The LDA+DMFT approach

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from the many-body problem to DFT
The theory of nearly everything

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} \]

(atomic units: Appendix A)

The underlying laws needed for the description of all chemistry as well as a large part of physics are now entirely known. The only problem that remains is that the exact equations of quantum mechanics are too difficult to be solved. It is therefore necessary to derive approximations that allow us to calculate the properties of complex molecular systems with an acceptable computational effort.

P.M.A. Dirac 1929

Paul Adrien Maurice Dirac
Nobel Prize in Physics 1933
the many-body problem

\[ \hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|r_i - r_{i'}|} - \sum_{i, \alpha} \frac{Z_\alpha}{|r_i - R_\alpha|} - \sum_\alpha \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|R_\alpha - R_{\alpha'}|} \]

(Born-Oppenheimer Ansatz)

\[ \Psi(\{r_i\}, \{R_\alpha\}) = \psi(\{r_i\}; \{R_\alpha\}) \Phi(\{R_\alpha\}) \]

(atomic units: Appendix A)

electronic Hamiltonian

\[ \hat{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|r_i - r_{i'}|} - \sum_{i, \alpha} \frac{Z_\alpha}{|r_i - R_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|R_\alpha - R_{\alpha'}|} \]

\[ = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \]
a single iron atom

26 electrons, 78 arguments, $10^{78}$ values
10 X 10 X 10 grid

$$\Psi_0(r_1, r_1, \ldots, r_{26})$$
independent electrons

exact solution for \( V_{ee}=0 \)

\[
\hat{h}_e^0(r) = -\frac{1}{2} \nabla^2 - \sum_{\alpha} \frac{Z_\alpha}{|r - R_\alpha|} = -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r)
\]

e.g. Bloch states, bands

many-body states

\[
\psi(\{r_i\}; \{R_\alpha\}) = \frac{1}{\sqrt{N_e}} \begin{pmatrix}
\psi_{k_1 \uparrow}(r_1) & \psi_{k_1 \uparrow}(r_2) & \cdots & \psi_{k_1 \uparrow}(r_{N_e}) \\
\psi_{k_1 \downarrow}(r_1) & \psi_{k_1 \downarrow}(r_2) & \cdots & \psi_{k_1 \downarrow}(r_{N_e}) \\
\vdots & \vdots & \vdots & \vdots \\
\psi_{k_{N_e} \uparrow}(r_1) & \psi_{k_{N_e} \uparrow}(r_2) & \cdots & \psi_{k_{N_e} \uparrow}(r_{N_e}) \\
\psi_{k_{N_e} \downarrow}(r_1) & \psi_{k_{N_e} \downarrow}(r_2) & \cdots & \psi_{k_{N_e} \downarrow}(r_{N_e})
\end{pmatrix}
\]

unfortunately Coulomb repulsion is large
density-functional theory

\[ E[n] = F[n] + \int d\mathbf{r} \, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) + E_{nn} = F[n] + V[n] + E_{nn} \]

universal

\[ n(\mathbf{r}) = n_0(\mathbf{r}) = \sum_{\text{occ}} \left| \psi_n(\mathbf{r}) \right|^2 \]

auxiliary independent electrons model

\[ F[n] = T_0[n] + E_H[n] + E_{xc}[n] = T_0[n] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \]

Hartree Coulomb energy
long range and large

\[ \hat{h}_e^0(\mathbf{r}) \psi_n(\mathbf{r}) = \left[ -\frac{1}{2} \nabla^2 + v_R(\mathbf{r}) \right] \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r}) \]

Kohn-Sham equations

\[ v_R(\mathbf{r}) = -\sum_{\alpha} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} + \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n} \]
exchange-correlation energy

\[ E_{xc}[n] = E_{ee}[n] - E_{H}[n] + T_{e}[n] - T_{0}[n] \]

coupling-constant integration \[ V_{ee} \to \lambda V_{ee} \]

(see Lecture Notes, 6.3)

\[ E_{xc}[n] = \int dr \int dr' \frac{n(r)n(r')(\bar{g}(r,r') - 1)}{|r - r'|} \]

\[ \bar{g}(r,r') = \int_{0}^{1} d\lambda g_{\lambda}(r,r') \]

pair-correlation function

\[ n(r,r') = \sum_{\sigma,\sigma'} n(r\sigma, r'\sigma') = n(r')n(r)g_{\lambda}(r,r') \]

joint probability of finding electrons at \( r \) and \( r' \)

short-range and small
from DFT to LDA, GGA,...

\[ E_{xc}[n] = \int dr \int dr' \frac{n(r)n(r')(\bar{g}(r, r') - 1)}{|r - r'|} \]

\[ E_{xc}[n] = \int dr \epsilon_{xc}^{LDA}(n(r))n(r) \]

homogeneous electron gas

Walter Kohn

Nobel Prize in Chemistry (1998)

Kohn-Sham equations

understand and predict properties of solids, molecules, biological systems, geological systems...
strongly correlated materials

example: Mott insulators metallic in LDA, GGA,..
localized electrons

\[ \psi_{nlm}(\rho, \theta, \phi) = R_{nl}(\rho)Y_{l}^{m}(\theta, \phi) \]

\[ R_{nl}(\rho) = \sqrt{\left( \frac{2Z}{n} \right)^{3} \frac{(n - l - 1)!}{2n[(n + l)]^{3}}} e^{-\rho/n} \left( \frac{2\rho}{n} \right)^{l} L_{n-l-1}^{2l+1} \left( \frac{2\rho}{n} \right) \]

