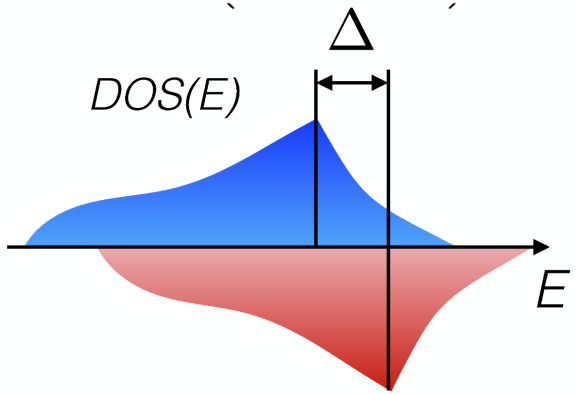
$$H = -J_{ij}\, \mathbf{m}_i\, \mathbf{m}_j$$

Expansion of the Hamiltonian in $\delta\vec{\theta}_i$ and $\delta\vec{\theta}_j$ gives

$$J_{ij} = \frac{-1}{4\pi}\int_{-\infty}^{E_F} \delta\epsilon \mathrm{Tr}_m \left[\Delta_i \cdot G_{ij}^{\uparrow}(\epsilon) \cdot \Delta_j \cdot G_{ij}^{\downarrow}(\epsilon)\right]$$

Local exchange field

$$\Delta_i = (\hat{H}_i^{\uparrow} - \hat{H}_i^{\downarrow})$$



Inter-site Greens function

$$G_{ij}^{\sigma} = \left\langle i \left| \hat{G}(z) \right| j \right\rangle = \left\langle i \left| \frac{1}{z - \hat{H}^{\sigma}} \right| j \right\rangle$$

Lichtenstein *et al* JMMM **67** 65 (1987),
Katsnelson *et al* PRB **61** 8906 (2000),
Kvashnin *et al* PRB **91** 125133 (2015)
A.Szilva et al. RMP 95, 035004 (2023)

hcp Gd

Ferromagnetic metal (T_C=292 K)