Exact Exchange in Density Functional Theory

S. Sharma, J. K. Dewhurst and C. Ambrosch-Draxl

Institut für Physik
Karl-Franzens-Universität Graz
Universitätsplatz 5
A-8010 Graz, Austria

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Density functional theory

Many-body theory involves solving for functions in $3N$ coordinates: $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$

Density functional theory (DFT) requires solving for functions in 3 coordinates: $n(\mathbf{r})$

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Hohenberg-Kohn Theorems (1964)

1. External potential $v(\mathbf{r})$ is uniquely determined by $n(\mathbf{r})$
2. The variational principle holds

$$E_0 = E_{v_0}[n_0] < E_{v_0}[n]$$

3. $E_{v_0}[n] = F[n] + \int d\mathbf{r}\, v_0(\mathbf{r}) n(\mathbf{r})$

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Density functional theory

DFT is an exact theory for interacting systems in the ground state

Kohn-Sham equations

Find set of auxilliary single particle orbitals such that

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathsf{s}}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

and

$$n(\mathbf{r}) = \sum_i^{\mathsf{occ}} |\phi_i(\mathbf{r})|^2.$$

If

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

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$$v_{\mathsf{s}}[n](\mathbf{r}) = v(\mathbf{r}) + \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\mathsf{xc}}[n](\mathbf{r})$$

where

$$v_{\mathsf{xc}}[n](\mathbf{r}) = \frac{\delta E_{\mathsf{xc}}[n]}{\delta n(\mathbf{r})}.$$

Many sins hidden in $E_{\mathsf{xc}}[n]$!

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Exchange-correlation functionals

First generation : Local density approximation (LDA)

$$E_{\text{xc}}^{\text{LDA}}[n] = \int d\mathbf{r}\; n(\mathbf{r}) e_{\text{xc}}^{\text{unif}}(n(\mathbf{r}))$$

Second generation : Generalised gradient approximations

$$E_{\text{xc}}^{\text{GGA}}[n] = \int d\mathbf{r}\; f(n(\mathbf{r}), \nabla n(\mathbf{r}))$$

$$E_{\text{xc}}^{\text{Meta-GGA}}[n] = \int d\mathbf{r}\; g(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r}))$$

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Exchange-correlation functionals

Development of new functionals leads not only to improved accuracy but also correct qualitative features

Exchange-correlation functionals

Third generation: Exact exchange (EXX)

Neglect correlation and use the Hartree-Fock exchange energy

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

To solve the Kohn-Sham system we require

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

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Exchange-correlation functionals

Using the functional derivative chain rule:

$$v_{\mathsf{x}}[n](\mathbf{r}) = \sum_{i}^{\mathsf{occ}} \int d\mathbf{r}\, d\mathbf{r}'' \left[\frac{\delta E_{\mathsf{x}}}{\delta \phi_i(\mathbf{r}'')} \frac{\delta \phi_i(\mathbf{r}'')}{\delta v_{\mathsf{s}}(\mathbf{r}')} + \frac{\delta E_{\mathsf{x}}}{\delta \phi_i^*(\mathbf{r}'')} \frac{\delta \phi_i^*(\mathbf{r}'')}{\delta v_{\mathsf{s}}(\mathbf{r}')} \right] \frac{\delta v_{\mathsf{s}}(\mathbf{r}')}{\delta n(\mathbf{r})}$$

$$= \int d\mathbf{r}' \left[\sum_{i}^{\mathsf{occ}} \sum_{j}^{\mathsf{unocc}} \langle \phi_i | \hat{v}_{\mathsf{x}}^{\mathsf{NL}} | \phi_j \rangle \frac{\phi_j^*(\mathbf{r}') \phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j} + \mathsf{c.c.} \right] \frac{\delta v_{\mathsf{s}}(\mathbf{r}')}{\delta n(\mathbf{r})},$$

where

$$\langle \phi_{i\mathbf{k}} | \hat{v}_{\mathsf{x}}^{\mathsf{NL}} | \phi_{j\mathbf{k}} \rangle = \sum_{l\mathbf{k}'}^{\mathsf{occ}} w_{\mathbf{k}'} \int d\mathbf{r}\, d\mathbf{r}' \frac{\phi_{i\mathbf{k}}^*(\mathbf{r}) \phi_{l\mathbf{k}'}(\mathbf{r}) \phi_{l\mathbf{k}'}^*(\mathbf{r}') \phi_{j\mathbf{k}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}.$$

LR

Exchange-correlation functionals

Using the linear-response operator

$$\chi(\mathbf{r},\mathbf{r}') \equiv \frac{\delta n(\mathbf{r})}{\delta v_{\mathsf{s}}(\mathbf{r}')}$$
$$= \sum_{i}^{\text{occ}} \sum_{j}^{\text{unocc}} \frac{\phi_i^*(\mathbf{r})\phi_j(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j} + \text{c.c.}$$

we have

$$\frac{\delta v_{\mathsf{s}}(\mathbf{r}')}{\delta n(\mathbf{r})} = \tilde{\chi}^{-1}(\mathbf{r},\mathbf{r}').$$

basis

Exchange-correlation functionals

Exact exchange is NOT

- Hartree-Fock
- a mean-field theory
- an attempt to solve the quasi-particle equation
- a parameterised correction to LDA
- easy to implement

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Practicalities

Pseudopotentials (PP)

- atomic core is frozen and represented by a non-local potential
- does not react properly to the solid state environment: no relaxation of core states
- planewaves are used as the basis

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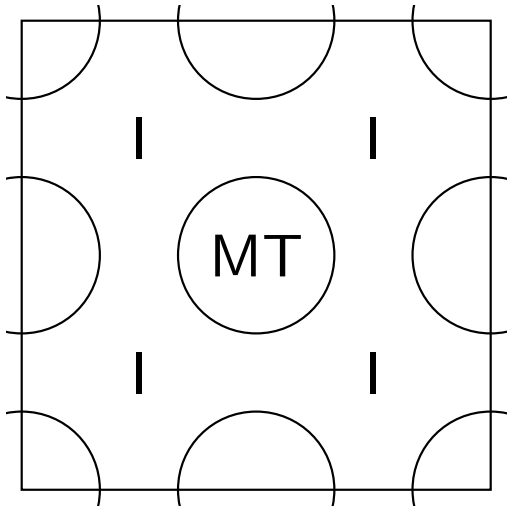
Practicalities

Full-potential linearised augmented planewaves (FP-LAPW)

- includes core orbitals
- potential is fully described
- space divided into muffin-tin and interstitial regions
- most precise method available



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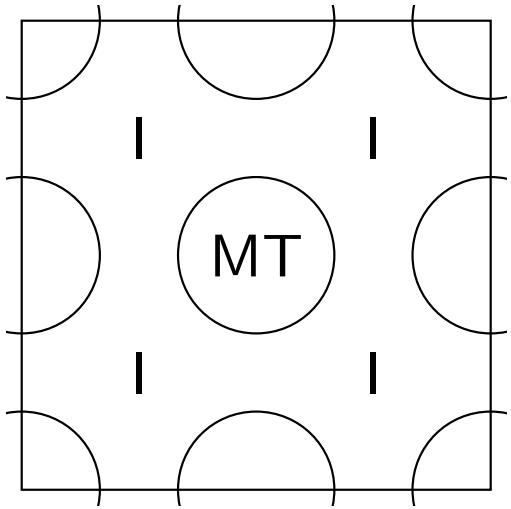

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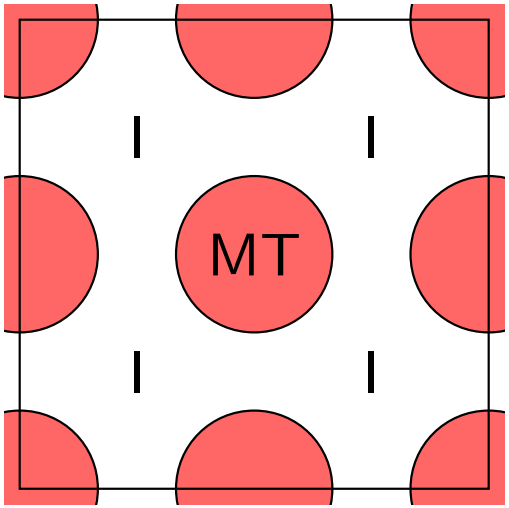