(hydrogen-like atom: Appendix B)
an example: KCuF$_3$

K$^+$ Cu$^{2+}$ F$^-$

K 4s$^0$ Cu 3d$^9$ F 2p$^6$

odd number of electrons
LDA band structure

partially filled d-like bands, metallic

LDA, GGA, ...

in reality: insulator, paramagnetic for T>40 K
back to the many-body problem

\[
\hat{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|}
\]

\[
= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}
\]
simple models
from ab-initio to simple model

energy scales

10^9 eV
quarks

10^7 eV
proton

10^5 eV
nucleus

10^3 eV
atom

simple low-energy models

10^{-8} eV
molecule

10^{-6} eV
crystal

energy (eV)

K \ s \ Cu \ s

Cu \ d

F \ p
simple models

real Hamiltonian

\[ \hat{H}_e = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|\mathbf{r}_i - \mathbf{r}_{i'}|} - \sum_{i\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_\alpha Z_{\alpha'}}{|\mathbf{R}_\alpha - \mathbf{R}_{\alpha'}|} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \]

Hubbard model

\[ \hat{H} = -t \sum_{\sigma \langle ii' \rangle} c_i^\dagger \sigma c_{i'}^\sigma + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} = \hat{H}_0 + \hat{U} \]

\( U=0 \) half-filled band \hspace{1cm} \( t=0 \) isolated atoms

metal-insulator transition
dynamical mean-field theory

\[ \hat{H} = -t \sum_{\sigma \langle ii' \rangle} c_{i\sigma}^{\dagger} c_{i'\sigma} + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} = \hat{H}_0 + \hat{U} \]

Hubbard model replaced by a self-consistent one-impurity Anderson model

Anderson model

\[ \hat{H}_{\text{eff}} = \sum_{k\sigma} \varepsilon_k \hat{n}_{k\sigma} + \varepsilon_d \sum_{\sigma} \hat{n}_{d\sigma} + U \hat{n}_{d\uparrow} \hat{n}_{d\downarrow} + \sum_{k\sigma} (V_{kd} c_{k\sigma}^{\dagger} d_{\sigma} + \bar{V}_{kd} d_{\sigma}^{\dagger} c_{k\sigma}) \]

self-consistent parameters

solution: Bethe Ansatz  NRG  ED/Lanczos  QMC
dynamical mean-field theory

\[ G_0^{-1} - G^{-1} = \Sigma(\omega) \]

- dynamics captured
- self-energy local
- exact in infinite dimensions

Metzner and Vollhardt, PRL 62, 324 (1989); Georges and Kotliar, PRB 45, 6479 (1992)
metal-insulator transition

![Bethe lattice](image)

**metallic phase**

\[
\text{Re}\Sigma(\omega+i0^+) = U/2 + (1 - 1/Z) \omega + O(\omega^3), \tag{226}
\]

\[
\text{Im}\Sigma(\omega+i0^+) = -B\omega^2 + O(\omega^4). \tag{227}
\]

The quasiparticle residue \(Z\) defines the renormalized Fermi energy of the problem:

\[
\epsilon^*_F = ZD \tag{228}
\]

This is also the Kondo temperature of the impurity model. Since the self-energy is momentum independent, \(Z\) directly yields the effective mass of quasiparticles (Müller-Hartmann, 1989c):

\[
\frac{m^*}{m} = \frac{1}{Z} = 1 - \frac{\partial}{\partial \omega} \text{Re}\Sigma(\omega+i0^+)\big|_{\omega=0}. \tag{229}
\]

**insulating phase**

\[
\text{Im}\Sigma(\omega+i0^+) = -\pi p_2 \delta(\omega) \quad \text{for} \quad \omega \in [-\Delta_g/2, \Delta_g/2] \tag{235}
\]

and that \(\text{Re}\Sigma\) has the following low-frequency behavior:

\[
\text{Re}\Sigma(\omega+i0^+) - U/2 = \frac{p_2}{\omega} + O(\omega). \tag{236}
\]

G. Koltiar and D. Vollhardt

A. Georges et al. RMP 63, 13 (1996)
and real materials?

\[ \hat{H} = -t \sum_{\sigma \langle ii' \rangle} c_{i\sigma}^\dagger c_{i'\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} = \hat{H}_0 + \hat{U} \]

\[ \begin{align*}
\hat{H}_e &= -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq i'} \frac{1}{|r_i - r_{i'}|} - \sum_{i\alpha} \frac{Z_{\alpha}}{|r_i - R_{\alpha}|} + \frac{1}{2} \sum_{\alpha \neq \alpha'} \frac{Z_{\alpha} Z_{\alpha'}}{|R_{\alpha} - R_{\alpha'}|} \\
&= \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}
\end{align*} \]

many bands
U tensor
crystal-field
non-local U
…….

increasing number of free parameters, difficult to test theory
from DFT to many-body models
realistic models

basis functions

\[ \psi_{in\sigma}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{R}_i \cdot \mathbf{k}} \psi_{n\mathbf{k}\sigma}(\mathbf{r}) \]

localized Wannier functions from LDA (GGA,...)

