Introduction To The Elk Code

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What is Elk?

- Elk is an all-electron (L)APW+l.o. code
- In development for about 13 years (originally the EXCITING code)
- Simple as possible ($\sim 55k$ lines of Fortran 90)
- Aims to be trustworthy
- Aims to be feature-complete
- Aims to be fully documented
- Released under the GPL
- Website: http://elk.sourceforge.net/

Contributors

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D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic Publishers, Boston, 1994)

Features

Basic aim of Elk is to solve the Kohn-Sham equations for external fields

External field	Conjugate field
$V_{\text{ext}}(\mathbf{r})$	$\rho(\mathbf{r})$
$\mathbf{B}_{\text{ext}}(\mathbf{r})$	$\mathbf{m}(\mathbf{r})$
$\mathbf{E}(\mathbf{r})$ $(= -\nabla V(\mathbf{r}))$	$\rho(\mathbf{r})$
$\mathbf{A}$	$\mathbf{j}$

Features

- Kohn-Sham equations solved in two-step process:

  First-variational step: scalar potential and $\mathbf{E}$ only

  $$\hat{H} = \hat{T}_s + \hat{V}_{\text{ext}} + \mathbf{E} \cdot \hat{\mathbf{r}} + \hat{V}_{\text{xc}}$$

  and solve $\hat{H}\phi_i = \epsilon_i \phi_i$

  Second-variational step: add magnetic fields, spin-orbit coupling and $\mathbf{A}$ field

  $$H_{ij} = \varepsilon_i \delta_{ij} + \langle \phi_i | \boldsymbol{\sigma} \cdot (\hat{\mathbf{B}}_{\text{ext}} + \hat{\mathbf{B}}_{\text{xc}}) + \boldsymbol{\sigma} \cdot \hat{L} + \mathbf{A} \cdot \hat{\nabla} | \phi_j \rangle$$

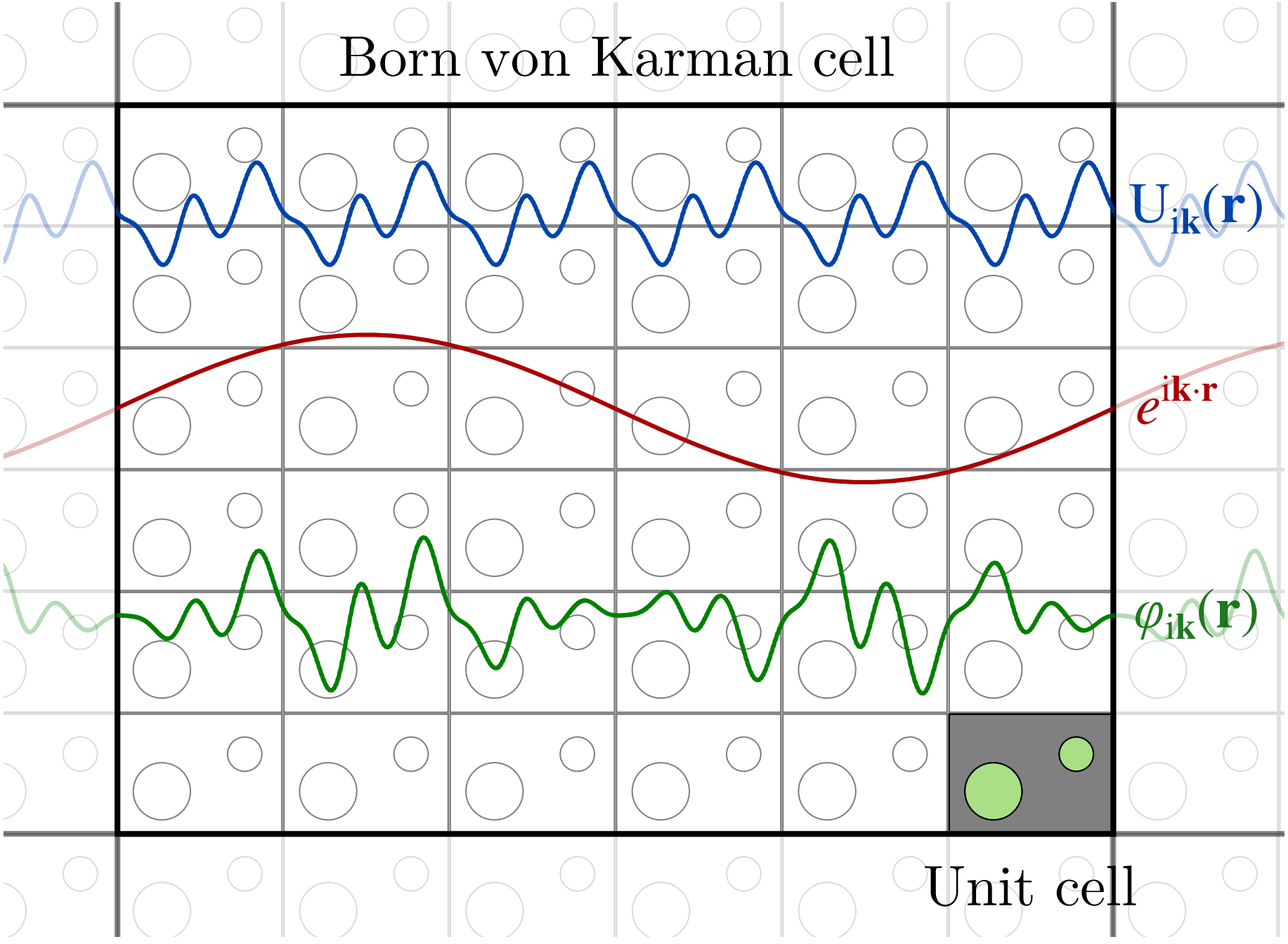
Features

- Full spinor wavefunctions:

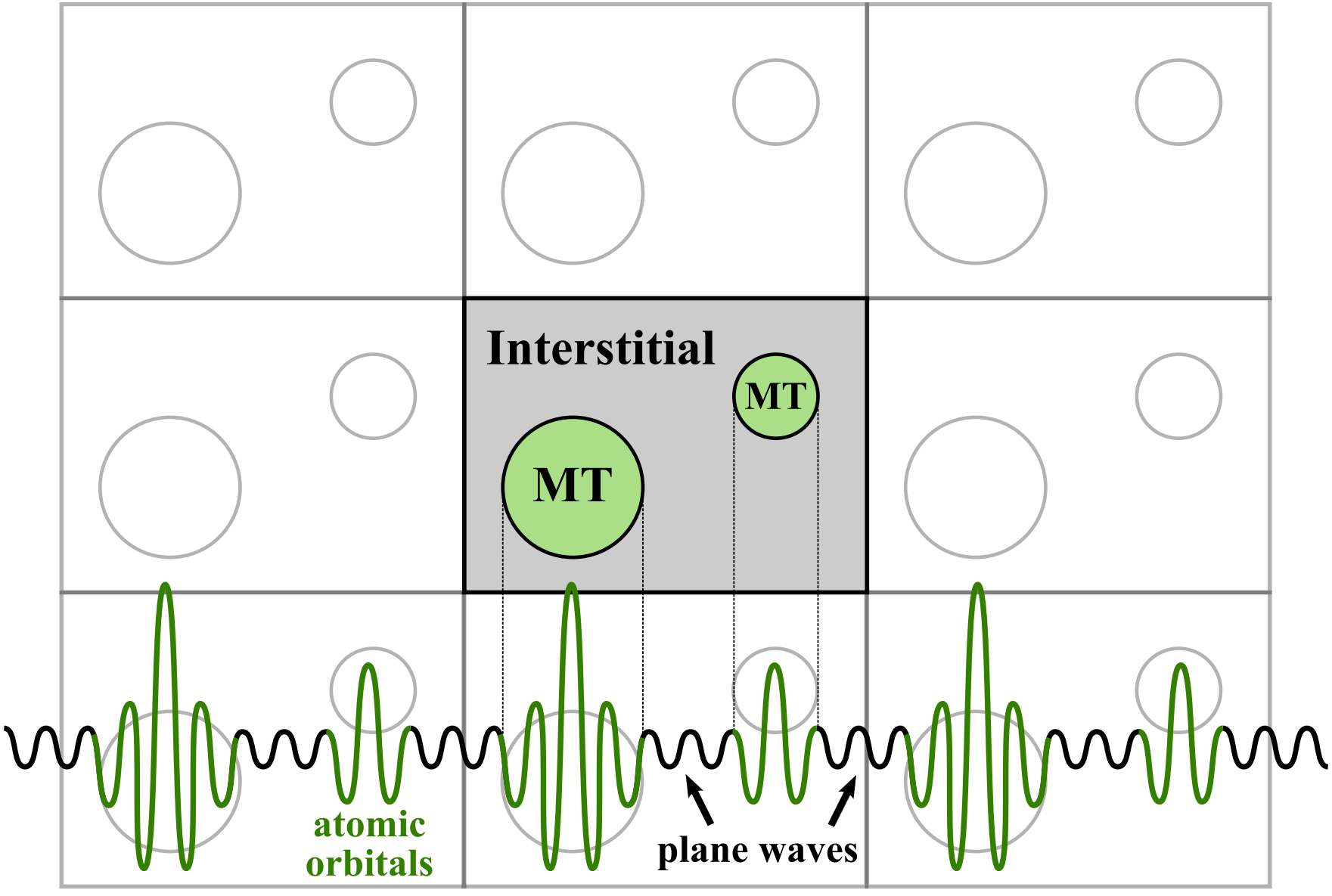
$$\phi_{i\mathbf{k}}(\mathbf{r}) = \begin{pmatrix} U^{\uparrow}_{i\mathbf{k}}(\mathbf{r}) \\ U^{\downarrow}_{i\mathbf{k}}(\mathbf{r}) \end{pmatrix} \times e^{i\mathbf{k}\cdot\mathbf{r}}$$

- Spin-spiral states also available:

$$\phi_{i\mathbf{k}}(\mathbf{r}) = \begin{pmatrix} U^{\uparrow}_{i\mathbf{k}}(\mathbf{r}) e^{i(\mathbf{k}+\mathbf{q}/2)\cdot\mathbf{r}} \\ U^{\downarrow}_{i\mathbf{k}}(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{q}/2)\cdot\mathbf{r}} \end{pmatrix}$$