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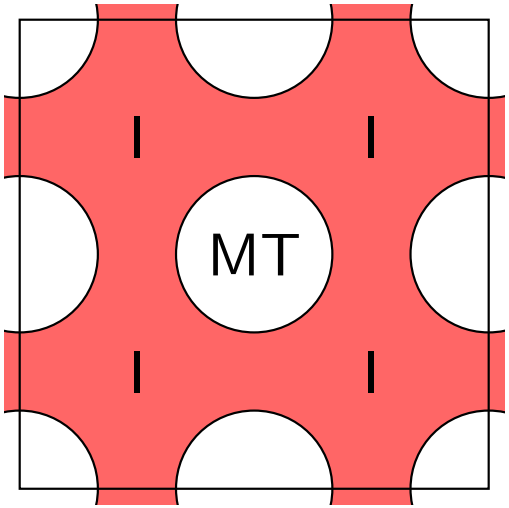

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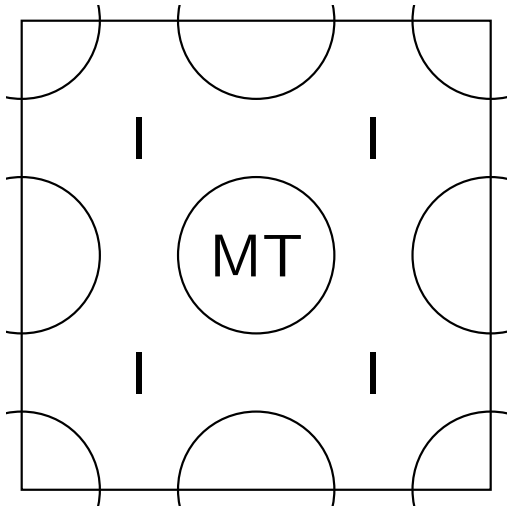

Practicalities

Basis set

- An efficient basis set is required so that the response

$$\chi(\mathbf{r},\mathbf{r}') \equiv \frac{\delta n(\mathbf{r})}{\delta v_{\mathrm{s}}(\mathbf{r}')}$$

  can be inverted

- Basis set should not contain constant functions

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Practicalities

Choose the overlap densities

$$\rho_\alpha(\mathbf{r}) \equiv \phi^*_{i\mathbf{k}}(\mathbf{r})\phi_{j\mathbf{k}}(\mathbf{r}),$$

and complex conjugates, where $\alpha \equiv (i\mathbf{k}, j\mathbf{k})$.

Diagonalise

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and eliminate eigenvectors with small eigenvalues.

Practicalities

Find transformation matrix C such that if

$$\tilde{\rho}_\alpha(\mathbf{r}) = \sum_\beta C_\beta^\alpha \sum_\gamma v_\gamma^\beta \rho_\gamma(\mathbf{r})$$

then

$$\int d\mathbf{r}\ \tilde{\rho}_\alpha^*(\mathbf{r})\tilde{\rho}_\beta(\mathbf{r}) = \delta_{\alpha\beta}.$$

The matrix equation

$$CC^\dagger = \left(v^\dagger O v\right)^{-1}$$

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By construction $\int d\mathbf{r}\ \tilde{\rho}_\alpha(\mathbf{r}) = 0$, so $\{\tilde{\rho}_\alpha\}$ form an ideal basis for inversion of χ

Practicalities

NL Lastly, given $\mathbf{q} \equiv \mathbf{k} - \mathbf{k}'$, the long range coulomb term of the NL matrix elements

$$\langle \phi_{i\mathbf{k}} | \hat{v}_{\mathrm{x}}^{\mathrm{NL}} | \phi_{j\mathbf{k}} \rangle_{\mathrm{LR}} = \sum_{l\mathbf{q}}^{\mathrm{occ}} w_{\mathbf{q}} \frac{4\pi\Omega}{q^2} \rho_{il}^*(\mathbf{q}) \rho_{lj}(\mathbf{q}),$$

where $\rho_{il}(\mathbf{q})$ and $\rho_{lj}(\mathbf{q})$ are the pseudo-charge densities.

Poor convergence with respect to the number of q-points.

Approximate it by an integral over a sphere of volume equivalent to that of the BZ

$$\langle \phi_{i\mathbf{k}} | \hat{v}_{\mathrm{x}}^{\mathrm{NL}} | \phi_{j\mathbf{k}} \rangle_{\mathrm{LR}} \simeq 2 \left(\frac{6\Omega^5}{\pi} \right)^{1/3} \sum_{l\mathbf{q}}^{\mathrm{occ}} w_{\mathbf{q}} \rho_{il}^*(\mathbf{q}) \rho_{lj}(\mathbf{q}).$$

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Applications

EXX Applied to

1. Magnetic metals
2. Semiconductors and insulators

Magnetic metals: introduction to the problem

Magnetic moment in Bohr magneton

Compound	FP-LDA	Experiment
FeAl	0.71	0.0

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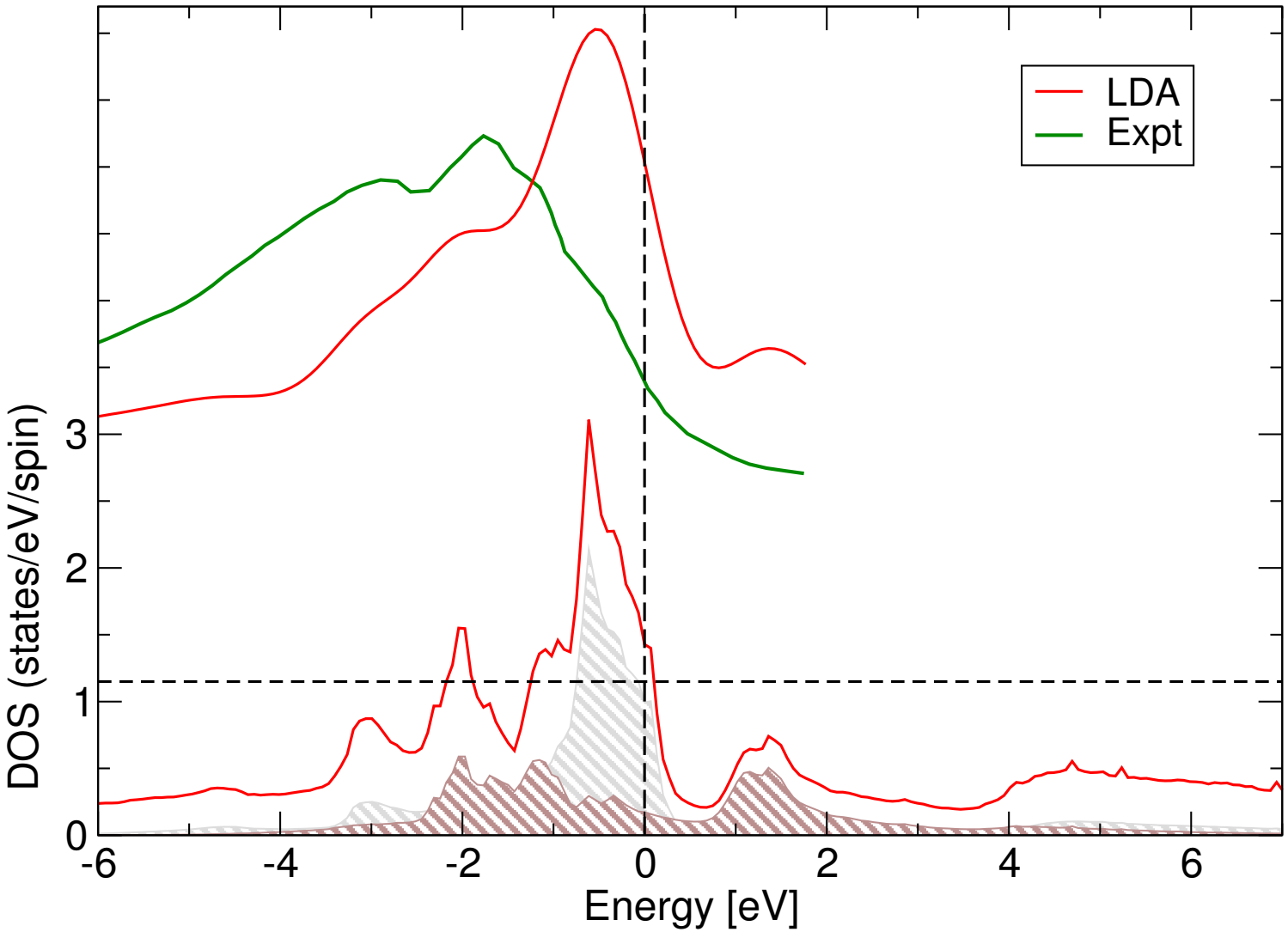