Hamiltonian

\[ \hat{H}_e = \hat{H}^{\text{LDA}} + \hat{U} - \hat{H}_{\text{DC}} \]

LDA Hamiltonian

\[ \hat{H}^{\text{LDA}} = - \sum_{\sigma} \sum_{in,i'n'} t^{i,i'}_{n,n'} c_{in\sigma}^\dagger c_{i'n'\sigma} \]

\[ t^{i,i'}_{n,n'} = - \int d\mathbf{r} \bar{\psi}_{in\sigma}(\mathbf{r}) \left[ -\frac{1}{2} \nabla^2 + v_R(\mathbf{r}) \right] \psi_{i'n'\sigma}(\mathbf{r}) \]
Coulomb and double counting

\[ \hat{U} = \frac{1}{2} \sum_{ii'jj'} \sum_{\sigma\sigma'} \sum_{nn'pp'} U_{npn'p'}^{ii'jj'} c_{in\sigma}^\dagger c_{jp\sigma'}^\dagger c_{j'p'\sigma'} c_{i'n'\sigma} \]

\[ \hat{U} = \frac{1}{2} U_{npn'p'}^{ii'jj'} = \langle in\sigma jp\sigma' | \hat{U} | i'n'\sigma j'p'\sigma' \rangle \]

\[ = \int dr_1 \int dr_2 \overline{\psi}_{in\sigma}(r_1) \overline{\psi}_{jp\sigma'}(r_2) \frac{1}{|r_1 - r_2|} \psi_{j'p'\sigma'}(r_2) \psi_{i'n'\sigma}(r_1) \]

\[ \hat{H}_{DC} \]

long range Hartree and mean-field exchange-correlation already are well described by LDA (GGA,..)

up to here all electrons are the same....
light and heavy electrons

light (weakly correlated): LDA (GGA,..)

heavy (strongly correlated): U

\[ \hat{H}_e = \hat{H}^{\text{LDA}} + \hat{U}^l - \hat{H}^{\text{DC}}_\text{l} \]

eg. l shell

short-range correction to LDA
local or almost local

for a l shell, the local Coulomb interaction is

\[ \hat{U}^l = \frac{1}{2} \sum_i \sum_{\sigma\sigma'} \sum_{m_\alpha m'_\alpha} \sum_{m_\beta m'_\beta} U_{m_\alpha m_\beta m'_\alpha m'_\beta} c^\dagger_{im_\alpha \sigma} c^\dagger_{im_\beta \sigma'} c_{im'_\beta \sigma'} c_{im'_\alpha \sigma} \]

screening? cRPA, cLDA
Coulomb interaction tensor

\[
\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{k=0}^{\infty} \frac{r_k^k}{r_{k+1}^k} \frac{4\pi}{2k+1} \sum_{q=-k}^{k} Y_q^k(\theta_2, \phi_2) \overline{Y}_q^k(\theta_1, \phi_1)
\]

\[
U_{m_\alpha m_\beta m'_\alpha m'_\beta} = \sum_{k=0}^{2l} a_k(m_\alpha m'_\alpha, m_\beta m'_\beta) F_k
\]

\[
a_k(m_\alpha m'_\alpha, m_\beta m'_\beta) = \frac{4\pi}{2k+1} \sum_{q=-k}^{k} \langle lm_\alpha | Y_q^k | lm'_\alpha \rangle \langle lm_\beta | \overline{Y}_q^k | lm'_\beta \rangle
\]

\[
F_k = \int dr_1 \ r_1^2 \int dr_2 \ r_2^2 \ R_{nl}^2(r_1) \frac{r_k^k}{r_{k+1}^k} R_{nl}^2(r_2).
\]

d electrons: $F_0$, $F_2$, $F_4$

Lecture Notes 3.12 and Appendix B
Coulomb interaction tensor

two-index terms

\[
U_{mm'm'} = U_{m,m'} = \sum_{k=0}^{2l} a_k (mm, m'm') F_k,
\]

\[
U_{mm'm'} = J_{m,m'} = \sum_{k=0}^{2l} a_k (mm', m'm) F_k
\]

direct and exchange integrals

\[
U_{m,m'} = \int dr_1 \int dr_2 \overline{\psi}_{m\sigma}(r_1) \overline{\psi}_{m'\sigma'}(r_2) \frac{1}{|r_1 - r_2|} \psi_{m'\sigma'}(r_2) \psi_{m\sigma}(r_1)
\]

\[
J_{m,m'} = \int dr_1 \int dr_2 \overline{\psi}_{m\sigma}(r_1) \overline{\psi}_{m'\sigma}(r_2) \frac{1}{|r_1 - r_2|} \psi_{m\sigma}(r_2) \psi_{m'\sigma}(r_1)
\]

density-density approximation

\[
\hat{U}^l \sim \frac{1}{2} \sum_{i\sigma} \sum_{mm'} U_{m,m'} \hat{n}_{i\sigma} \hat{n}_{im'\sigma} + \frac{1}{2} \sum_{i\sigma} \sum_{m \neq m'} (U_{m,m'} - J_{m,m'}) \hat{n}_{i\sigma} \hat{n}_{im'\sigma}
\]

Lecture Notes 3.12 and Appendix B
real harmonics

\[ s = y_{00} = Y_0^0 = \sqrt{\frac{1}{4\pi}} \]

\[ p_y = y_{1-1} = \frac{i}{\sqrt{2}} (Y_1^1 + Y_{-1}^1) = \sqrt{\frac{3}{4\pi}} \]

\[ p_z = y_{10} = Y_2^0 = \sqrt{\frac{3}{4\pi}} \]

\[ p_x = y_{11} = \sqrt{\frac{3}{4\pi}} \]

\[ d_{xy} = y_{2-2} = \frac{i}{\sqrt{2}} (Y_2^2 - Y_{-2}^2) = \sqrt{\frac{15}{4\pi}} \]

\[ d_{yz} = y_{2-1} = \frac{i}{\sqrt{2}} (Y_1^2 + Y_{-1}^2) = \sqrt{\frac{15}{4\pi}} \]

\[ d_{3z^2-r^2} = y_{20} = Y_2^0 = \sqrt{\frac{15}{4\pi}} \]

\[ d_{xz} = y_{21} = \sqrt{\frac{15}{4\pi}} \]

\[ d_{x^2-y^2} = y_{22} = \frac{1}{\sqrt{2}} (Y_2^2 + Y_{-2}^2) = \sqrt{\frac{15}{4\pi}} \]

