Introduction to exciting

Claudia Draxl, HU Berlin

The most exciting code

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone,
S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl
J. Phys: Condens. Matter **26**, 363202 (2014).

exciting

a full-potential all-electron package implementing linearized augmented planewave methods

DOWNLOAD FORUM

About exciting

exciting is a full-potentia
density-functional-theory p
implementing linearized aug
planewave methods. It can b
all kinds of materials, irresp
atomic species involved and
exploring the physics of core electrons.
As the name tells, exciting has a
particular focus on excitations.

READ MORE

- Iterative eigensolver
- Speedy BSE

DEVELOPMENT TEAM

GET STARTED

exciting is a full-potential all-electron density-functional-theory package implementing the families of linearized augmented planewave methods. It can be applied to all kinds of materials, irrespective of the atomic species involved, and also allows for exploring the physics of core electrons. A particular focus are excited states within many-body perturbation theory.

http://exciting-code.org

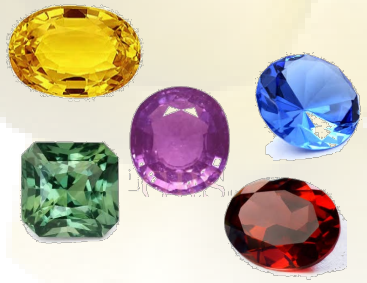
What limits us?

Many materials and/or properties require methods better than semi-local DFT

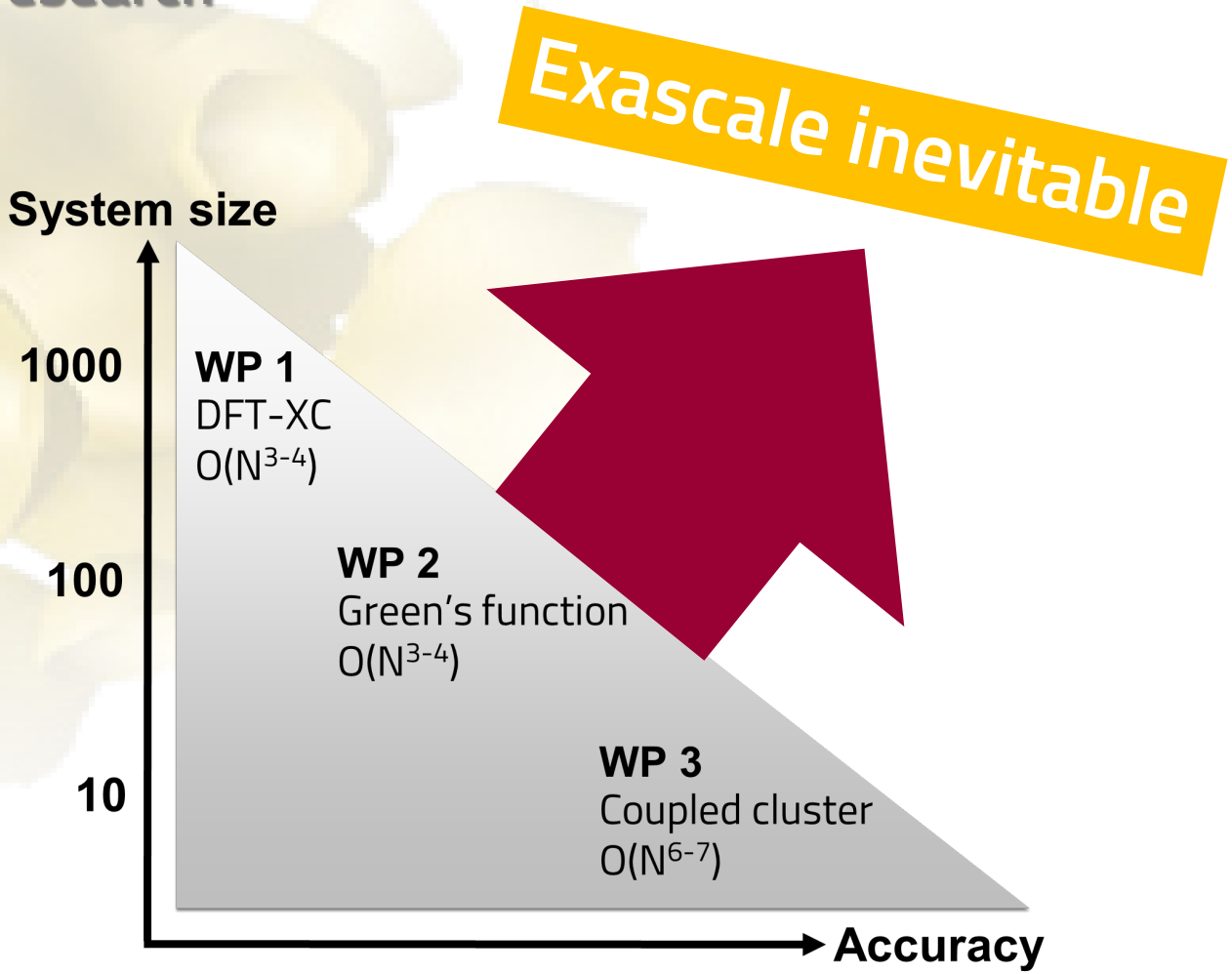
Basically everything relevant for energy research