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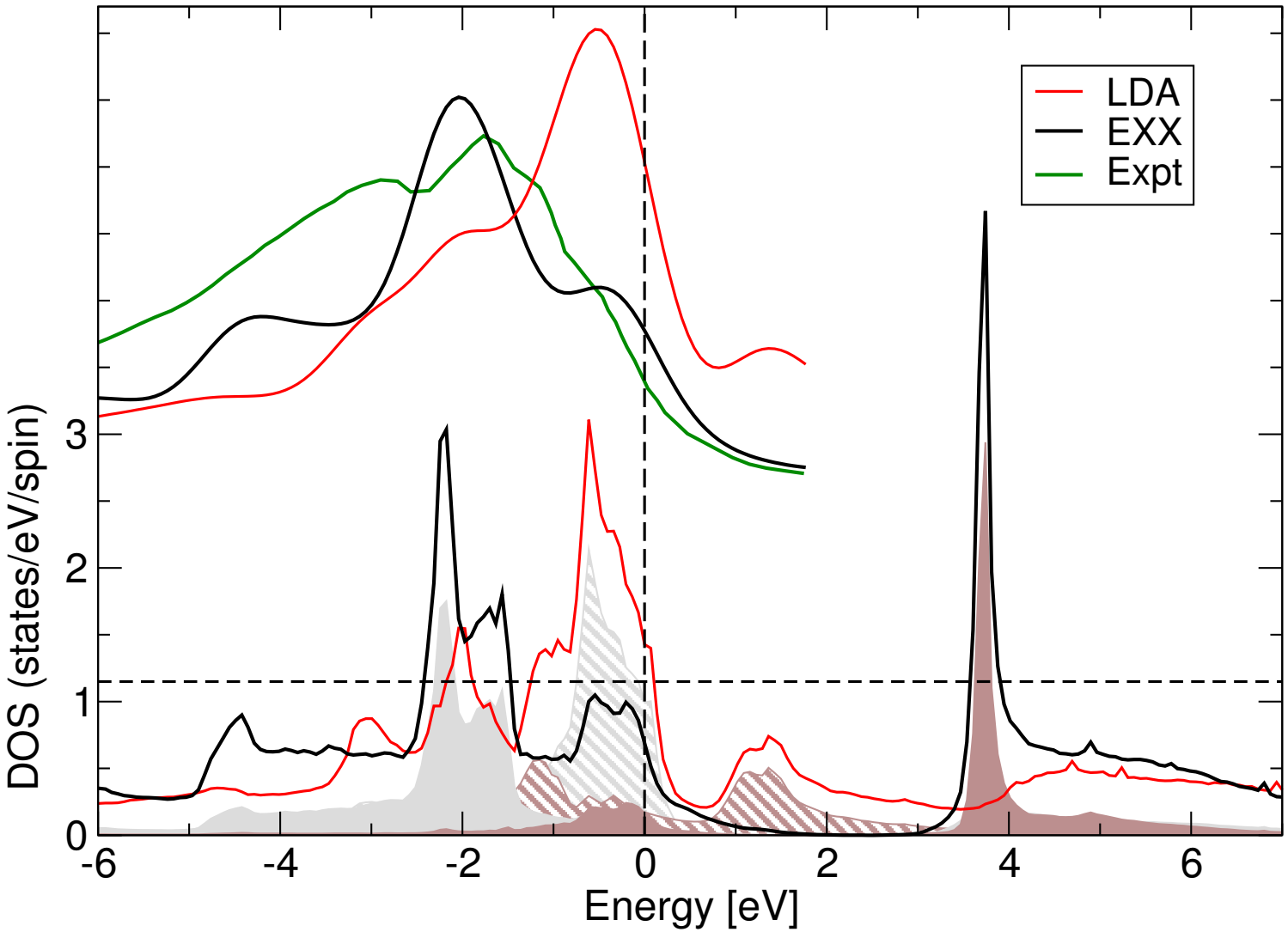

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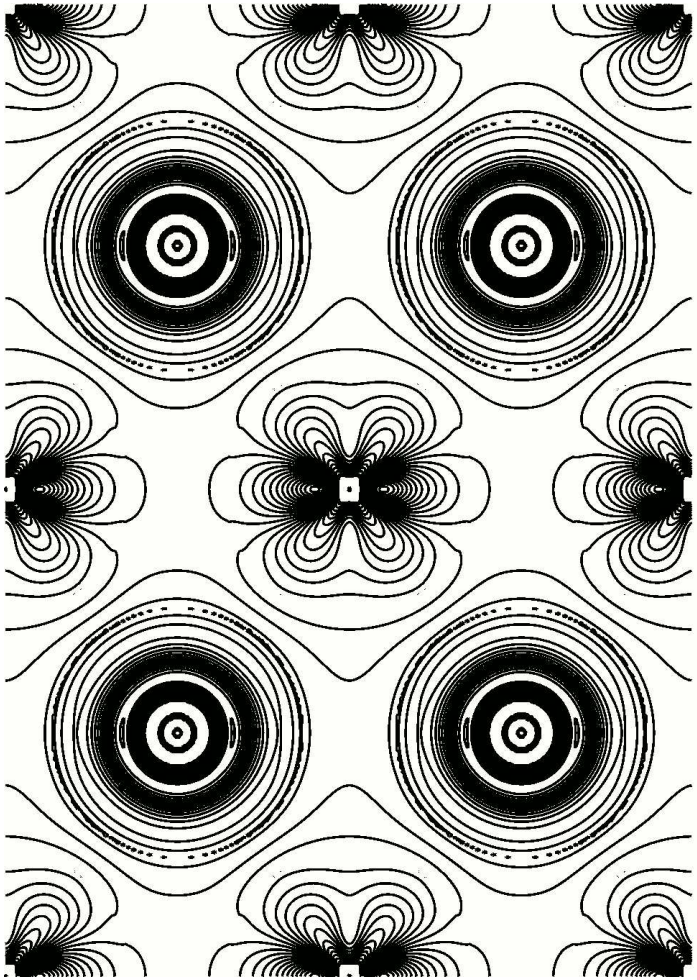