Born von Karman cell
$U_{ik}(\mathbf{r})$
$e^{i\mathbf{k}\cdot\mathbf{r}}$
$\varphi_{ik}(\mathbf{r})$
Unit cell

Augmented plane waves



Augmented plane waves

Densities and potentials are expanded in real spherical harmonics inside the muffin-tins:

$$V(\mathbf{r}) = \sum_{l=0}^{l_{\max}} \sum_{m=-l}^{l} V_{lm}(r) R_{lm}(\hat{\mathbf{r}})$$

Augmented plane waves

The APW radial functions are obtained from the radial Schrödinger equation solved in the $l = m = 0$ part of the Kohn-Sham potential V_s

$$\left(\frac{\partial}{\partial r} + \frac{l(l+1)}{r} + V_{00}^{s}(r) R_{00} - \epsilon_l \right) u_l(r) = 0$$

(Note: no m dependence)

This is not an eigenvalue problem: the linearisation energies ϵ_l have to be supplied

Augmented plane waves

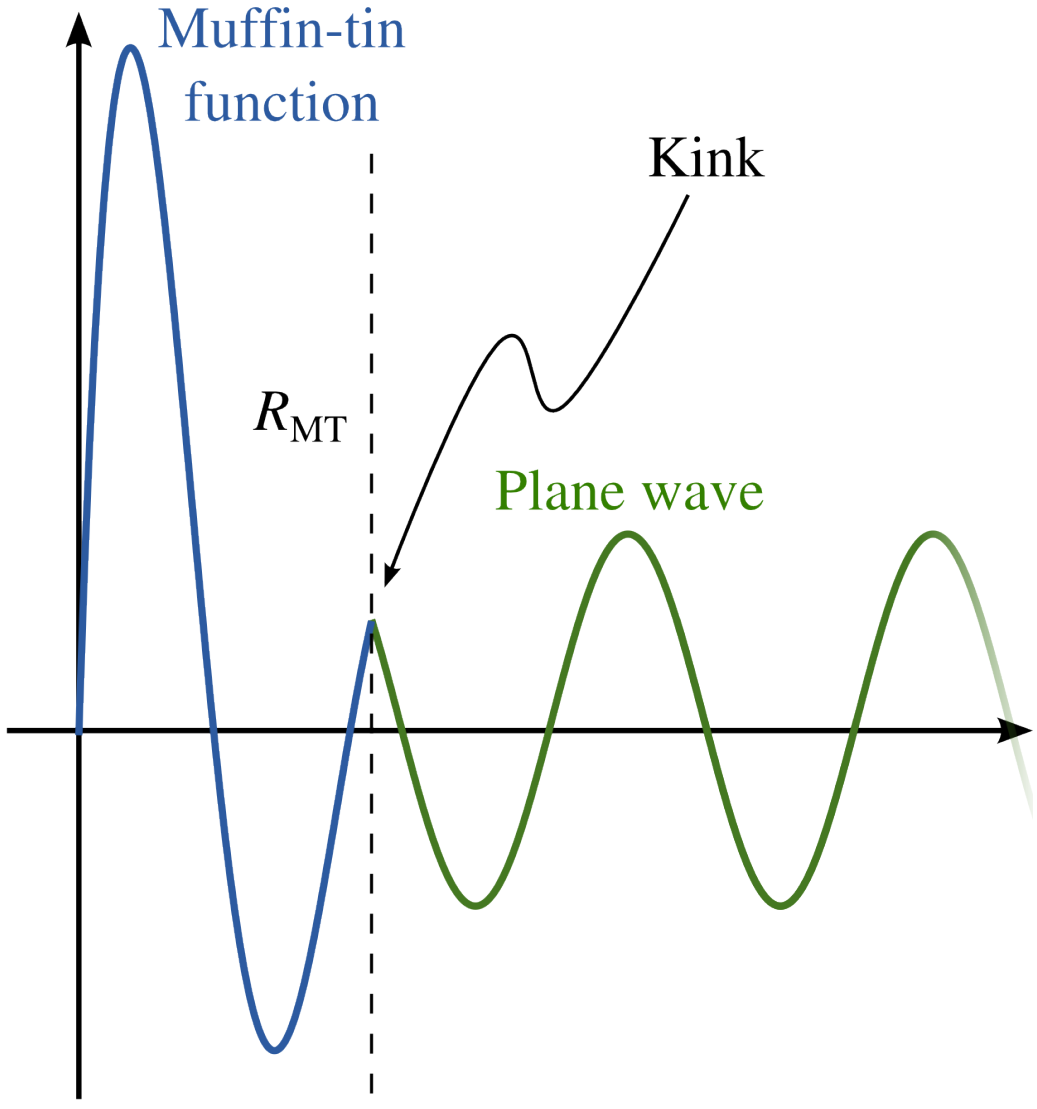
These functions are plane waves in the interstitial region and radial functions times spherical harmonics in the muffin-tin region:

$$B_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \dfrac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} & \mathbf{r} \in \text{interstitial} \\ \displaystyle\sum_{l=0}^{l_{\max}} u_l^\alpha(r) \sum_{m=-l}^{l} A_{lm}(\mathbf{G}+\mathbf{k})^\alpha Y_{lm}(\hat{\mathbf{r}}) & \mathbf{r} \in \text{muffin-tin } \alpha \end{cases}$$

where u_l^α are radial functions and Y_{lm} are spherical harmonics.

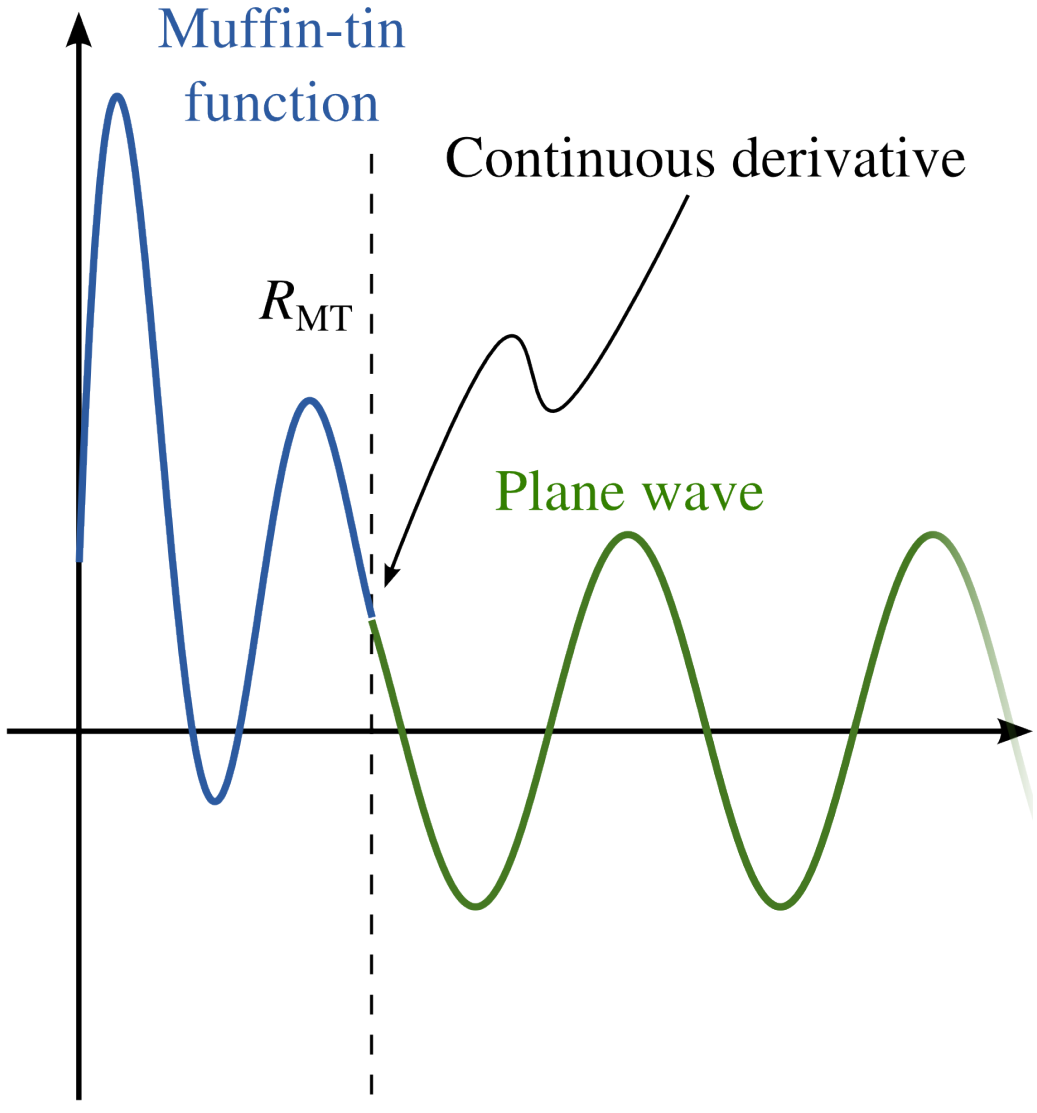
The coefficients A_{lm}^α are chosen so that the APW functions are continuous at the muffin-tin boundary

Augmented plane waves



The kink has infinite kinetic energy density!