Lecture Notes Appendix B
Coulomb tensor $d$ shell

\[
\begin{align*}
U_{m,m'} & \quad |xy\rangle & |yz\rangle & |3z^2 - r^2\rangle & |xz\rangle & |x^2 - y^2\rangle \\
|xy\rangle & U_0 & U_0 - 2J_1 & U_0 - 2J_2 & U_0 - 2J_1 & U_0 - 2J_3 \\
|yz\rangle & U_0 - 2J_1 & U_0 & U_0 - 2J_4 & U_0 - 2J_1 & U_0 - 2J_1 \\
|3z^2 - r^2\rangle & U_0 - 2J_2 & U_0 - 2J_4 & U_0 & U_0 - 2J_4 & U_0 - 2J_2 \\
xz & U_0 - 2J_1 & U_0 - 2J_1 & U_0 - 2J_4 & U_0 & U_0 - 2J_1 \\
x^2 - y^2 & U_0 - 2J_3 & U_0 - 2J_1 & U_0 - 2J_2 & U_0 - 2J_1 & U_0 \\
\end{align*}
\]

\[
U_{\text{avg}} = \frac{1}{(2l + 1)^2} \sum_{m,m'} U_{m,m'} = F_0
\]

\[
U_{\text{avg}} - J_{\text{avg}} = \frac{1}{2l(2l + 1)} \sum_{m,m'} (U_{m,m'} - J_{m,m'})
\]

\[
J_{\text{avg}} = (F_2 + F_4)/14
\]

atomic $3d$ \quad $F_4/F_2 = 15/23$

\[
U_0 = U_{\text{avg}} + \frac{8}{7} J_{\text{avg}} = U_{\text{avg}} + \frac{8}{5} J_{\text{avg}}
\]

\[
J_1 = \frac{3}{49} F_2 + \frac{20}{9} \frac{1}{49} F_4
\]

\[
J_2 = -2J_{\text{avg}} + 3J_1
\]

\[
J_3 = 6J_{\text{avg}} - 5J_1
\]

\[
J_4 = 4J_{\text{avg}} - 3J_1
\]

Lecture Notes 3.12 and Appendix B
minimal material-specific model
minimal material-specific models

example: 3d⁹ cubic perovskite

K⁺ Cu²⁺ F⁻  

K 4s⁰ Cu 3d⁹ F 2p⁶
cubic crystal-field

$\text{Cu}^{3+} \ 3d^9$

$e_g^3$

$t_{2g}^6$

$\Delta$

"Wannier functions"
tight-binding model

Slater integrals: Appendix B
### Tight-Binding Model

The **tight-binding model** (TB) is a method for describing the electronic structure of materials, particularly in the context of solid-state physics. It simplifies the complex interactions of electrons in a lattice by approximating them as discrete, localized states.

#### Hamiltonian Matrix

The Hamiltonian matrix $H^{\text{TB}}$ in the tight-binding model is given by:

| $H^{\text{TB}}$ | $|k_z\rangle$ | $|k_x\rangle$ | $|k_y\rangle$ | $|k\ 3z^2-r^2\rangle$ | $|k\ x^2-y^2\rangle$ |
|-----------------|---------------|---------------|---------------|----------------|---------------|
| $|k_z\rangle$   | $\epsilon_p$  | 0             | 0             | $-2V_{pd\sigma}s_z$ | 0             |
| $|k_x\rangle$   | 0             | $\epsilon_p$  | 0             | $V_{pd\sigma}s_x$   | $-\sqrt{3}V_{pd\sigma}s_x$ |
| $|k_y\rangle$   | 0             | 0             | $\epsilon_p$  | $V_{pd\sigma}s_y$   | $\sqrt{3}V_{pd\sigma}s_y$ |
| $|k\ 3z^2-r^2\rangle$ | $-2V_{pd\sigma}s_z$ | $V_{pd\sigma}s_x$ | $V_{pd\sigma}s_y$ | $\epsilon_d$   | 0             |
| $|k\ x^2-y^2\rangle$ | 0             | $-\sqrt{3}V_{pd\sigma}s_x$ | $\sqrt{3}V_{pd\sigma}s_y$ | 0             | $\epsilon_d$   |

#### Transition from $(0,0,0)$ to $(0,0,\pi)$

The transition matrix elements are given by:

- $\epsilon_2 = \epsilon_p$
- $\epsilon_3 = \epsilon_p$
- $\epsilon_4 = \epsilon_d$
- $\epsilon_{1,5} = \epsilon_p + \frac{1}{2} \Delta_{pd} \pm \frac{1}{2} \sqrt{\Delta_{pd}^2 + 16V_{pd\sigma}^2 |s_z|^2}$