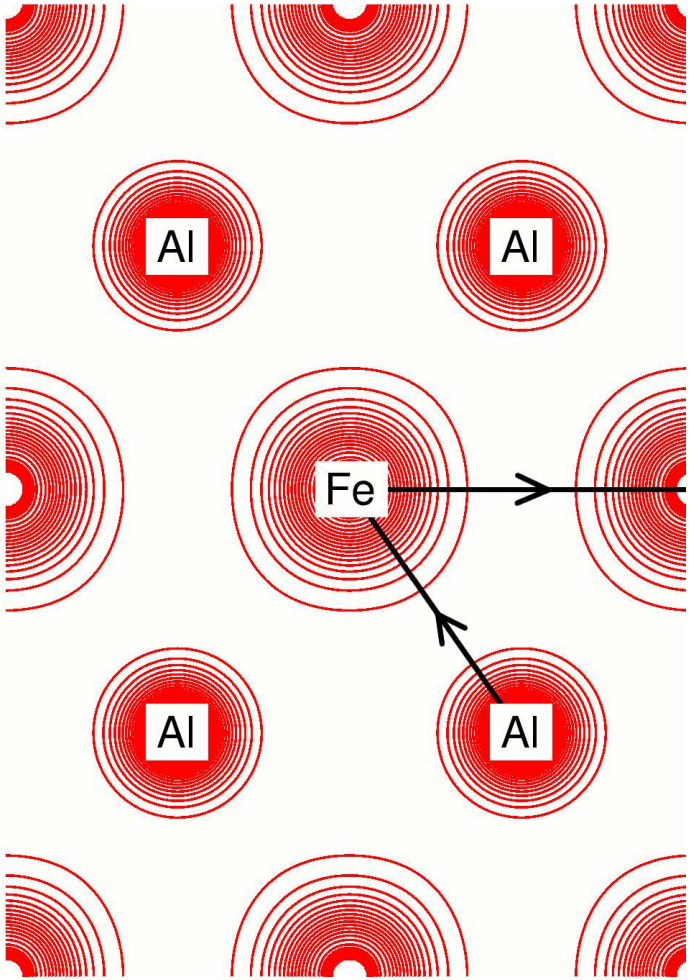

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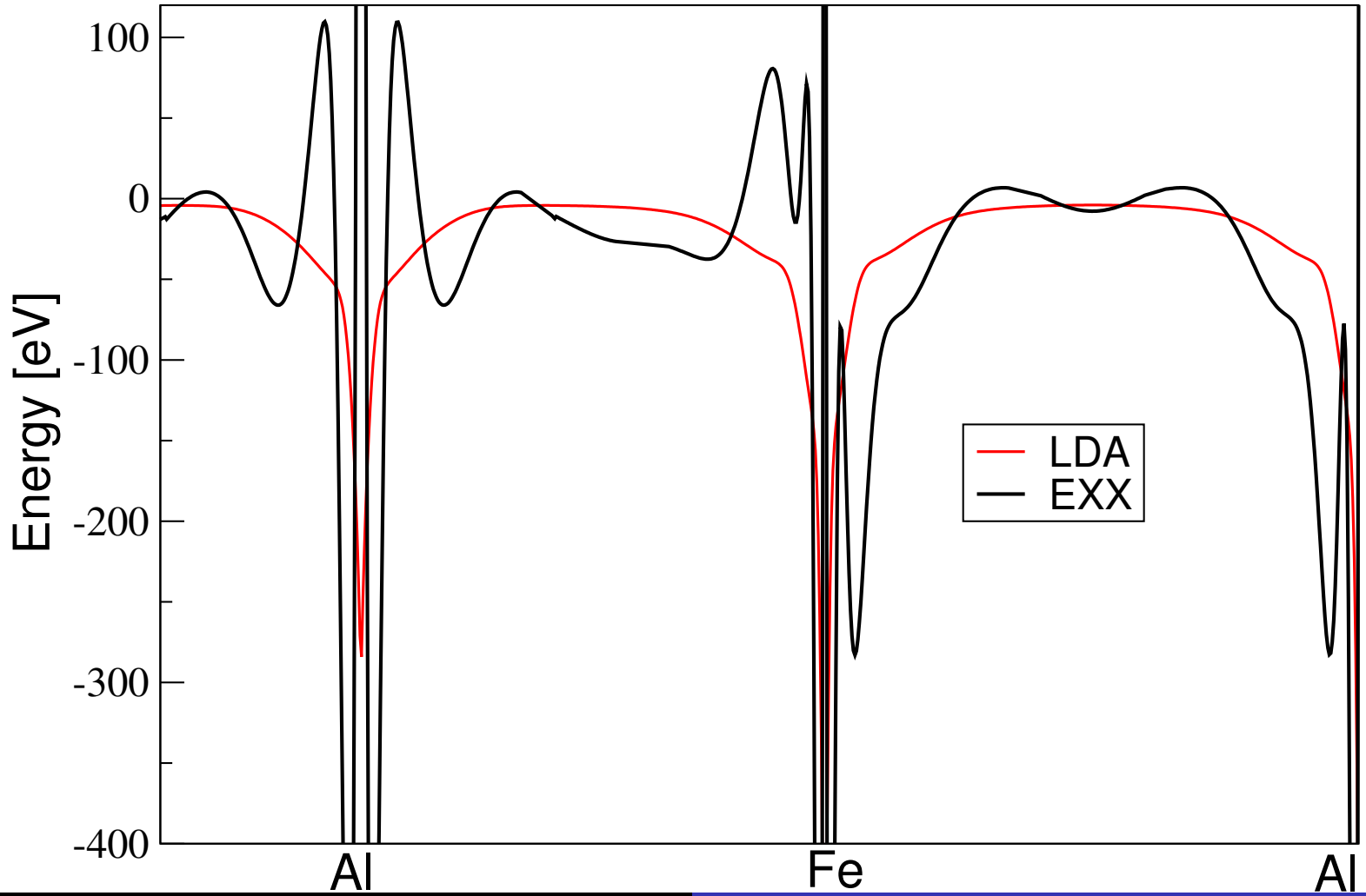

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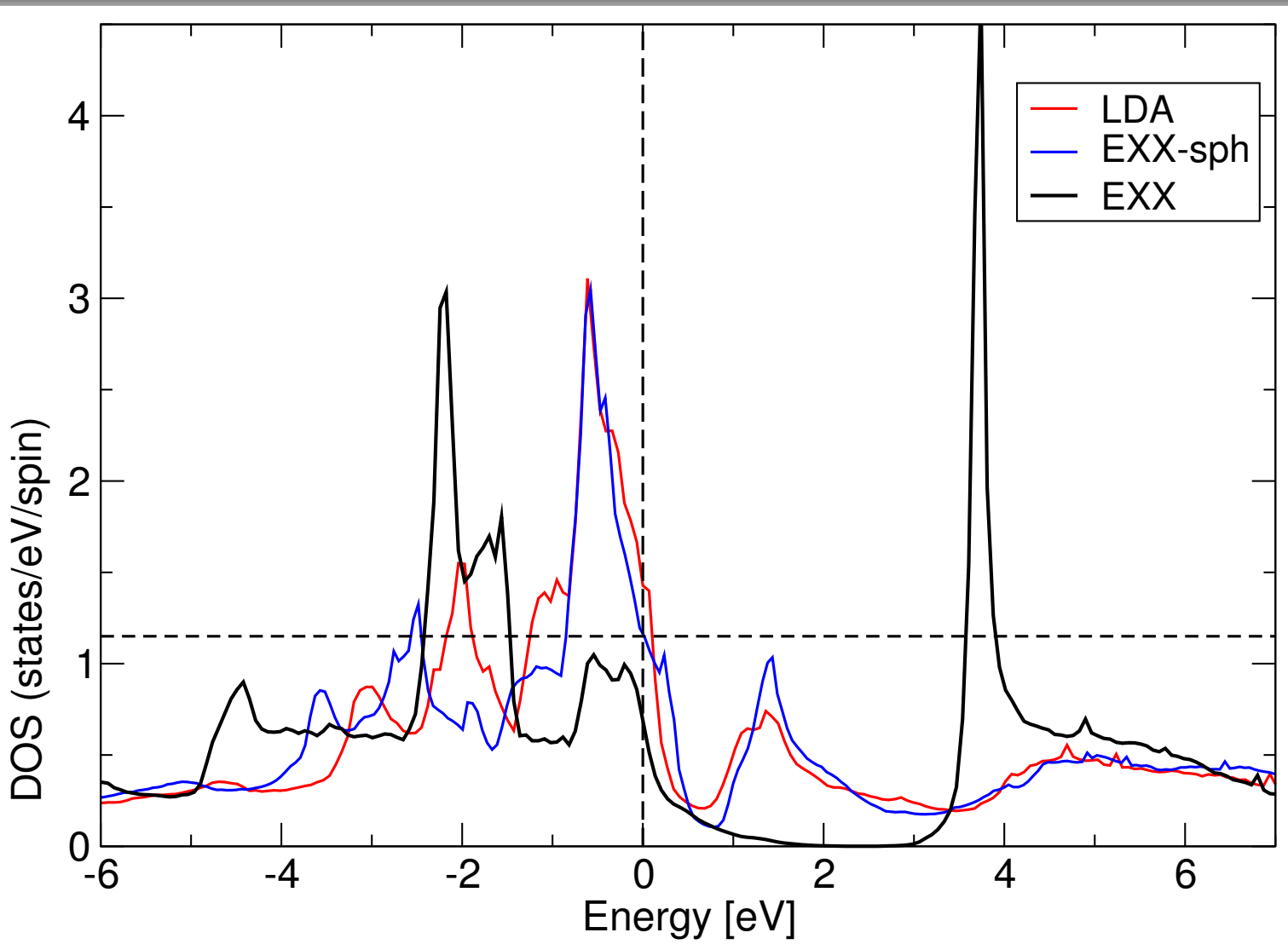