Linearised augmented plane waves (LAPW)



Local-orbitals

More flexibility can be added to the APW basis in the form of local-orbitals:

$$B_i^\alpha(\mathbf{r}) = v_{l_i}^\alpha(r) Y_{l_i m_i}(\hat{\mathbf{r}}),$$

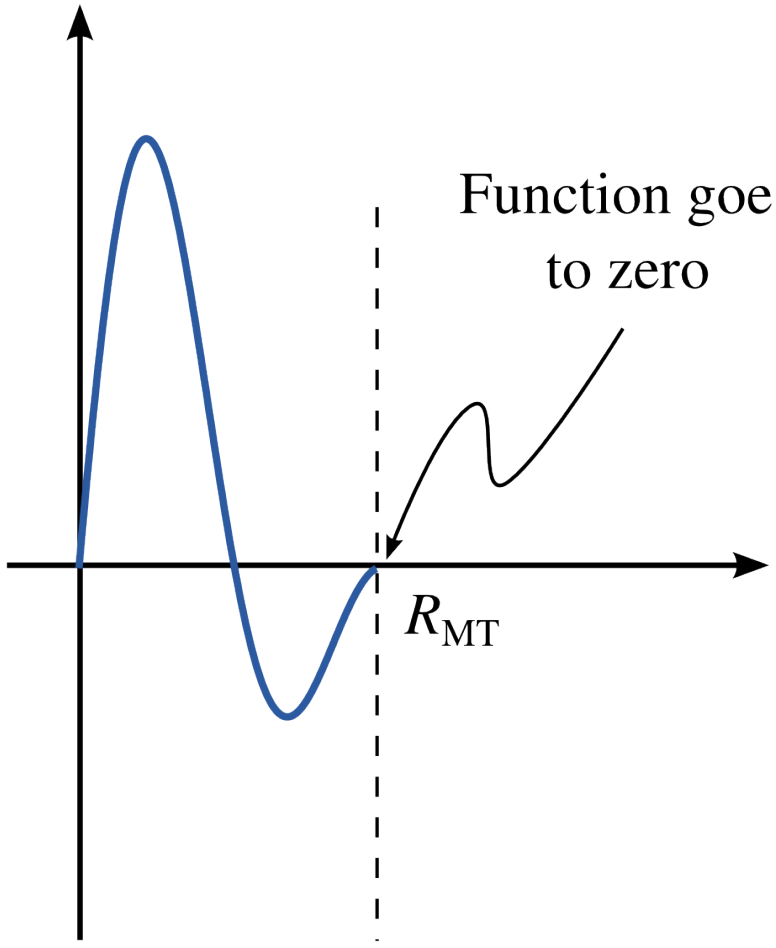
where α labels the muffin-tin

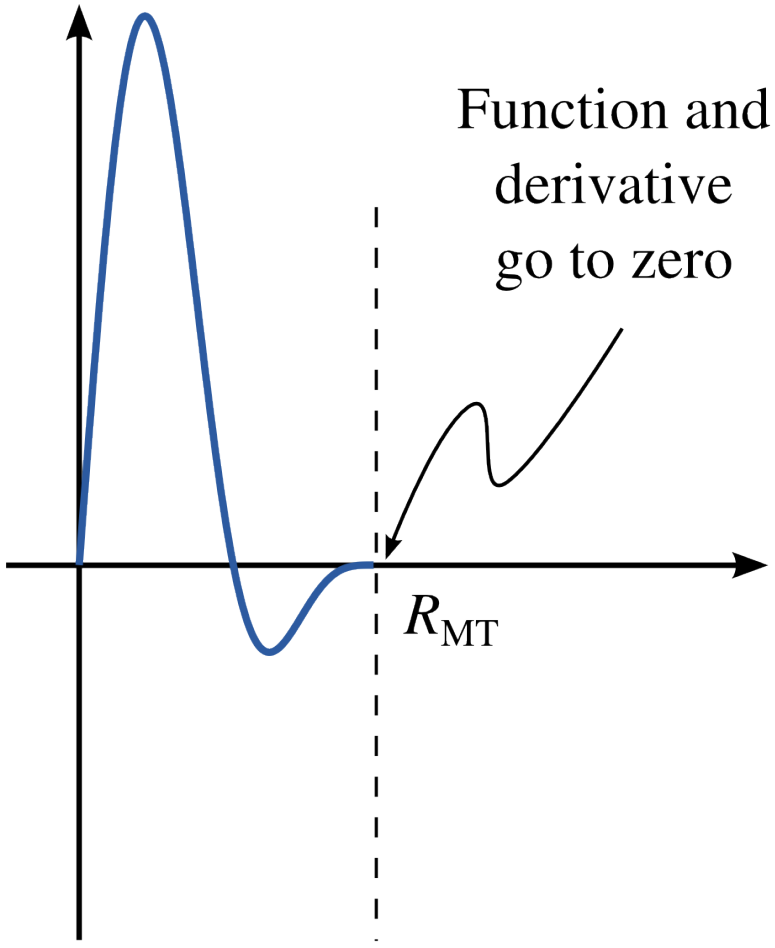
Local-orbitals are zero at the muffin-tin boundary R_{MT}

Higher derivatives can also be set to zero at R_{MT}

These functions can be used for semi-core or even core states

Local-orbitals

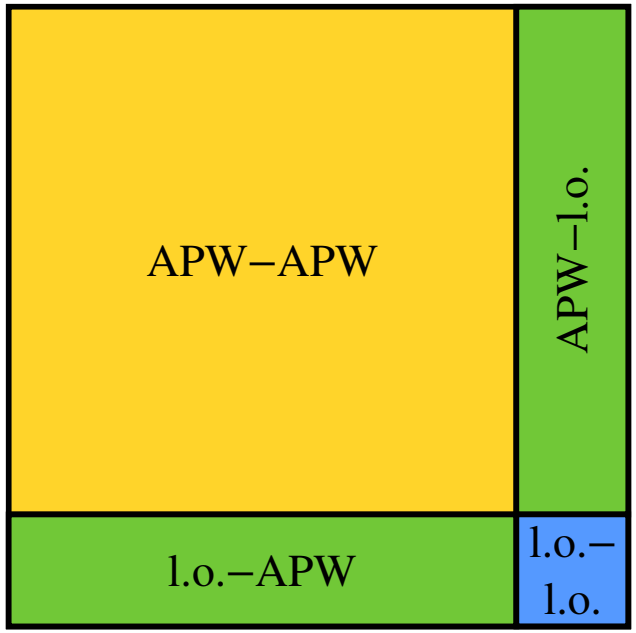




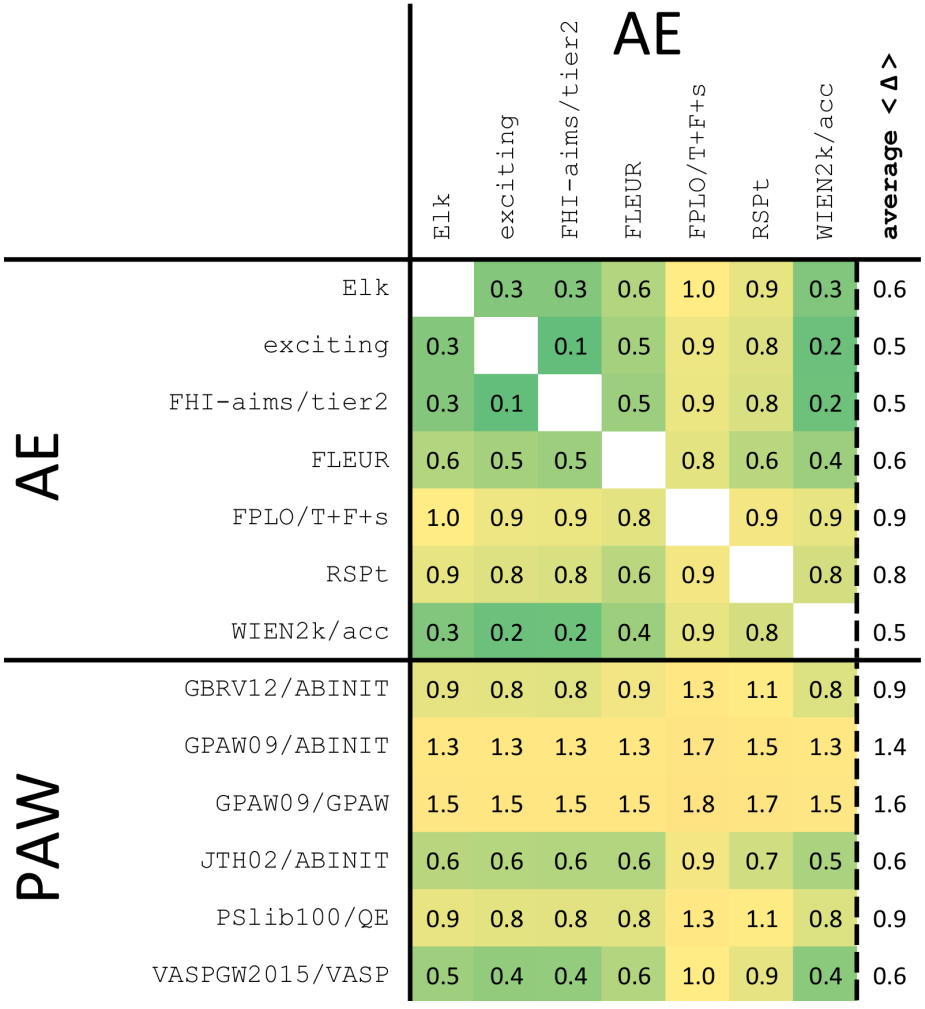
Augmented plane waves

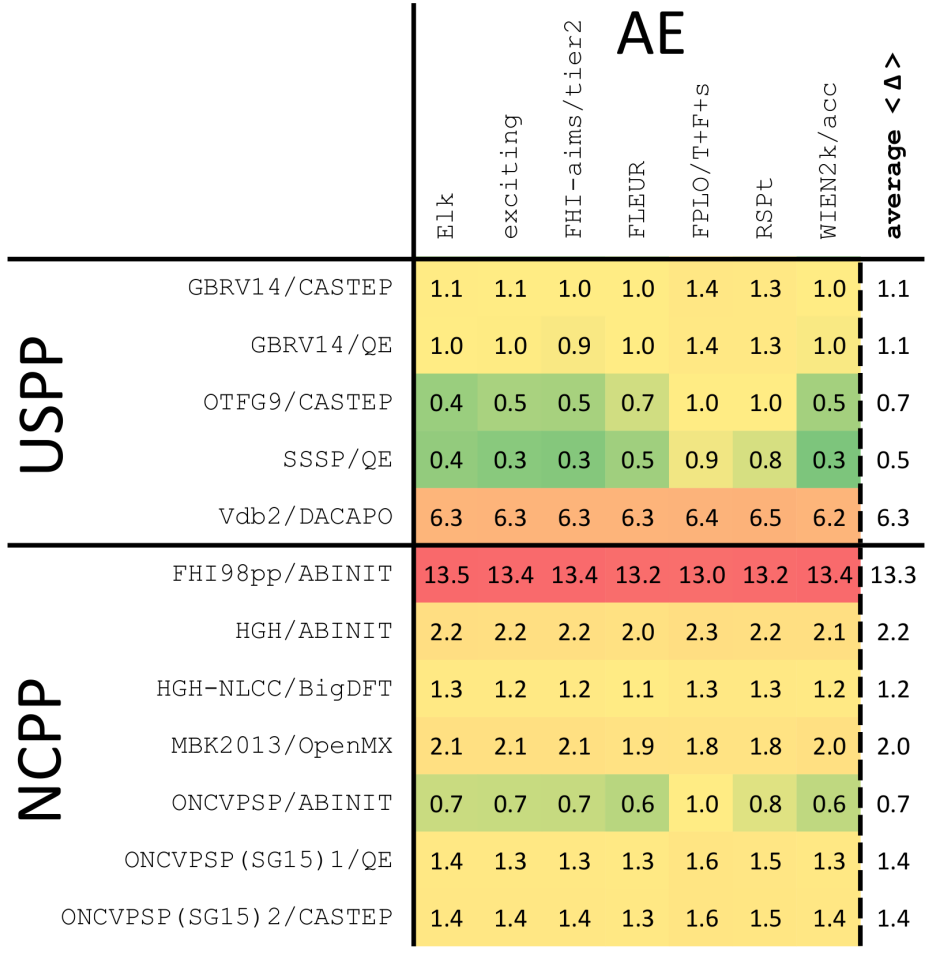
The Hamiltonian matrix H has contributions from