#### Calculation of $s_\alpha$

$s_\alpha = i e^{-ik_\alpha a/2} \sin k_\alpha a/2$

#### Values

- $\Delta = 5$
- $\Delta_{pd} = 4$
- $\Delta = 2,3$
- $\Delta = 1$
the $e_g$ bands
downfolding

\[
\begin{bmatrix}
H_{pp} & H_{pd} \\
H_{dp} & H_{dd}
\end{bmatrix}
\begin{bmatrix}
|k p\rangle \\
|k d\rangle
\end{bmatrix}
= \varepsilon
\begin{bmatrix}
I_{pp} & 0 \\
0 & I_{dd}
\end{bmatrix}
\begin{bmatrix}
|k p\rangle \\
|k d\rangle
\end{bmatrix}
\]

\[
H_{dd}^{\varepsilon} = H_{dd} - H_{dp}(H_{pp} - \varepsilon I_{pp})^{-1}H_{pd},
\]

| $H_{dd}^{\varepsilon}$ | $|k \ 3z^2 - r^2\rangle_\varepsilon$ | $|k \ x^2 - y^2\rangle_\varepsilon$ |
|----------------------|-----------------|-----------------|
| $|k \ 3z^2 - r^2\rangle_\varepsilon$ | $\varepsilon'_d - 2t\varepsilon\left[\frac{1}{4}(\cos k_x a + \cos k_y a) - \cos k_z a\right]$ | $2t\varepsilon\left[\frac{\sqrt{3}}{4}(\cos k_x a - \cos k_y a)\right]$ |
| $|k \ x^2 - y^2\rangle_\varepsilon$ | $2t\varepsilon\left[\frac{\sqrt{3}}{4}(\cos k_x a - \cos k_y a)\right]$ | $\varepsilon'_d - 2t\varepsilon\left[\frac{3}{4}(\cos k_x a + \cos k_y a)\right]$ |
ab-initio downfolding

NMTO Wannier functions

LaTiO$_3$

$E = 0$ meV

$E = 190$ meV

$E = 205$ meV

YTiO$_3$

$E = 0$ meV

$E = 200$ meV

$E = 330$ meV
model for \( e_g \) (or \( t_{2g} \)) systems

\[
H = - \sum_{m,m',i,i',\sigma} t_{mm',i,i',\sigma} \hat{c}_{im\sigma}' c_{im'\sigma}' + U \sum_{i m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} \\
+ \frac{1}{2} \sum_{i \sigma \sigma'} \sum_{m \neq m'} (U - 2J - J \delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \\
- J \sum_{i m \neq m'} \left[ \hat{c}_{im\uparrow} \hat{c}_{im\downarrow} c_{im'\uparrow} c_{im'\downarrow} + \hat{c}_{im\uparrow} c_{im\downarrow} \hat{c}_{im'\uparrow} \hat{c}_{im'\downarrow} \right] - \hat{H}_{DC}^{e_g}
\]

pair-hopping \hspace{1cm} \text{spin-flip}

\[
U = U_0 \hspace{2cm} J = J_2 \text{ or } J_1
\]
methods of solution: LDA+U
Hartree-Fock and LDA+$U$

\[
\hat{H}^\text{LDA} + \hat{U}^l - \hat{H}^l_{\text{DC}} = \hat{H}^\text{LDA} + \frac{1}{2}U \sum_{im\sigma} \sum_{m'\sigma'} \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} - \frac{1}{2}U \sum_{im\sigma} \sum_{m'\sigma'} \langle \hat{n}_{im\sigma} \rangle \langle \hat{n}_{im'\sigma'} \rangle
\]

\text{Coulomb energy} \quad \text{Hartree part}

\[
\hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \rightarrow \langle \hat{n}_{im\sigma} \rangle \langle \hat{n}_{im'\sigma'} \rangle + \hat{n}_{im\sigma} \langle \hat{n}_{im'\sigma'} \rangle - \langle \hat{n}_{im\sigma} \rangle \langle \hat{n}_{im'\sigma'} \rangle
\]

\text{mean-field (Hartree-like)}

\[
H = \hat{H}^\text{LDA} + \sum_{im\sigma} t^\sigma_m \hat{n}_{im\sigma}, \quad \text{with} \quad t^\sigma_m = U \left( \frac{1}{2} - \langle \hat{n}_{im\sigma} \rangle \right)
\]

\[
E_{\text{LDA}+U}[n] = E_{\text{LDA}}[n] + \sum_i \left[ \frac{1}{2}U \sum_{m\sigma \neq m'\sigma'} \langle \hat{n}_{im\sigma} \rangle \langle \hat{n}_{im'\sigma'} \rangle - E_{\text{DC}} \right]
\]

\[
\varepsilon_{im\sigma}^{\text{LDA}+U} = \frac{\partial E_{\text{LDA}+U}}{\partial \langle \hat{n}_{im\sigma} \rangle} = \varepsilon_{im\sigma}^{\text{LDA}} + U \left( \frac{1}{2} - \langle \hat{n}_{im\sigma} \rangle \right)
\]