Magnetic metals: stringent tests for EXX

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Ni_3Ga	0.79	?	0.0
Ni_3Al	0.70	?	0.23

http://arxiv.org/abs/cond-mat/0501258

Magnetic metals: FeAl, Ni_3Ga and Ni_3Al

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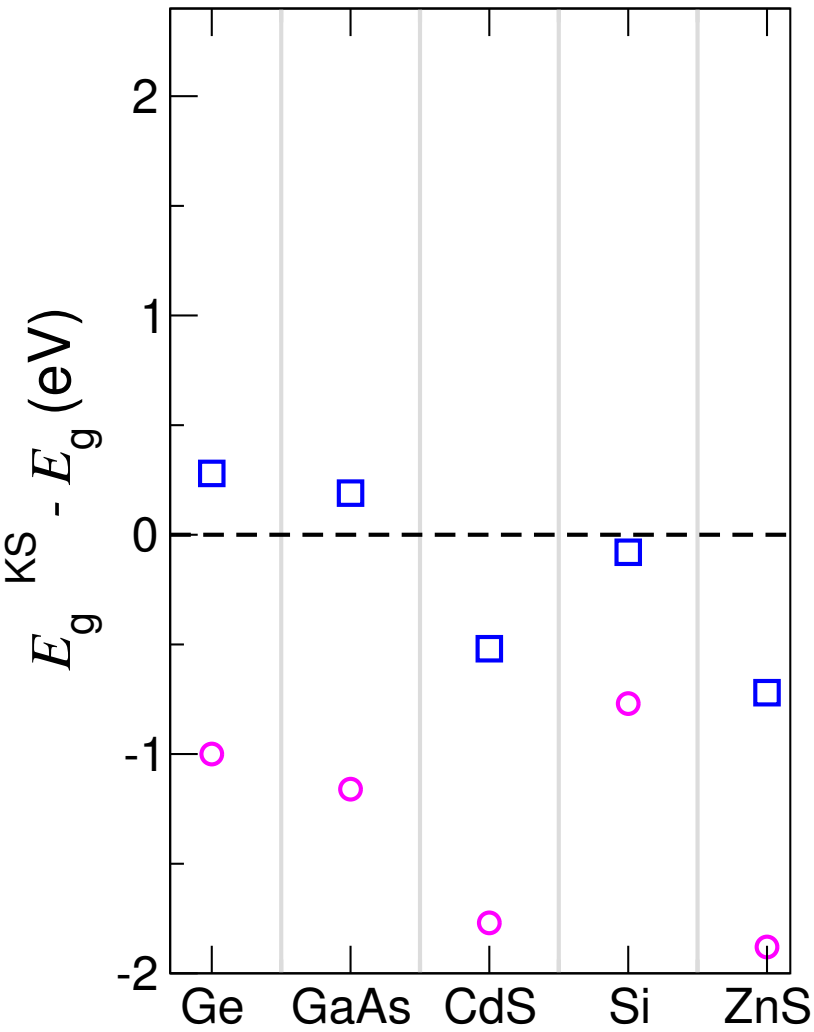
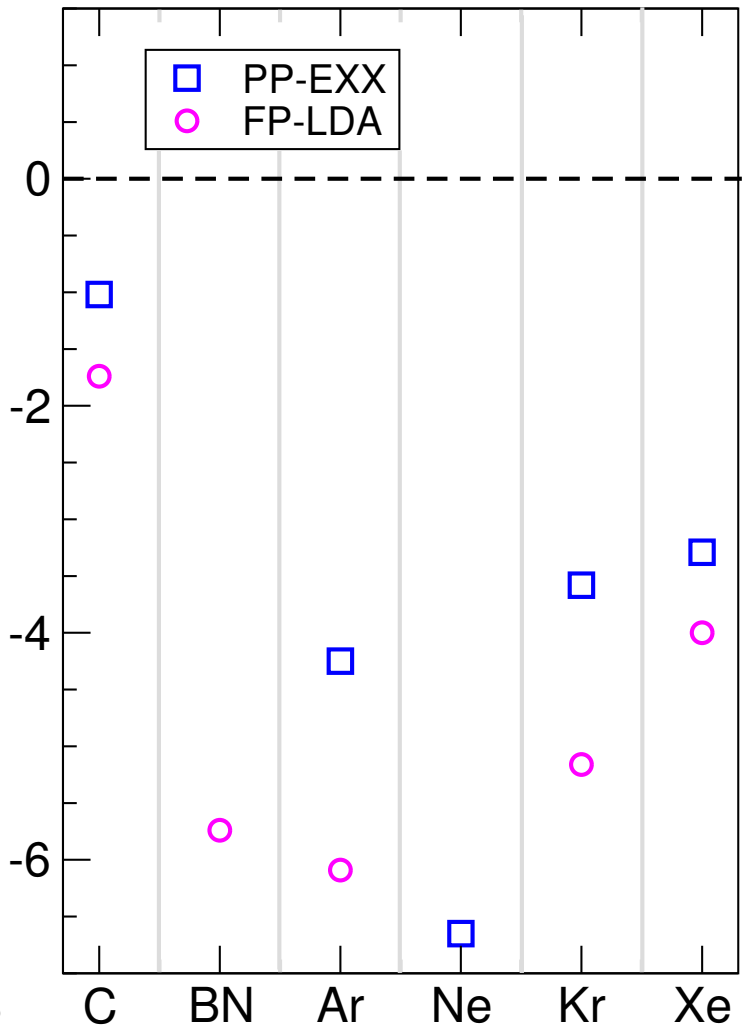
Semiconductors and insulators: band-gaps

PP-EXX : Städele et al. PRB 59 10031



PP-EXX: Magyar et al. PRB 69 045111



The fundamental band-gap for materials:

$$E_g = A - I = (E_{N+1} - E_N) - (E_N - E_{N-1})$$

$$E_g = \frac{\delta E}{\delta n^+} - \frac{\delta E}{\delta n^-}$$

$$E[n] = T[n] + U_{\mathsf{s}}[n] + E_{\mathsf{xc}}[n]$$

$$E_g = \left(\frac{\delta T}{\delta n^+} - \frac{\delta T}{\delta n^-}\right) + \left(\frac{\delta v_{\mathsf{xc}}}{\delta n^+} - \frac{\delta v_{\mathsf{xc}}}{\delta n^-}\right)$$

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$$E[n] = T[n] + U_{\mathsf{s}}[n] + E_{\mathsf{xc}}[n]$$

$$E_g = \left(\frac{\delta T}{\delta n^+} - \frac{\delta T}{\delta n^-}\right) + \left(\frac{\delta v_{\mathsf{xc}}}{\delta n^+} - \frac{\delta v_{\mathsf{xc}}}{\delta n^-}\right)$$