- APW–APW
- APW–APW surface term
- interstitial–interstitial
- APW–local-orbital
- local-orbital–local-orbital



The Kohn-Sham equation of state for elemental solids: a solved problem, Kurt Lejaeghere *et al.* Science 351, 6280 (2016)





Ground state DFT:
Exact EXchange functional

Goerling-Levy expansion of total energy functional

$$E[n] = \int d\mathbf{r}\; v_0(\mathbf{r}) n(\mathbf{r}) + \sum_{j=0}^{\infty} E_j[n]$$

$$\sum_{j=0}^{\infty} E_j[n] = T_s[n] + \left[\int d\mathbf{r}' d\mathbf{r} \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + E_{\mathrm{x}}[n] \right] + \sum_{j=2}^{\infty} E_j[n]$$

Orbital dependent exchange-correlation functional

Neglect correlation and use the Hartree-Fock exchange energy

$$E_{\rm x}[n] = -\frac{1}{2}\sum_{i,j}^{\rm occ}\int d\mathbf{r}\; d\mathbf{r}'\,\frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r})\phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

This is automatically self-interaction free!!

To solve the Kohn-Sham system we require

$$v_{\rm x}[n](\mathbf{r}) = \frac{\delta E_{\rm x}[n]}{\delta n(\mathbf{r})}$$

Functionals for non-collinear magnetism

$$\overleftrightarrow{\rho}(\mathbf{r}) \equiv \begin{pmatrix} \rho^{\uparrow\uparrow}(\mathbf{r}) & \rho^{\uparrow\downarrow}(\mathbf{r}) \\ \rho^{\downarrow\uparrow}(\mathbf{r}) & \rho^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

LSDA and Kübler trick:

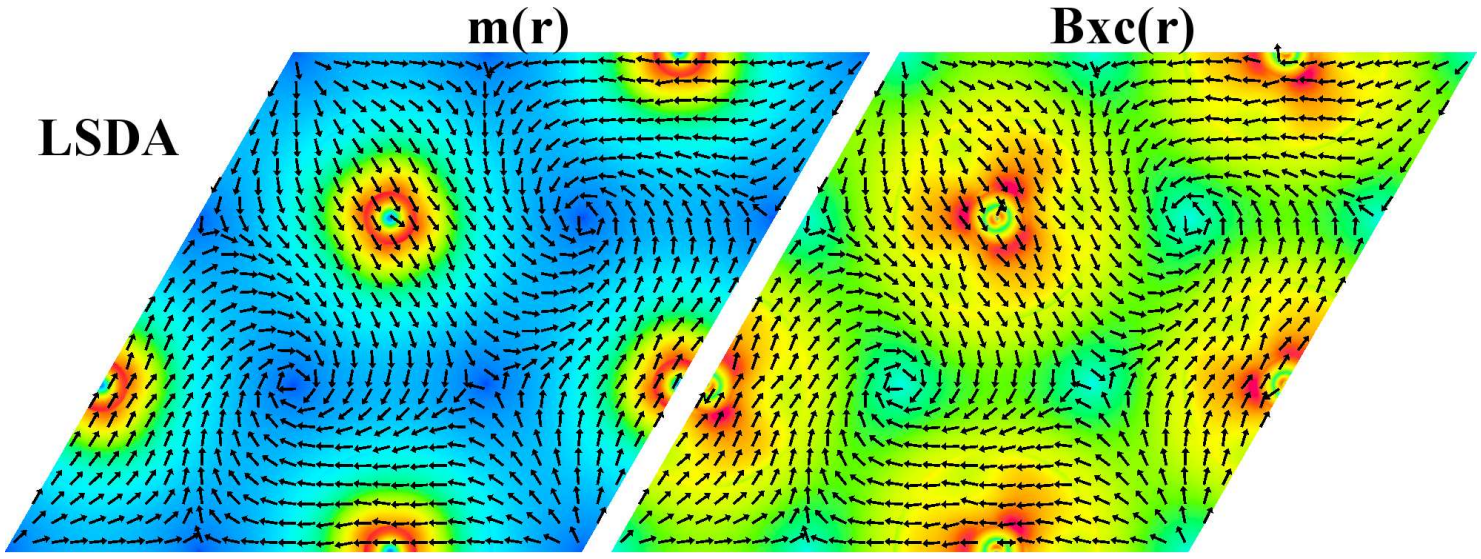
$$U \begin{pmatrix} \rho^{\uparrow\uparrow}(\mathbf{r}) & \rho^{\uparrow\downarrow}(\mathbf{r}) \\ \rho^{\downarrow\uparrow}(\mathbf{r}) & \rho^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix} U^{\dagger} = \begin{pmatrix} \tilde{\rho}^{\uparrow\uparrow}(\mathbf{r}) & 0 \\ 0 & \tilde{\rho}^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

$$\begin{pmatrix} \tilde{\rho}^{\uparrow\uparrow}(\mathbf{r}) & 0 \\ 0 & \tilde{\rho}^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix} \overset{\text{LSDA}}{\longrightarrow} \begin{pmatrix} \tilde{v}_{\text{xc}}^{\uparrow\uparrow}(\mathbf{r}) & 0 \\ 0 & \tilde{v}_{\text{xc}}^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

$$U^{\dagger} \begin{pmatrix} \tilde{v}_{\text{xc}}^{\uparrow\uparrow}(\mathbf{r}) & 0 \\ 0 & \tilde{v}_{\text{xc}}^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix} U = \begin{pmatrix} v_{\text{xc}}^{\uparrow\uparrow}(\mathbf{r}) & v_{\text{xc}}^{\uparrow\downarrow}(\mathbf{r}) \\ v_{\text{xc}}^{\downarrow\uparrow}(\mathbf{r}) & v_{\text{xc}}^{\downarrow\downarrow}(\mathbf{r}) \end{pmatrix}$$

$$\mathbf{m}(\mathbf{r}) \overset{\text{LSDA}}{\longrightarrow} \mathbf{B}_{\text{xc}}(\mathbf{r})$$

LSDA: non-collinearity in Cr-monolayer



Sharma et. al Phys. Rev. Lett. **98** 196405 (2007)

Spin-dynamics

Landau-Lifschitz equation in absence of spin-currents

$$\frac{\partial \mathbf{m}(\mathbf{r},t)}{\partial t} = \gamma \mathbf{m}(\mathbf{r},t) \times (\mathbf{B}_{\rm xc}(\mathbf{r},t) + \mathbf{B}_{\rm ext}(\mathbf{r},t))$$

Within the LSDA $\mathbf{B}_{\rm xc}$ is locally parallel to $\mathbf{m}$,
so no spin dynamics!!

Non-collinear magnetism within OEP

Iterative solution of following equations:

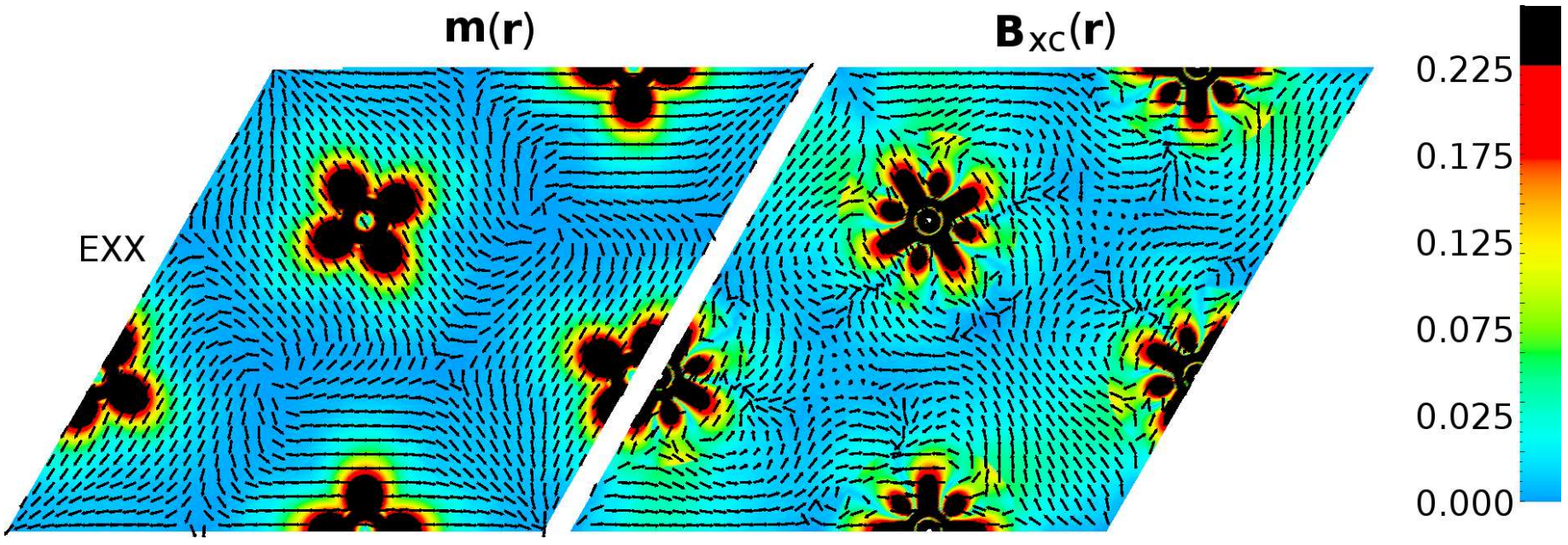
$$R_v(\mathbf{r}) \equiv \left.\frac{\delta E[\rho,\mathbf{m}]}{\delta v_{\rm s}(\mathbf{r})}\right|_{\mathbf{B}_{\rm s}} = \sum_i^{\rm occ}\sum_j^{\rm un}\left(\Lambda_{ij}\frac{\rho_{ij}(\mathbf{r})}{\varepsilon_i-\varepsilon_j}+{\rm c.c.}\right)=0$$

$$\mathbf{R_B}(\mathbf{r}) \equiv \left.\frac{\delta E[\rho,\mathbf{m}]}{\delta \mathbf{B}_{\rm s}(\mathbf{r})}\right|_{v_{\rm s}} = \sum_i^{\rm occ}\sum_j^{\rm un}\left(\Lambda_{ij}\frac{\mathbf{m}_{ij}(\mathbf{r})}{\varepsilon_i-\varepsilon_j}+{\rm c.c.}\right)=0,$$

$$\Lambda_{ij} = \left(V_{ij}^{\rm NL}\right)^* - \int \rho_{ij}^*(\mathbf{r})v_{\rm x}(\mathbf{r})\,d\mathbf{r} - \int \mathbf{m}_{ij}^*(\mathbf{r})\cdot\mathbf{B}_{\rm x}(\mathbf{r})\,d\mathbf{r},$$