\text{charge self-consistent}
\[ E_{\text{LDA+U}}[n] = E_{\text{LDA}}[n] + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m'''} U_{mm''m'''} \langle \hat{n}_{iim'}^\sigma \rangle \langle \hat{n}_{iim''m'''}^\sigma \rangle \]

\[ + \frac{1}{2} \sum_{i\sigma} \sum_{mm'm''m'''} \left[ U_{mm''m'''} - U_{mm''m''m'} \right] \langle \hat{n}_{iim'}^\sigma \rangle \langle \hat{n}_{iim''m'''}^\sigma \rangle - E_{\text{DC}} \]

\[ E_{\text{DC}} = \frac{1}{2} U_{\text{avg}} N_l (N_l - 1) - \frac{1}{2} J_{\text{avg}} \sum_{\sigma} N_{\sigma}^l (N_{\sigma}^l - 1) \]

\[ \hat{H} = \hat{H}^{\text{LDA}} + \sum_{imm'\sigma} t_{mm'}^\sigma c_{im\sigma}^\dagger c_{im'\sigma} \]

\[ t_{mm'}^\sigma = \sum_{i\sigma} \sum_{m''m'''} U_{mm''m'''} \langle \hat{n}_{iim''m'''}^\sigma \rangle + \left[ U_{mm''m''m'} - U_{mm''m'''} \right] \langle \hat{n}_{iim''m'''}^\sigma \rangle \]

\[ - \left[ U_{\text{avg}} (N_l^l - \frac{1}{2}) - J_{\text{avg}} (N_{\sigma}^l - \frac{1}{2}) \right] \delta_{m,m'} \]
LDA+\(U\) for a \(e_g\) model

\[
H = - \sum_{m,m',i,i',\sigma} t_{m,m'}^{i,i'} c_{im\sigma}^\dagger c_{im'\sigma} + U \sum_{i,m} \hat{n}_{im\uparrow} \hat{n}_{im\downarrow} \\
+ \frac{1}{2} \sum_{i\sigma\sigma'} \sum_{m \neq m'} (U - 2J - J\delta_{\sigma,\sigma'}) \hat{n}_{im\sigma} \hat{n}_{im'\sigma'} \\
- J \sum_{i,m \neq m'} \left[ c_{im\uparrow}^\dagger c_{im\downarrow}^\dagger c_{im'\downarrow} c_{im'\uparrow} + c_{im\uparrow}^\dagger c_{im\downarrow}^\dagger c_{im'\downarrow} c_{im'\uparrow} \right] - \hat{H}^{e_g}_{DC}
\]

\[
\Sigma^{i\sigma} = \begin{bmatrix}
\Sigma_{\alpha,\alpha}^{i\sigma} & \Sigma_{\alpha,\beta}^{i\sigma} \\
\Sigma_{\beta,\alpha}^{i\sigma} & \Sigma_{\beta,\beta}^{i\sigma}
\end{bmatrix}
\]

\[
\Sigma^{i\sigma} = U \begin{bmatrix}
\frac{1}{2} - \langle \hat{n}_{i\alpha\alpha} \rangle & -\langle \hat{n}_{i\beta\alpha} \rangle \\
-\langle \hat{n}_{i\alpha\beta} \rangle & \frac{1}{2} - \langle \hat{n}_{i\beta\beta} \rangle
\end{bmatrix}
\]

at site \(i\)

other sites: symmetries!

only correlated electrons: double counting incorporated in chemical potential

\[
E_{DC} = \frac{1}{2} U_{avg} N_l^t(N^l - 1) - \frac{1}{2} J_{avg} \sum_{\sigma} N_{\sigma}^t(N_{\sigma}^l - 1)
\]
### KCuF₃

#### Hole Orbital Order

| \( \Sigma/U \) | \( |\alpha\sigma\rangle_{1u} \) | \( |\beta\sigma\rangle_{1u} \) | \( |\alpha\sigma\rangle_{2u} \) | \( |\beta\sigma\rangle_{2u} \) | \( |\alpha\sigma\rangle_{1d} \) | \( |\beta\sigma\rangle_{1d} \) | \( |\alpha\sigma\rangle_{2d} \) | \( |\beta\sigma\rangle_{2d} \) |
|---|---|---|---|---|---|---|---|---|
| \( |\alpha\sigma\rangle_{1u} \) | \(-2\delta_{\sigma,\downarrow} - \delta_{\sigma,\uparrow}\) | \(\frac{\sqrt{3}\delta_{\sigma,\uparrow}}{4}\) | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |\beta\sigma\rangle_{1u} \) | \(\frac{\sqrt{3}\delta_{\sigma,\uparrow}}{4}\) | \(-2\delta_{\sigma,\downarrow} + \delta_{\sigma,\uparrow}\) | 0 | 0 | 0 | 0 | 0 | 0 |
| \( |\alpha\sigma\rangle_{2u} \) | 0 | 0 | \(-2\delta_{\sigma,\downarrow} - \delta_{\sigma,\uparrow}\) | \(-\frac{\sqrt{3}\delta_{\sigma,\uparrow}}{4}\) | 0 | 0 | 0 | 0 |
| \( |\beta\sigma\rangle_{2u} \) | 0 | 0 | \(-\frac{\sqrt{3}\delta_{\sigma,\uparrow}}{4}\) | \(-2\delta_{\sigma,\downarrow} + \delta_{\sigma,\uparrow}\) | 0 | 0 | 0 | 0 |
| \( |\alpha\sigma\rangle_{1d} \) | 0 | 0 | 0 | 0 | \(-2\delta_{\sigma,\downarrow} - \delta_{\sigma,\uparrow}\) | \(\frac{\sqrt{3}\delta_{\sigma,\downarrow}}{4}\) | 0 | 0 |
| \( |\beta\sigma\rangle_{1d} \) | 0 | 0 | 0 | 0 | \(\frac{\sqrt{3}\delta_{\sigma,\downarrow}}{4}\) | \(-2\delta_{\sigma,\downarrow} + \delta_{\sigma,\uparrow}\) | 0 | 0 |
| \( |\alpha\sigma\rangle_{2d} \) | 0 | 0 | 0 | 0 | 0 | 0 | \(-2\delta_{\sigma,\downarrow} - \delta_{\sigma,\uparrow}\) | \(-\frac{\sqrt{3}\delta_{\sigma,\downarrow}}{4}\) |
| \( |\beta\sigma\rangle_{2d} \) | 0 | 0 | 0 | 0 | 0 | 0 | \(-\frac{\sqrt{3}\delta_{\sigma,\downarrow}}{4}\) | \(-2\delta_{\sigma,\downarrow} + \delta_{\sigma,\uparrow}\) |