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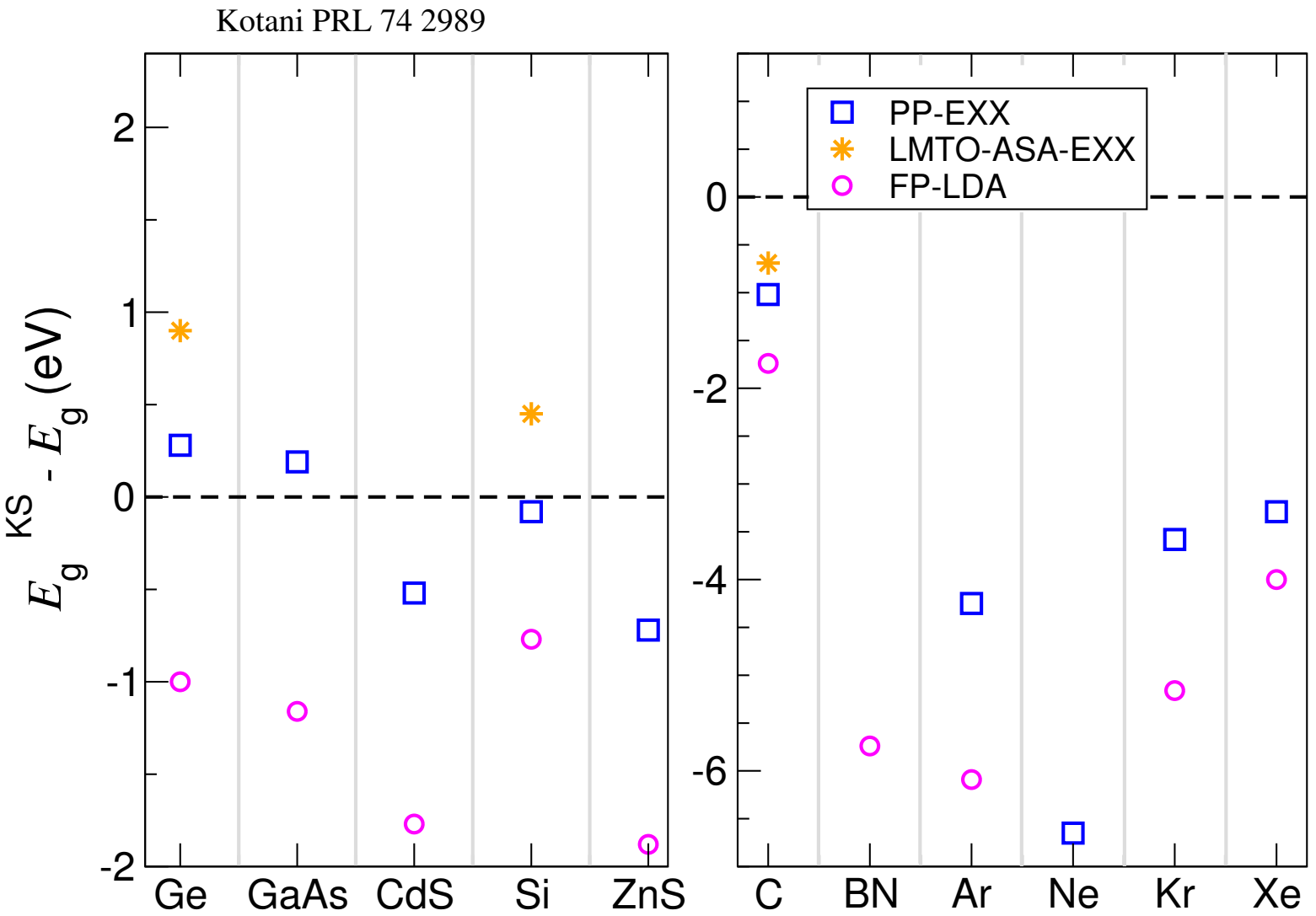
Semiconductors and insulators: band-gaps



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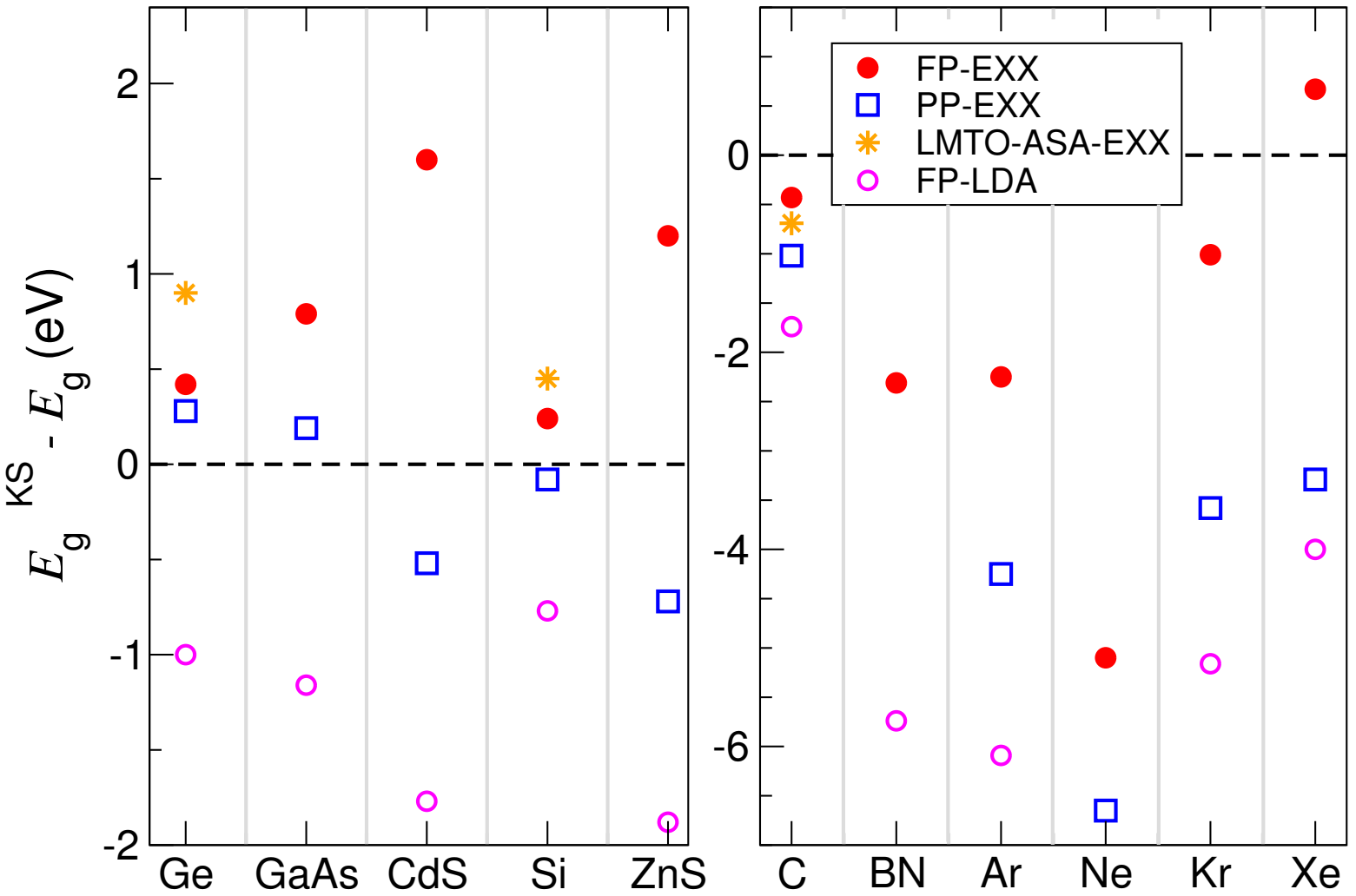