Sharma et. al Phys. Rev. Lett. **98** 196405 (2007)

OEP: non-collinearity in Cr-monolayer



Sharma et. al Phys. Rev. Lett. **98** 196405 (2007)

Ground state DFT: DFT+U functionals

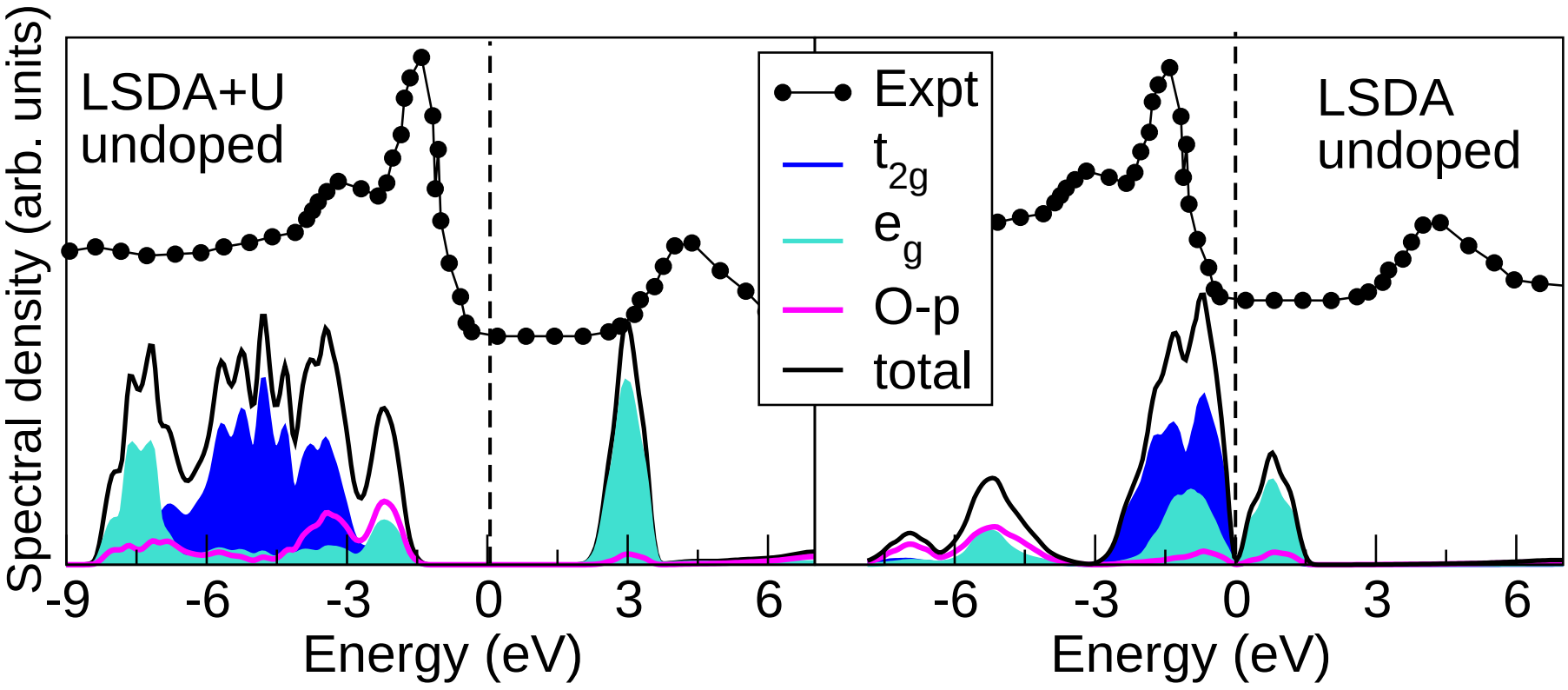
Strong correlations:
Transition metal oxides–prototypical Mott insulators

Solid	T_N(K)	Band gap(eV)
MnO	118	3.6
FeO	198	2.4
CoO	292	3.4
NiO	523	4.3

Table: Néel temperatures (in K) and band gaps (in eV) of TMO.

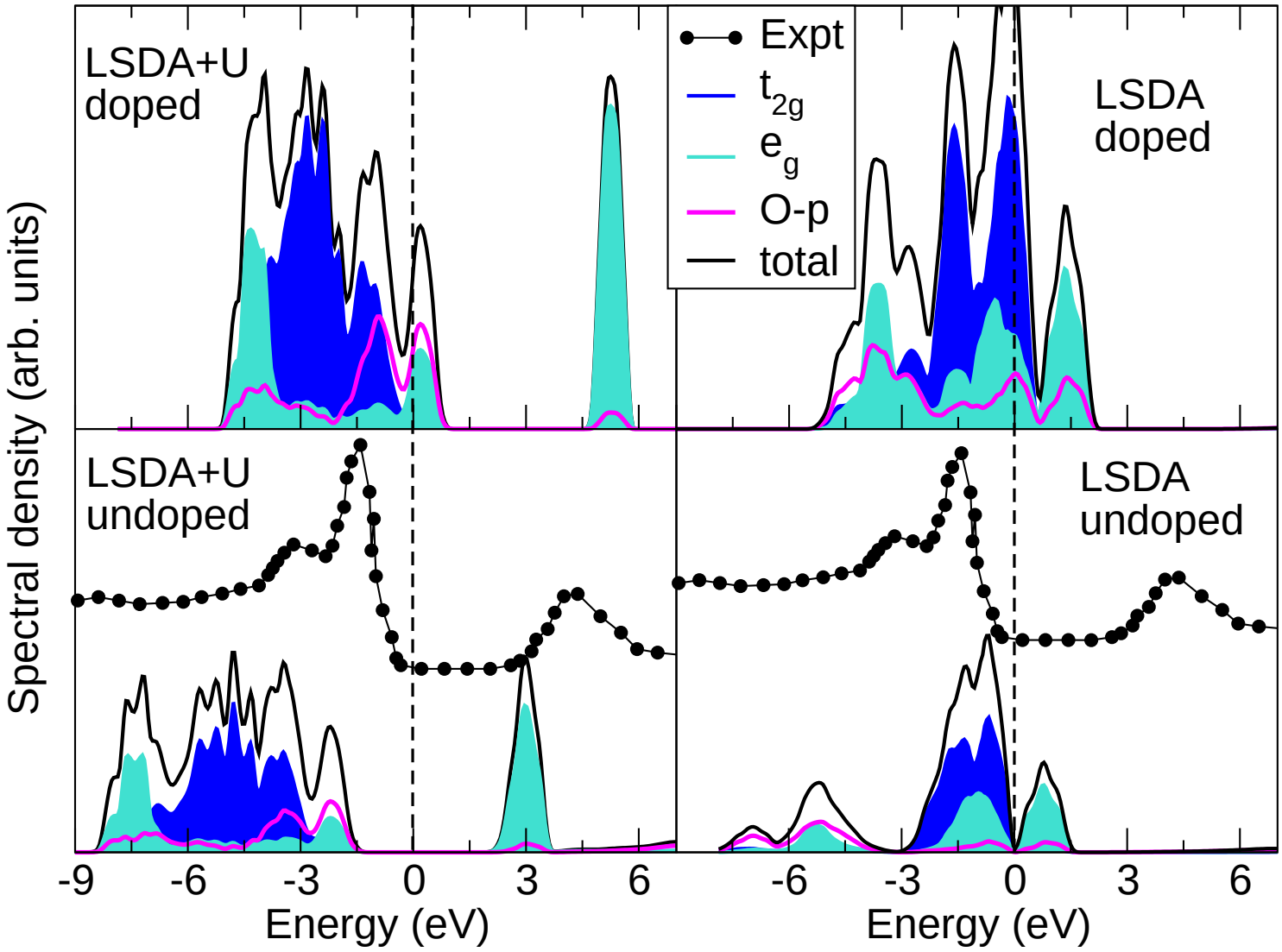
Long range magnetic order is just a co-existing phenomena.
It is NOT the reason for existence of gap in TMO.