#### Spin Order
LDA+\(U\) bands

LDA+\(U\) e\(_g\) bands
(no charge self-consistency)

Lda e\(_g\) bands
supercell 4 formula units

infinite lifetime and static self-energy
AFM linear Hubbard chain

\[ \hat{H} = -t \sum_{\sigma \langle ii' \rangle} c_{i\sigma}^\dagger c_{i'\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} = \hat{H}_0 + \hat{U} \]
methods of solution: LDA+DMFT
KCuF$_3$ paramagnetic massive downfolding to e$_g$

\[ H^\varepsilon_{dd} \]

<table>
<thead>
<tr>
<th>k $3z^2 - r^2$ $\varepsilon$</th>
<th>( \varepsilon'_d - 2t\varepsilon [\frac{1}{4}(\cos k_xa + \cos k_ya) - \cos k_z a] )</th>
<th>( 2t\varepsilon [\frac{\sqrt{3}}{4}(\cos k_xa - \cos k_ya)] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>k $x^2 - y^2$ $\varepsilon$</td>
<td>( 2t\varepsilon [\frac{\sqrt{3}}{4}(\cos k_xa - \cos k_ya)] )</td>
<td>( \varepsilon'_d - 2t\varepsilon [\frac{3}{4}(\cos k_xa + \cos k_ya)] )</td>
</tr>
</tbody>
</table>

\[ e_g H^{LDA} \]

2 equivalent sites

\[ \Sigma^1 \]

| $|\alpha\sigma\rangle_1$ | $\Sigma^1_{\alpha\alpha}$ | $\Sigma^1_{\alpha\beta}$ | $|\alpha\sigma\rangle_2$ | $|\beta\sigma\rangle_2$ |
|----------------------|----------------------|----------------------|----------------------|----------------------|
| $|\alpha\sigma\rangle_1$ | 0 | $\Sigma^1_{\alpha\beta}$ | 0 | 0 |
| $|\beta\sigma\rangle_1$ | $\Sigma^1_{\beta\alpha}$ | 0 | 0 | 0 |
| $|\alpha\sigma\rangle_2$ | 0 | 0 | $\Sigma^1_{\alpha\alpha}$ | $-\Sigma^1_{\alpha\beta}$ |
| $|\beta\sigma\rangle_2$ | 0 | 0 | $-\Sigma^1_{\beta\alpha}$ | $\Sigma^1_{\beta\beta}$ |
paramagnetic LDA+DMFT

\[ G_{i_c m \sigma, i'_c m' \sigma}(\omega) = \frac{1}{N_k} \sum_{\mathbf{k}} \left( \left[ \omega + \mu I - \hat{H}_{\mathbf{k}}^{\text{LDA}} - \Sigma^l(\omega) + \hat{H}_{\text{DC}} \right]^{-1} \right)_{i_c m \sigma, i'_c m' \sigma} \]

- **lattice green-function matrix**

- **symmetries**

- **local green-function matrix**

- **bath green-function matrix**

- **quantum impurity solver**

- **self-energy**

\[ \Sigma(\omega) = G^{-1}(\omega) - G^{-1}(\omega) \]
quantum impurity solvers

QMC

$G(\omega) = \int d\tilde{k} \left( \omega + \mu - H(\tilde{k}) - \Sigma(\omega) \right)^{-1} G^{-1}(\omega) \Sigma(c(\omega)) + G^{-1}(\omega)$

$\Sigma(c(\omega)) = G^{-1}(\omega) - G^{-1}(\omega) c(\omega)$

warmup

sampling
KCuF$_3$
extensions

- ferro and anti ferro magnetism
- charge self-consistency
- cluster DMFT
- GW+DMFT
- ....
example: orbital order in KCuF₃
orbital order in KCuF$_3$

problem to solve: why a co-operative Jahn-Teller distortion?
Electronic reconstruction at an interface between a Mott insulator and a band insulator

Satoshi Okamoto & Andrew J. Millis

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Surface science is an important and well-established branch of materials science involving the study of changes in material...
Crystal Distortion in Magnetic Compounds

JUNJIRO KANAMORI*
Institute for the Study of Metals, University of Chicago, Chicago 37, Illinois

The crystal distortion which arises from the Jahn-Teller effect is discussed in several examples. In the case of compounds containing Cu$^{2+}$ or Mn$^{3+}$ at octahedral sites, the lowest orbital level of these ions is doubly degenerate in the undistorted structure, and there is no spin-orbit coupling in this level. It is shown that, introducing a fictitious spin to specify the degenerate orbital states, we can discuss the problem by analogy with the magnetic problems. The “ferromagnetic” and “antiferromagnetic” distortions are discussed in detail. The transition from the distorted to the undistorted structure is of the first kind for the former and of the second kind for the latter. Higher approximations are discussed briefly. In compounds like FeO, CoO, and CuCr$_2$O$_4$, the lowest orbital level is triply degenerate, and the spin-orbit coupling is present in this level. In this case the distortion is dependent on the magnitude of the spin-orbit coupling relative to the strength of the Jahn-Teller effect term. The distortion at absolute zero temperature and its temperature dependence are discussed.

\[ H_1 = -g \sqrt{C} (\sigma_z Q_x + \sigma_x Q_z) \]

\[
\begin{align*}
E_0 + \Delta/2 & \quad \Delta \\
E_0 - \Delta/2 & \quad \theta
\end{align*}
\]

\[ |\theta\rangle = \sin \frac{\theta}{2} |3z^2 - 1\rangle + \cos \frac{\theta}{2} |x^2 - y^2\rangle \]
do we need a large crystal-field?