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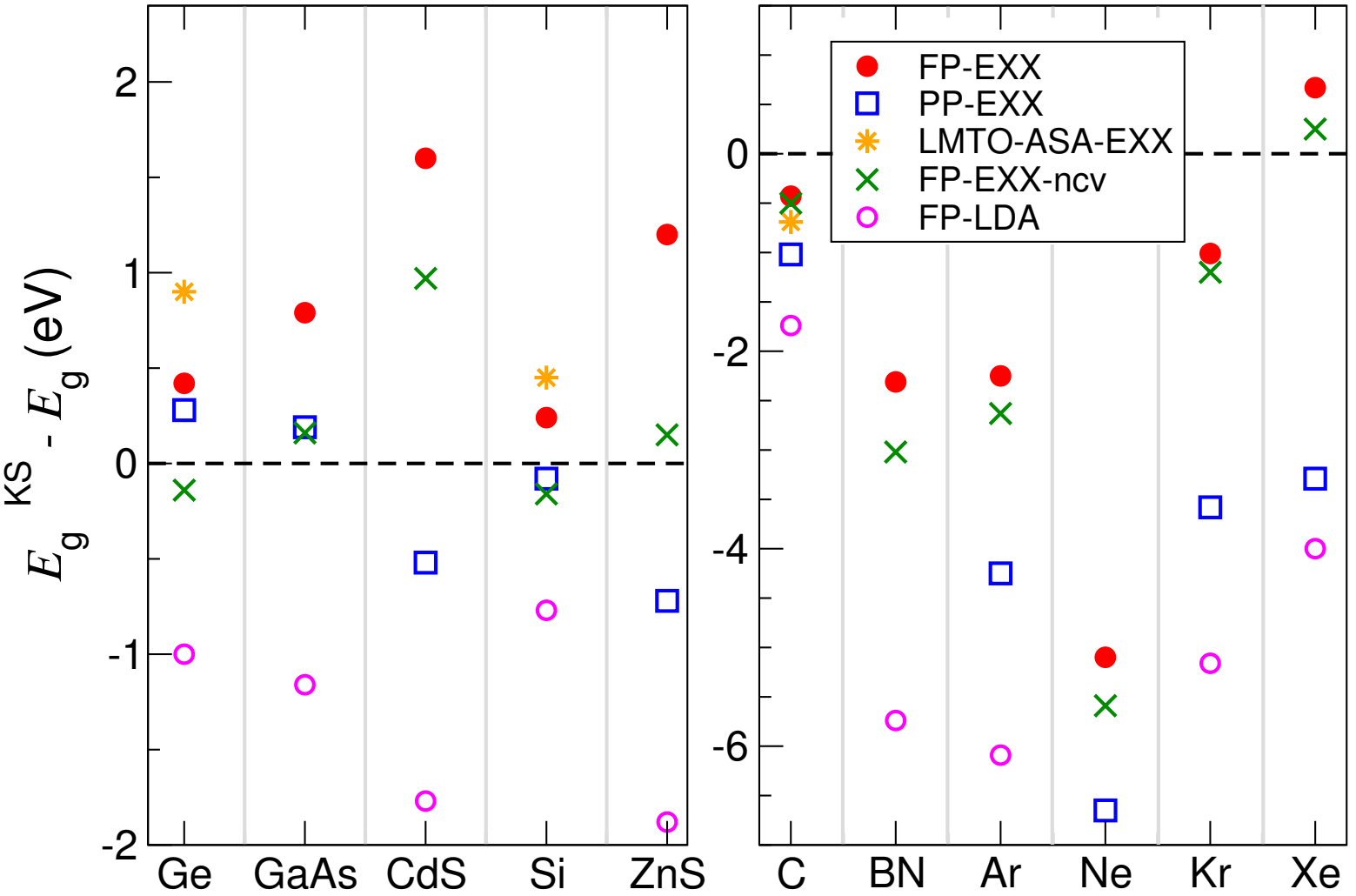
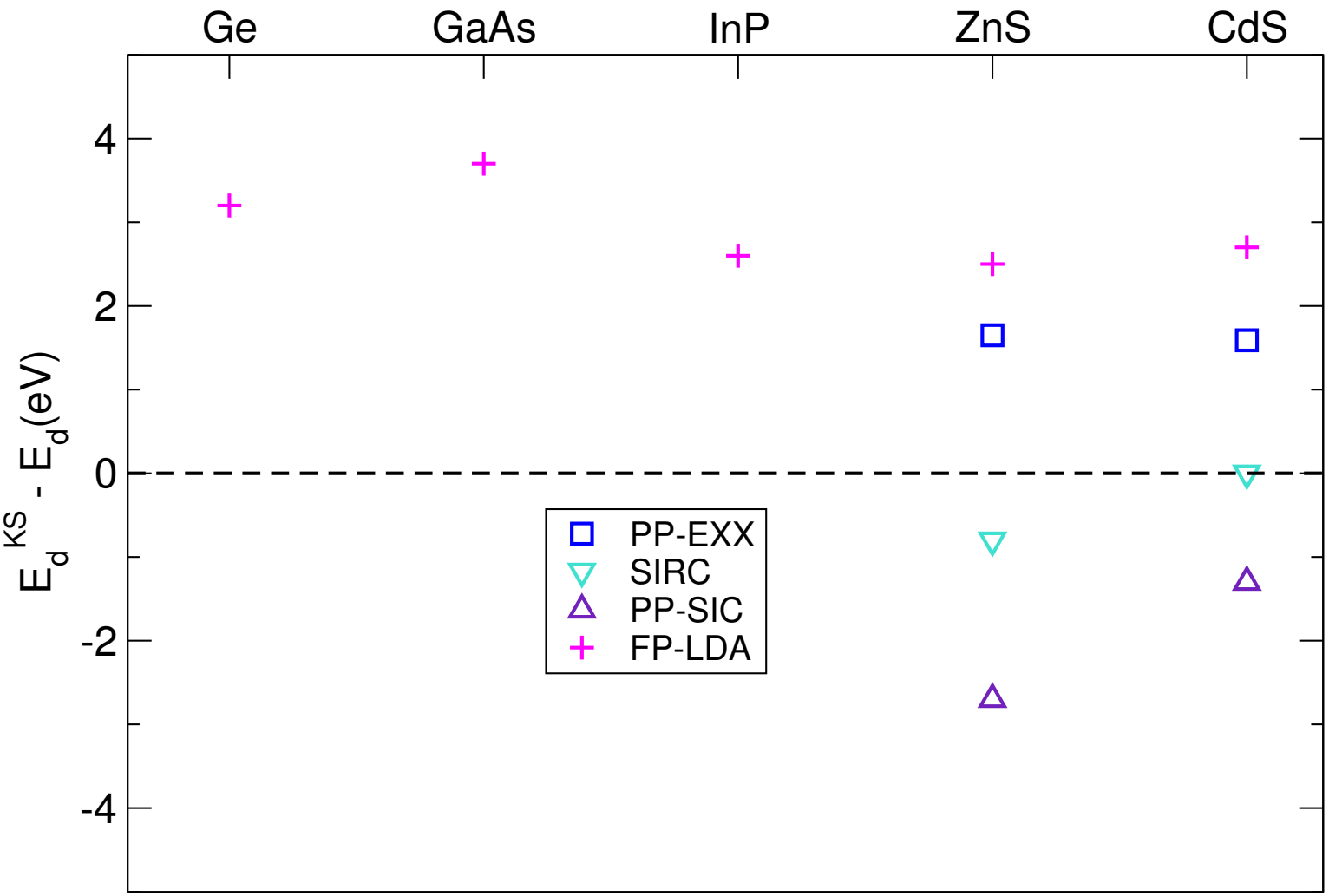
http://arxiv.org/abs/cond-mat/0501353