Strong correlations with LDA+U



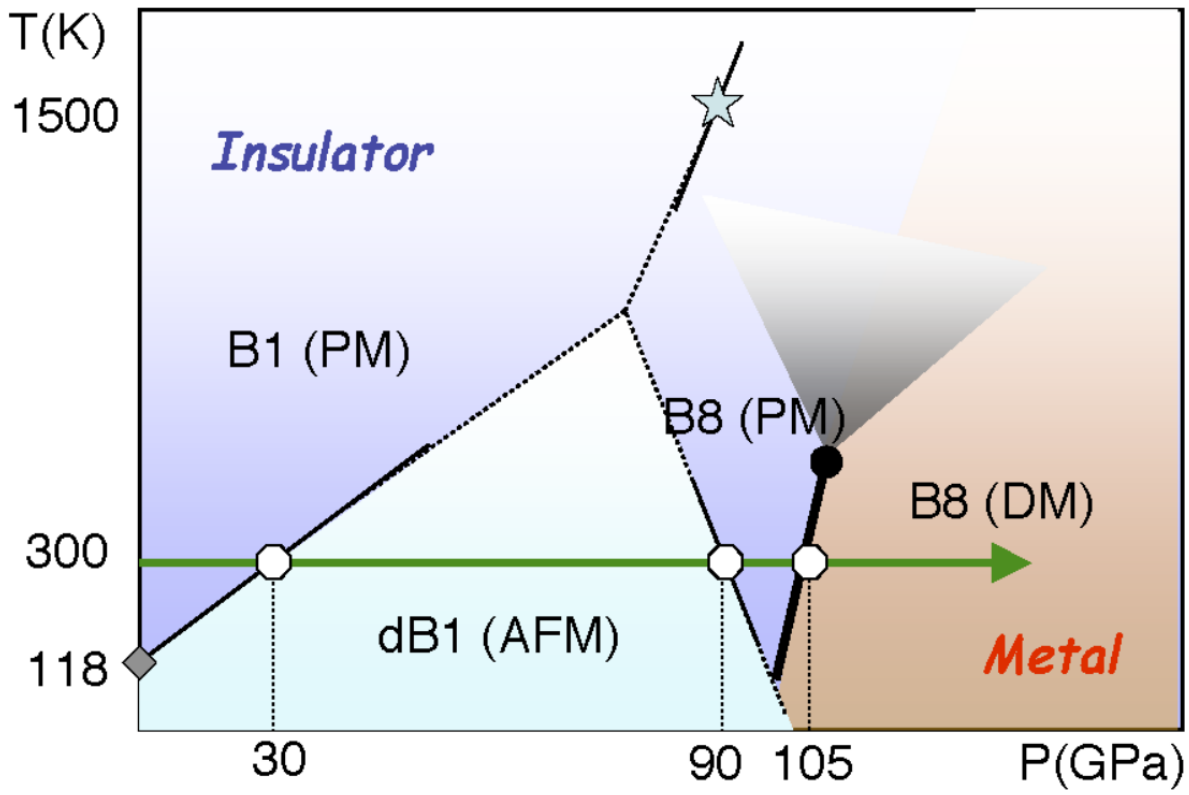
Y. Shinohara, S. Sharma, J. K. Dewhurst, S. Shallcross, N. N. Lathiotakis and E K U Gross, New J. Phys. 17, 093038 (2015)

Phase transition in NiO: LDA+U fails



Y. Shinohara, S. Sharma, J. K. Dewhurst, S. Shallcross, N. N. Lathiotakis and E K U Gross, New J. Phys. 17, 093038 (2015)

Phase transition in MnO: LDA+U fails



Experiments: Moment collapse (5 to 1 μ_B) and volume collapse (6.6%) at ∼100GPa

[Yoo et al. Phys. Rev. Lett. 94, 115502 (2005)]

Beyond ground state DFT:
Reduced Density Matrix Functional Theory

Reduced density matrix

- 1-RDM for integer particle number

$$\gamma(\mathbf{r}, \mathbf{r}') = N \int \Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \Psi^*(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\mathbf{r}_2 \ldots d\mathbf{r}_N.$$

$$\rho(\mathbf{r}) = \gamma(\mathbf{r}, \mathbf{r})$$

Diagonalising the density matrix gives the natural orbitals and occupation numbers

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i n_i \phi_i(\mathbf{r}) \phi_i^*(\mathbf{r}')$$

$$\int \gamma(\mathbf{r}, \mathbf{r}') \phi_i(\mathbf{r}') d\mathbf{r}' = n_i \phi_i(\mathbf{r})$$

Reduced density matrix functional theory

Gilbert's Theorem (PRB 12 2111 (75)) (HK for 1-RDM)

- Total energy is a unique functional $E[\gamma]$ of the 1-RDM
- Ground-state energy can be calculated by minimizing

$$F[\gamma] \equiv E_{\rm tot}[\gamma] - \mu \left[\int \gamma(\mathbf{r}, \mathbf{r})\, d\mathbf{r} - N \right]$$

Must ensure that γ is N-representable!
hence an additional constraint that $0 \leq n_i \leq 1$, $\sum_i n_i = N$
Proof by A. J. Coleman Rev. Mod. Phys. 35, 668 (1963)

Reduced density matrix functional theory

Three major differences to DFT

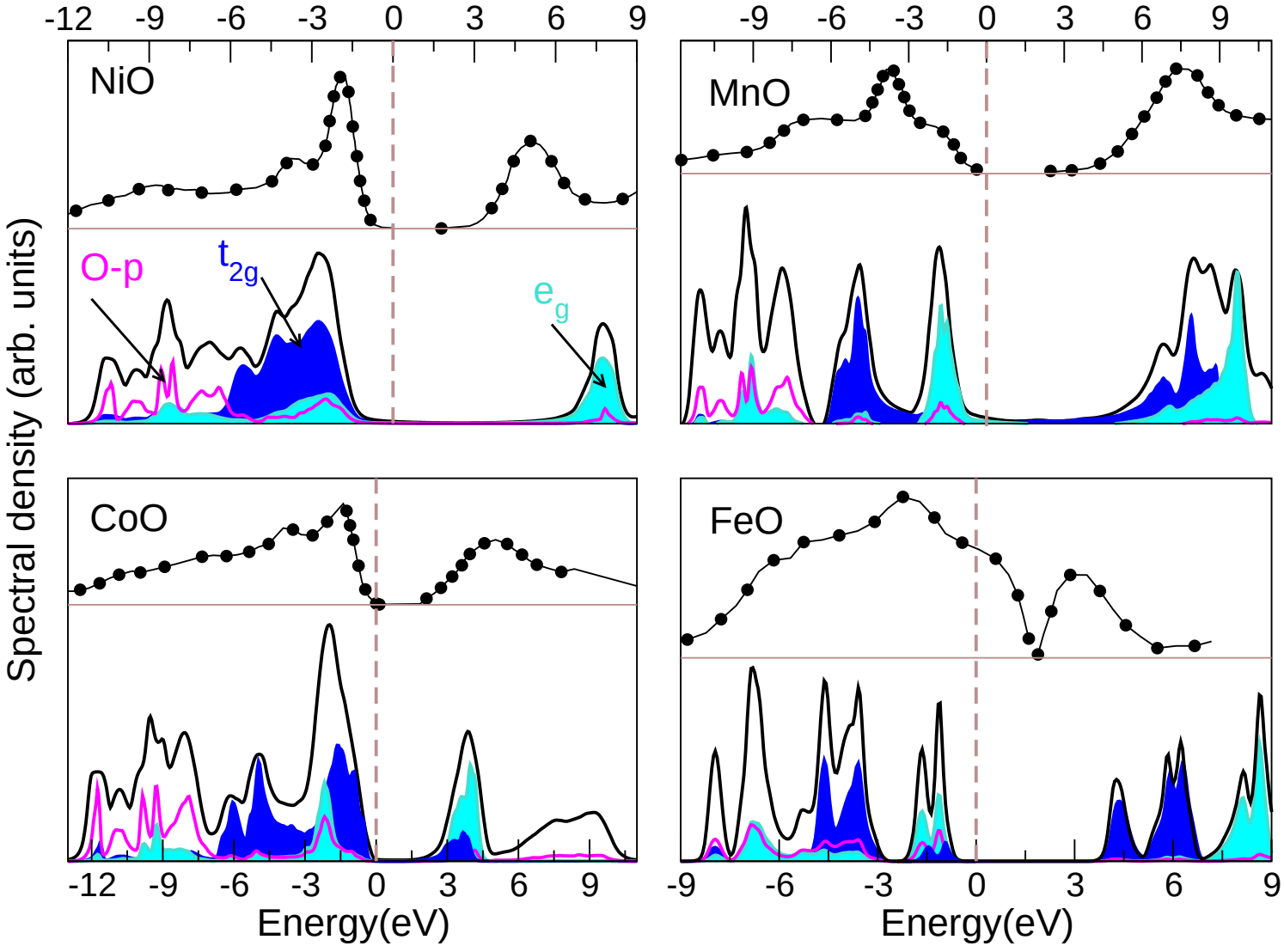
- Exact kinetic-energy functional is known explicitly

$$E_{\mathrm{kin}}[\gamma] = -\frac{1}{2}\int \delta(\mathbf{r}-\mathbf{r}')\nabla^2\gamma(\mathbf{r},\mathbf{r}')\,d\mathbf{r}\,d\mathbf{r}'$$

  so no kinetic energy in E_{xc}
- There exists no Kohn-Sham system reproducing the exact γ (because γ^{KS} is idempotent)
- There exists no variational equation