Mott Transition and Suppression of Orbital Fluctuations in Orthorhombic 3d¹ Perovskites

E. Pavarini,¹ S. Biermann,² A. Poteryaev,³ A. I. Lichtenstein,³ A. Georges,² and O. K. Andersen⁴

LaTiO₃

YTiO₃

t_{2g}¹

LDA+DMFT 770 K

Δ=200-300 meV

a 100 meV crystal-field could be enough
Crystal structure and magnetic properties of substances with orbital degeneracy

K. I. Kugel' and D. I. Khomskii
P. N. Lebedev Physics Institute
(Submitted November 13, 1972)
Zh. Eksp. Teor. Fiz. 64, 1429-1439 (April 1973)

Exchange interaction in magnetic substances containing ions with orbital degeneracy is considered. It is shown that, among with spin ordering, superexchange also results in cooperative ordering of Jahn-Teller ion orbitals, which, generally speaking, occurs at a higher temperature and is accompanied by distortion of the lattice (which is a secondary effect here). Concrete studies are performed for substances with a perovskite structure (KCuF₃, LaMnO₃, MnF₃). The effective spin Hamiltonian is obtained for these substances and the properties of the ground state are investigated. The orbital and magnetic structures obtained in this way without taking into account interaction with the lattice are in accord with the structures observed experimentally. The approach employed also permits one to explain the strong anisotropy of the magnetic properties of these compounds and to obtain a reasonable estimate for the critical temperatures.

\[
H = - \sum_{imjm'\sigma} t_{imjm'} c_{im\sigma}^\dagger c_{jm'\sigma} + U \sum_{im\sigma jm'\sigma'} n_{im\sigma} n_{jm'\sigma'}
\]

perturbation t/U \[\rightarrow\] super-exchange Hamiltonian

\[
H = J_{ss} S_i \cdot S_j + J_{oo} Q_i Q_j + J_{so} Q_i S_j
\]
Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators

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(Received 15 May 1995)

The situation changes drastically if we allow for orbital polarization. Because $U$ exceeds the bandwidth, the orbital sector is already strongly polarized (as are the spins) before the lattice is allowed to react. Overlooking some unimportant details concerning the coherence of the intermediate states, the well-known rule that electronic MFT in strong coupling maps onto the classical “spin” problem holds also in this case. In other words, we find the quadrupolar orbital-ferromagnetic spin phase to be most stable (for the same reasons as Kugel and Khomskii\(^a\)). Obviously the cubic lattice is unstable in the presence of this orbital order parameter. In fact, despite large-scale changes in the electronic system the deformation is modest, indicating a rather weak electron-phonon coupling.

KK-like mechanism!
Structural Relaxation due to Electronic Correlations in the Paramagnetic Insulator KCuF₃

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(Received 7 April 2008; published 29 August 2008)
two scenarios

• super-exchange
  • why $T_N$ (40K) much smaller than $T_{OO}$ (800-1400 K) ?

• electron-phonon coupling
  • what about LDA+U, HF, GGA+DMFT results?

Our approach: single out Kugel-Khomskii mechanism using LDA+DMFT
KCuF$_3$

ideal structures
\[ \delta = \frac{(l-s)}{(l+s)/2} \] Jahn-Teller distortion
\[ \lambda = \frac{c}{a}/2 \text{ tetragonal distortion} \]

LDA bands
NMTO-based downfolding method
ab-initio model for e$_g$ bands
Mechanism for orbital ordering in KCuF$_3$

orbital polarization $p=n_1-n_2$ for decreasing e-ph coupling $g$

orbital ordering R structure
conclusions

KCuF$_3$ and LaMnO$_3$

what is the mechanism of orbital-order?

$T_{KK}$ remarkably large

but el-ph coupling essential

PRL 101, 266405 (2008); PRL 104, 086402 (2010); to be published
final remarks
Finding a good approximation is virtually impossible. By the nature of the Kohn-Sham approach, density-functional calculations are largely confined to materials for which the picture of individual electrons is adequate, and Fermi-liquid theory, which models weakly interacting quasi-particles, applies. There is, however, a remarkable variety of strongly correlated materials for which this standard model of electronic structure theory breaks down. The hallmark of these materials is that some of their electrons are neither perfectly localized, nor fully itinerant. These electrons can no longer be considered individually. The resulting behavior presents some of the deepest intellectual challenges in physics. At the same time, interest in strongly correlated materials is fueled by the astounding possibilities for technological applications. Prominent examples are the transition-metal oxides, e.g., the high-temperature superconductors, and molecular crystals [13].
The effectiveness of this message may be indicated by the fact that I heard it quoted recently by a leader in the field of materials science, who urged the participants at a meeting dedicated to "fundamental problems in condensed matter physics" to accept that there were few or no such problems and that nothing was left but extensive science, which he seemed to equate with device engineering.

The main fallacy in this kind of thinking is that the reductionist hypothesis does not by any means imply a "constructionist" one: The ability to reduce everything to simple fundamental laws does not imply the ability to start from those laws and reconstruct the universe. In fact, the more the ele-