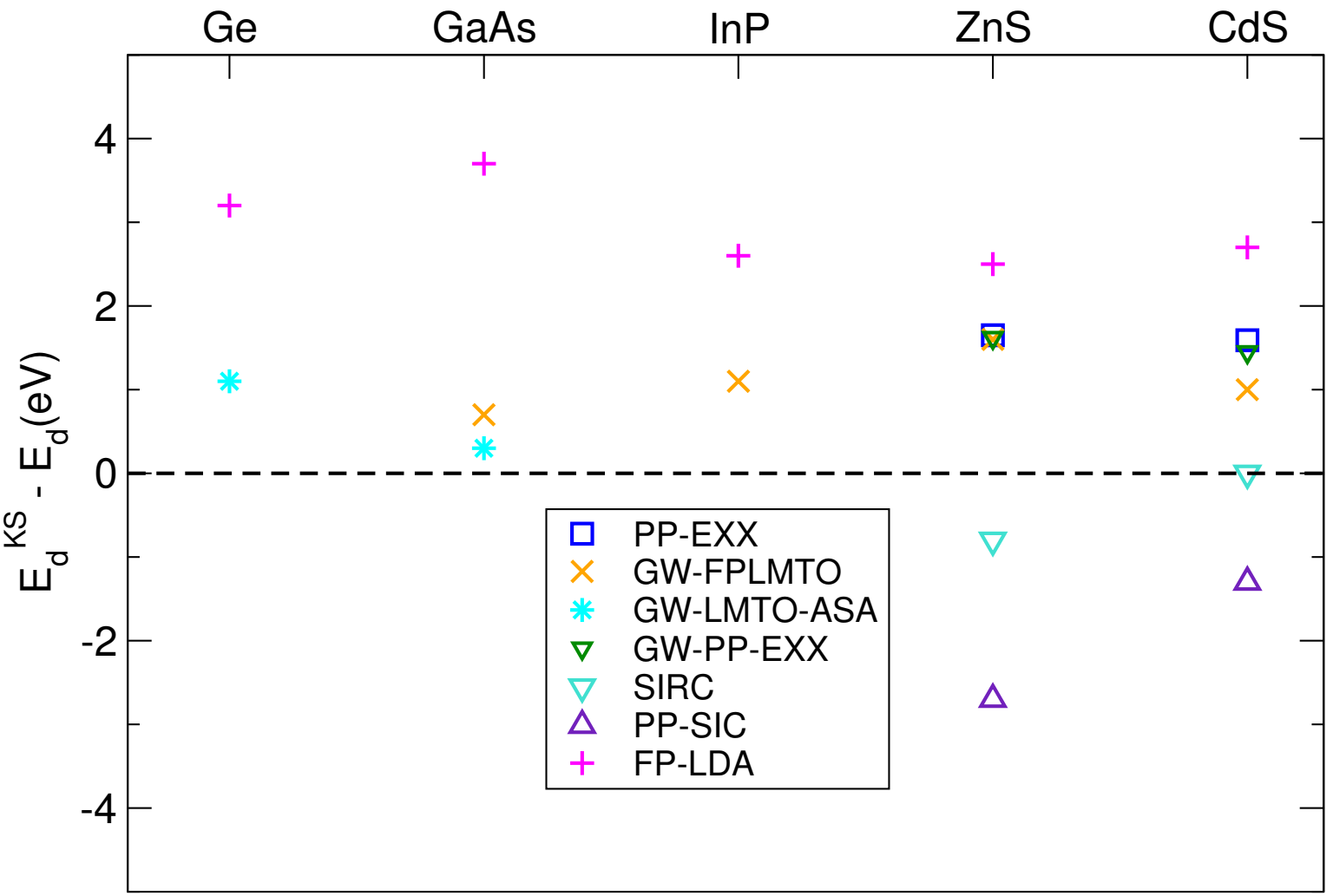
Semiconductors and insulators: d-band position



SIC: Vogle et al. PRB 54 5495

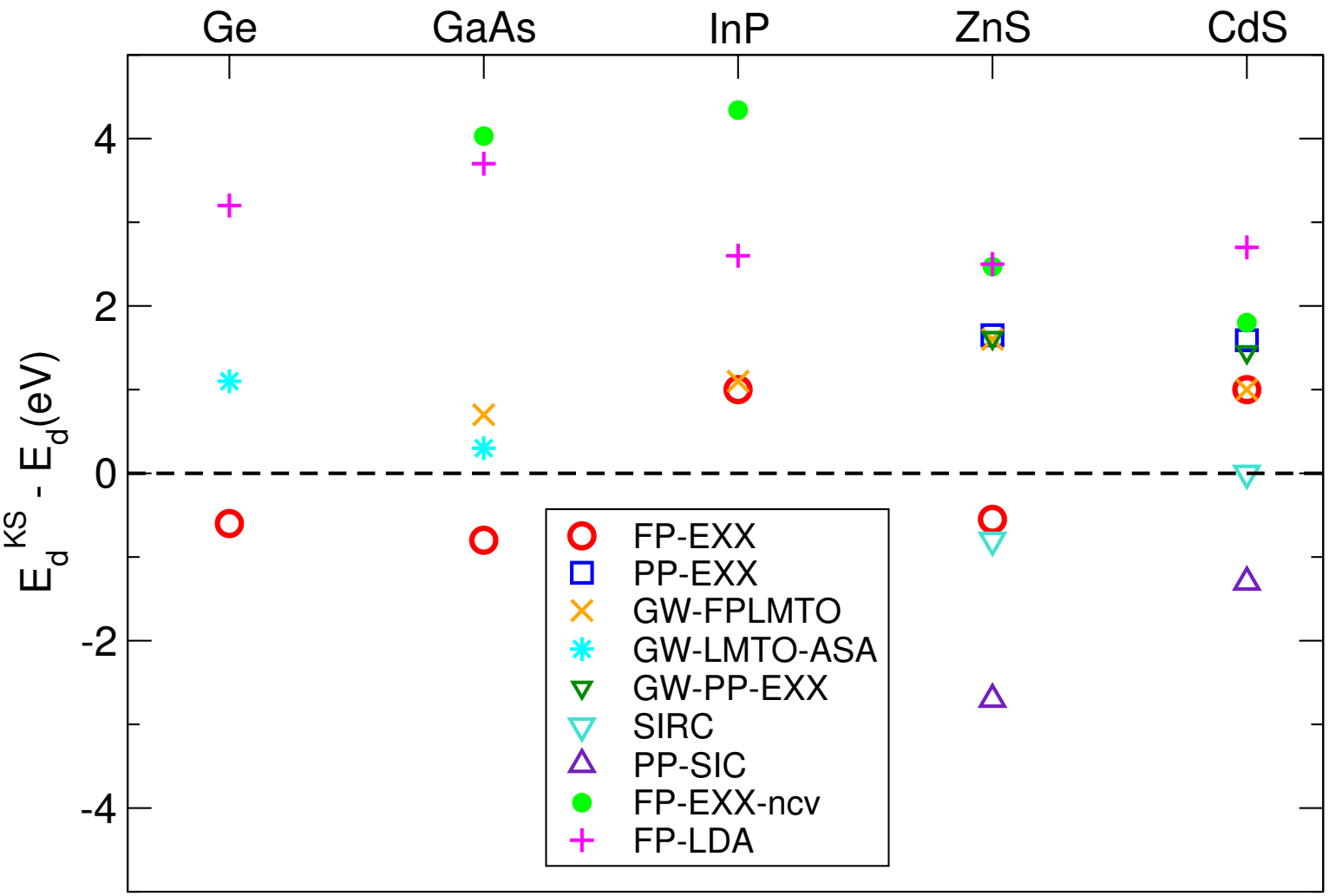
PP-EXX: Rinke et al. (unpublished)

Semiconductors and insulators: d-band position



GW LMTO-ASA: Aryasetiawan et al. PRB 54 17564 FPLMTO: Kotani et al. SSC 121

Semiconductors and insulators: d-band position



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Conclusions

1. EXX within an all electron full potential method is implemented within **EXC!TING** code. Right now this is the only FP code to be able to do EXX.
2. A new and one of the most optimal basis is proposed for calculating and inverting the response. This basis may be useful for future TD-DFT and GW calculations.
3. Magnetic metals: **Asymmetry** in exchange potential is very important to get the correct ground-state.
4. Semiconductors and insulators: **Core-valence interaction** is crucial for correct treatment of the EXX.
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Code available at:
http://physik.kfunigraz.ac.at/~kde/secret_garden/exciting.html