$$\frac{\delta F[\gamma]}{\delta\gamma(\mathbf{r},\mathbf{r}')} = 0$$

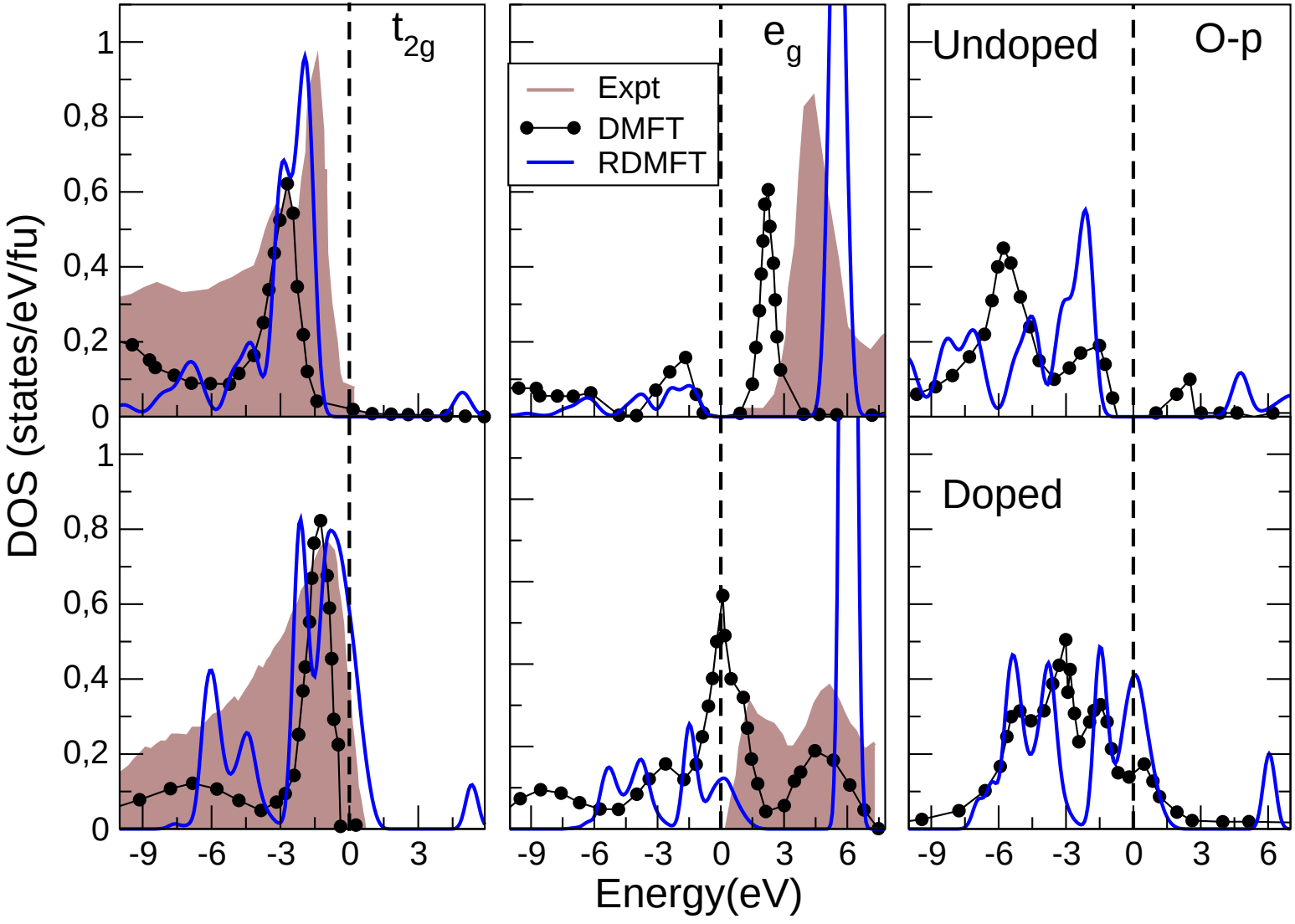
Spectral density of magnetic TMO



[Sharma et al. Phys. Rev. Lett. 110, 116403 (2013) and

Phys. Rev. A 85, 032504 (2012)]

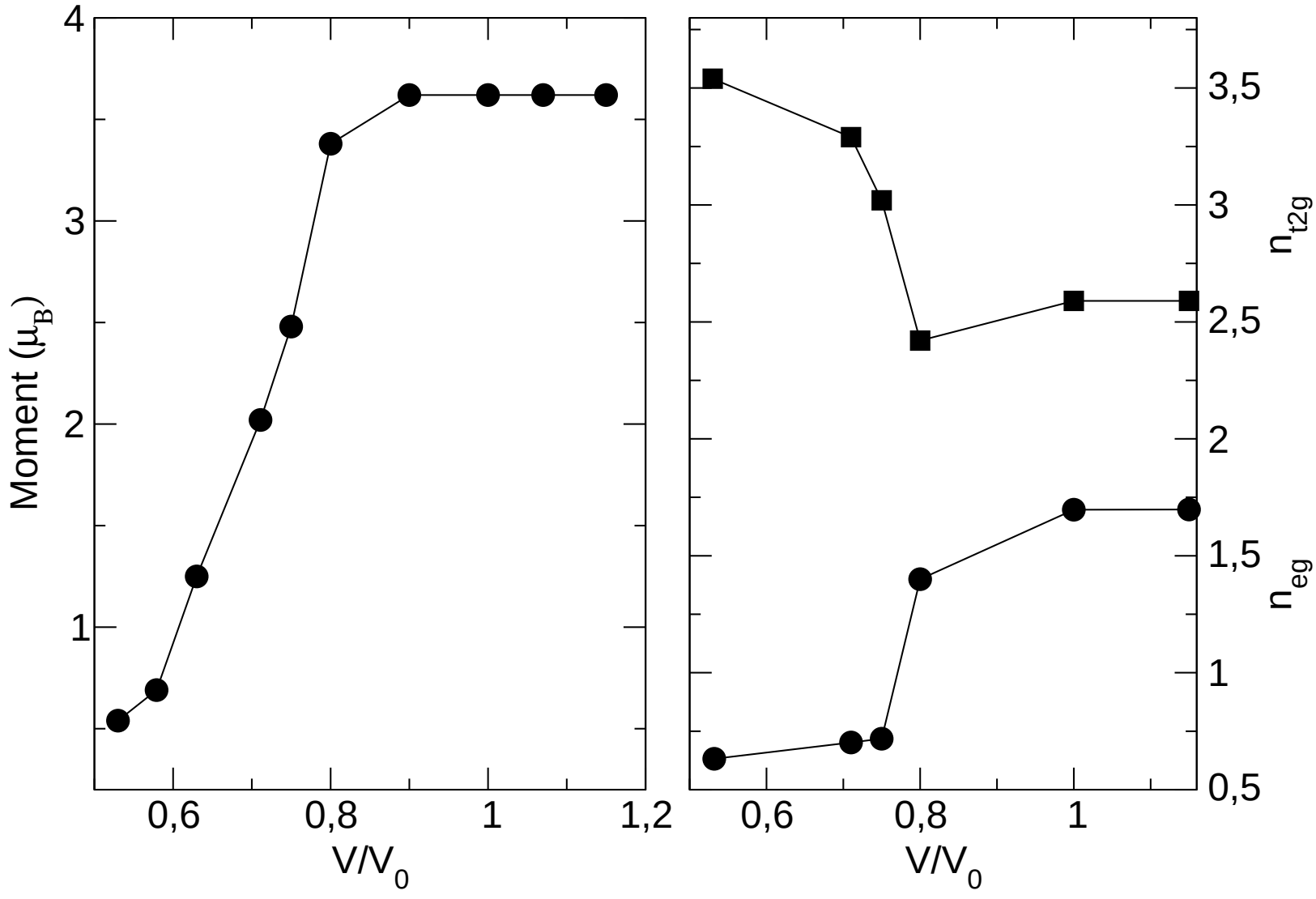
Doping induced phase transition in NiO



Y. Shinohara, S. Sharma, J. K. Dewhurst, S. Shallcross, N. N. Lathiotakis and E K U Gross,

New J. Phys. 17, 093038 (2015)

Pressure induced phase transition in MnO



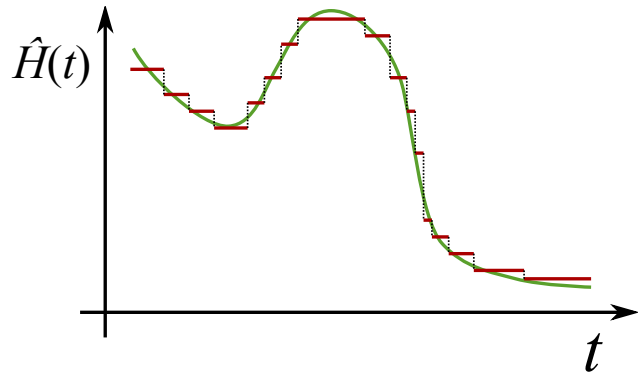
Sharma et al. Phys. Rev. Lett. 110, 116403 (2013)

Beyond ground state DFT:
Time Dependent Density Functional Theory

Time-evolution in practice

Time-evolution method should be energy-conserving and unitary

Assume time-dependence of the Hamiltonian $H_s(t)$ is step-like:



If $|\phi_i(t)\rangle$ are orbitals which diagonalize $H_s(t)$ instantaneously:

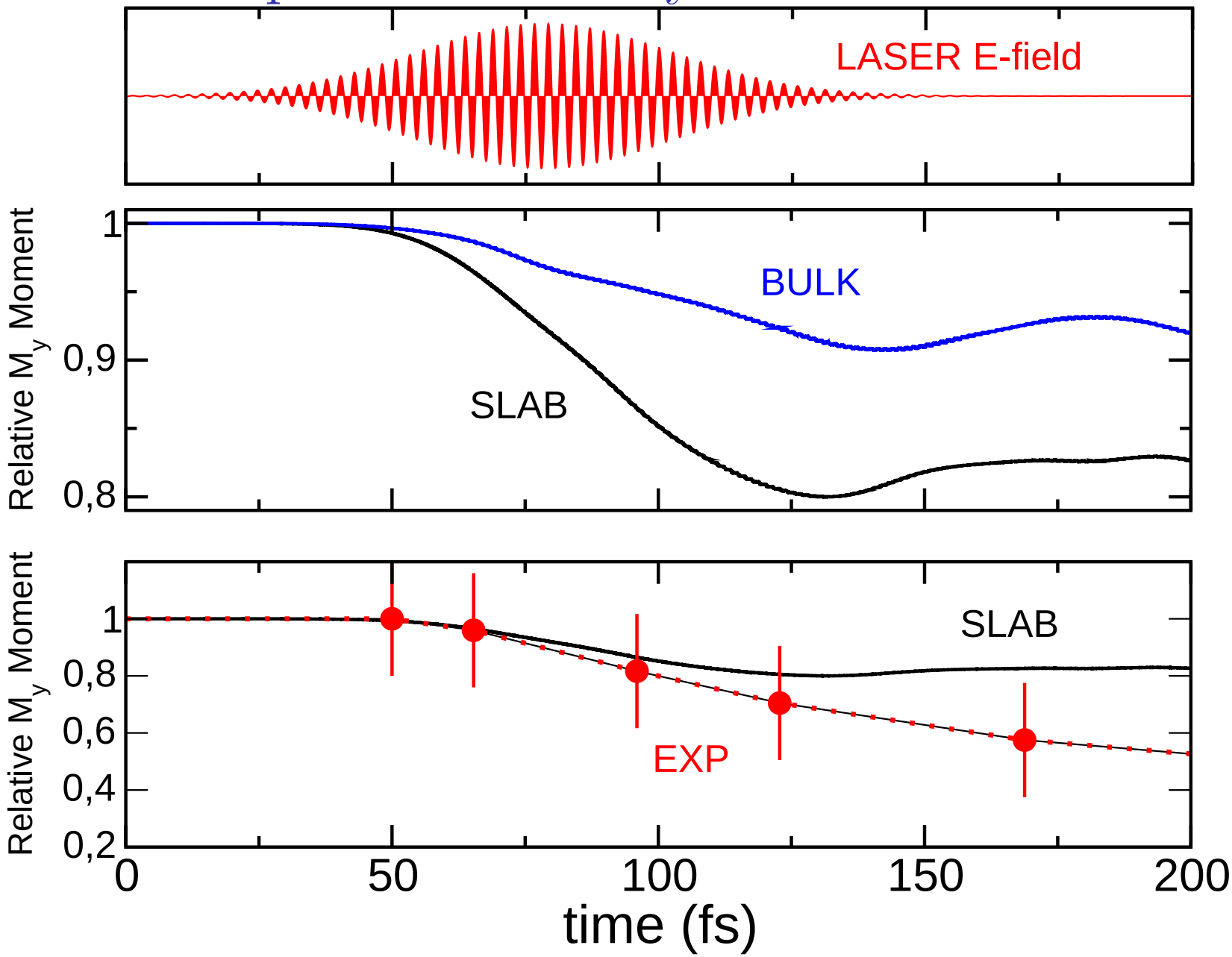
$$H_s(t)|\phi_i(t)\rangle = \varepsilon_i(t)|\phi_i(t)\rangle$$

Then expansion in these states gives time evolution which is simple and exact:

$$|\psi_i(t+\Delta t)\rangle = \sum_j a_j^i(t) e^{-i\varepsilon_i(t)\Delta t}|\phi_j(t)\rangle.$$

Dewhurst et al. arxiv.org/1412.0996

Experimental pulse and a 5-layer slab of Ni



Experiment: Stamm *et al.* Nat. Mat. 6 740 (2007)

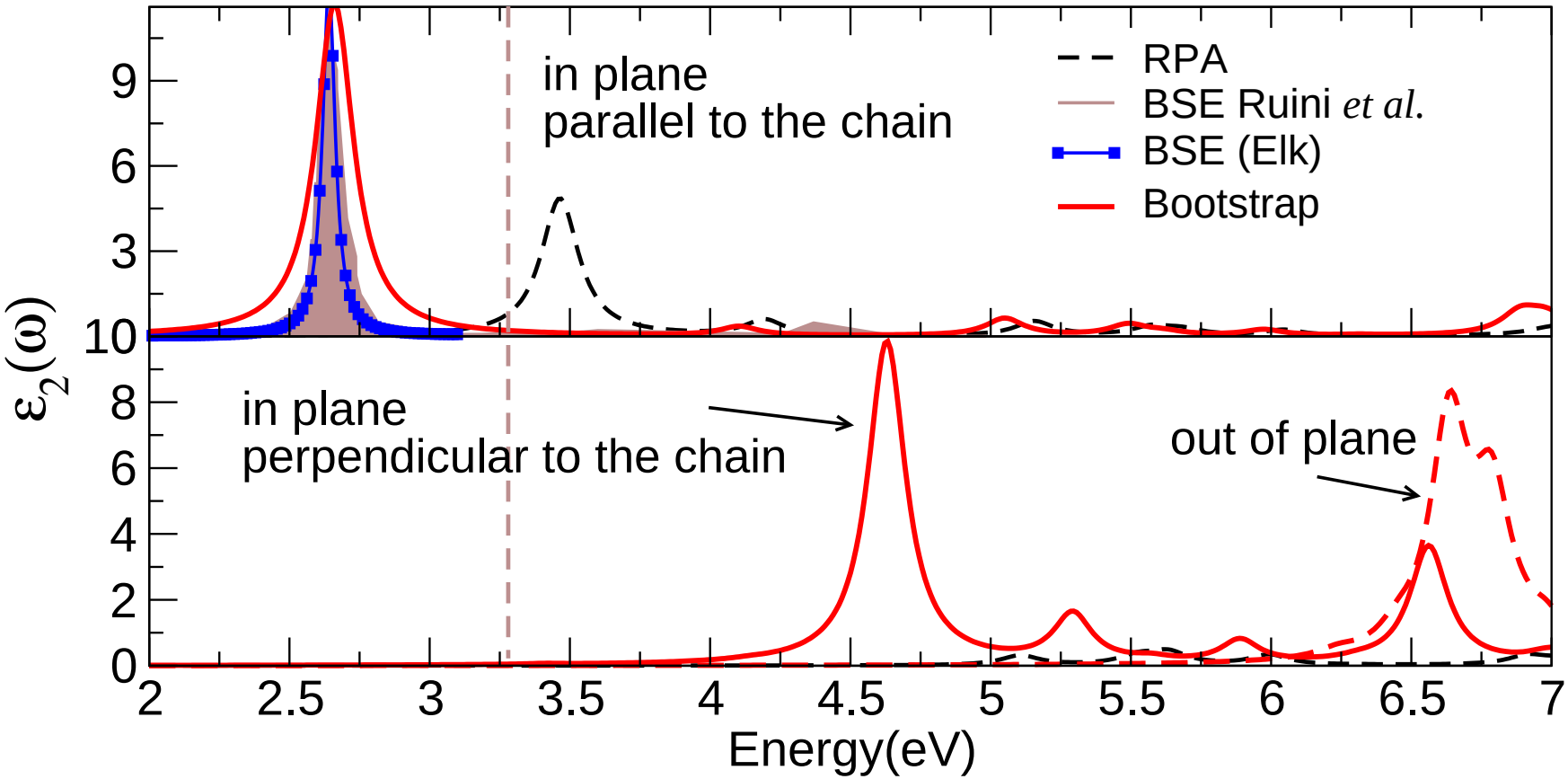
Response functions:
Excitons

Density-density reponse function

$$\chi_0 = \frac{\delta\rho}{\delta v} = \left[\begin{array}{ccc|c} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} & \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} & \text{Wings} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} & 3 \times (n_G - 1) \\ \hline & & & \\ & \text{Wings} & & \text{Body} \\ & (n_G - 1) \times 3 & & (n_G - 1) \times (n_G - 1) \\ & & & \end{array}\right]$$

$$\chi = \chi_0 + \chi_0(v + f_{\text{xc}})\chi$$

Excitons from TDLR and BSE: linear chain of PPV



S. Sharma et al. J. Chem. Theory Comput. 11, 1710 (2015)

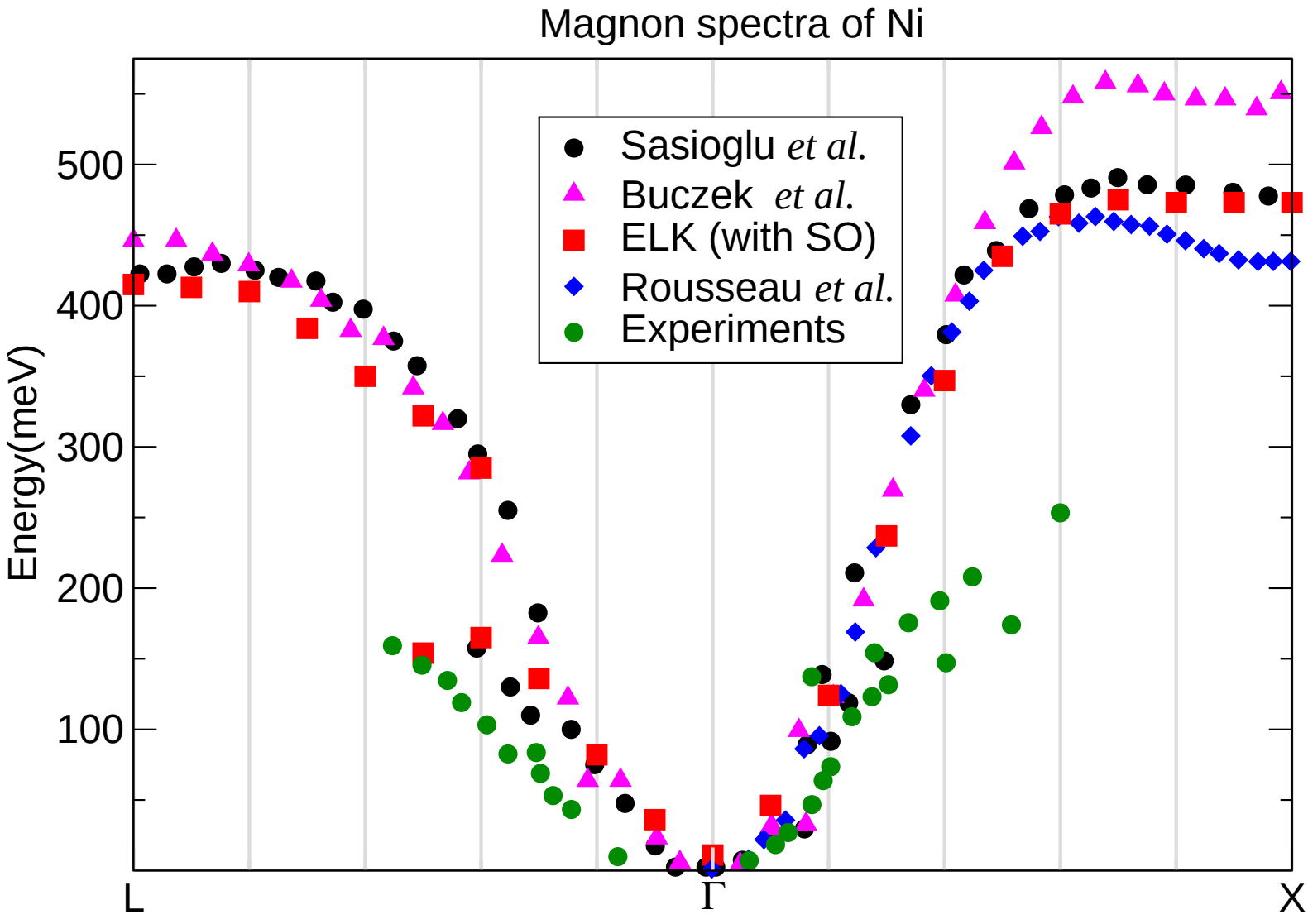
Response functions:
Magnons

magneitisation-magnetisation reponse function

$$\chi_0 = \left[\begin{array}{c|c} \frac{\delta\rho}{\delta v} & \frac{\delta\rho}{\delta \mathbf{B}} \\ \hline \frac{\delta \mathbf{m}}{\delta v} & \frac{\delta \mathbf{m}}{\delta \mathbf{B}} \end{array}\right]$$

$$\chi = \chi_0 + \chi_0(v + f_{\mathrm{xc}})\chi$$

Linear response magnons



Response functions:
Linear response phonons

Linear response phonons