Complex systems require larger simulation cells

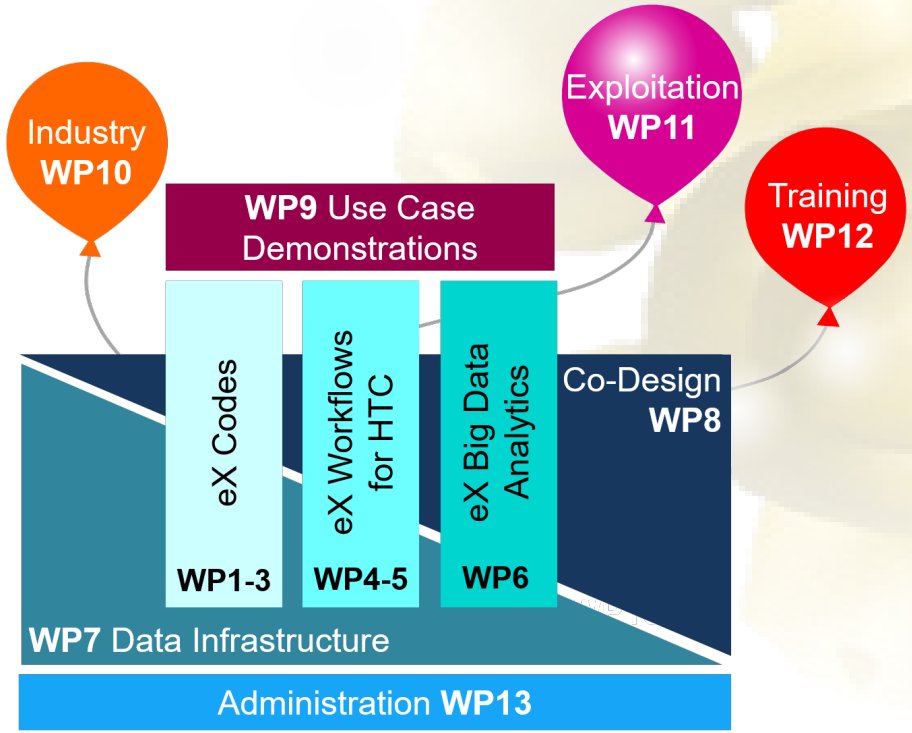
1 atom out of thousand(s) may determine the color



... and/or better methodology



NOMAD CoE



Exascale Codes

- Bringing DFT, Green-function methods, and coupled-cluster theory to exascale
- Supporting entire code families, covering planewaves (PW), linearized augmented PWs, and atom-centred orbitals
- NOMAD demonstrator codes

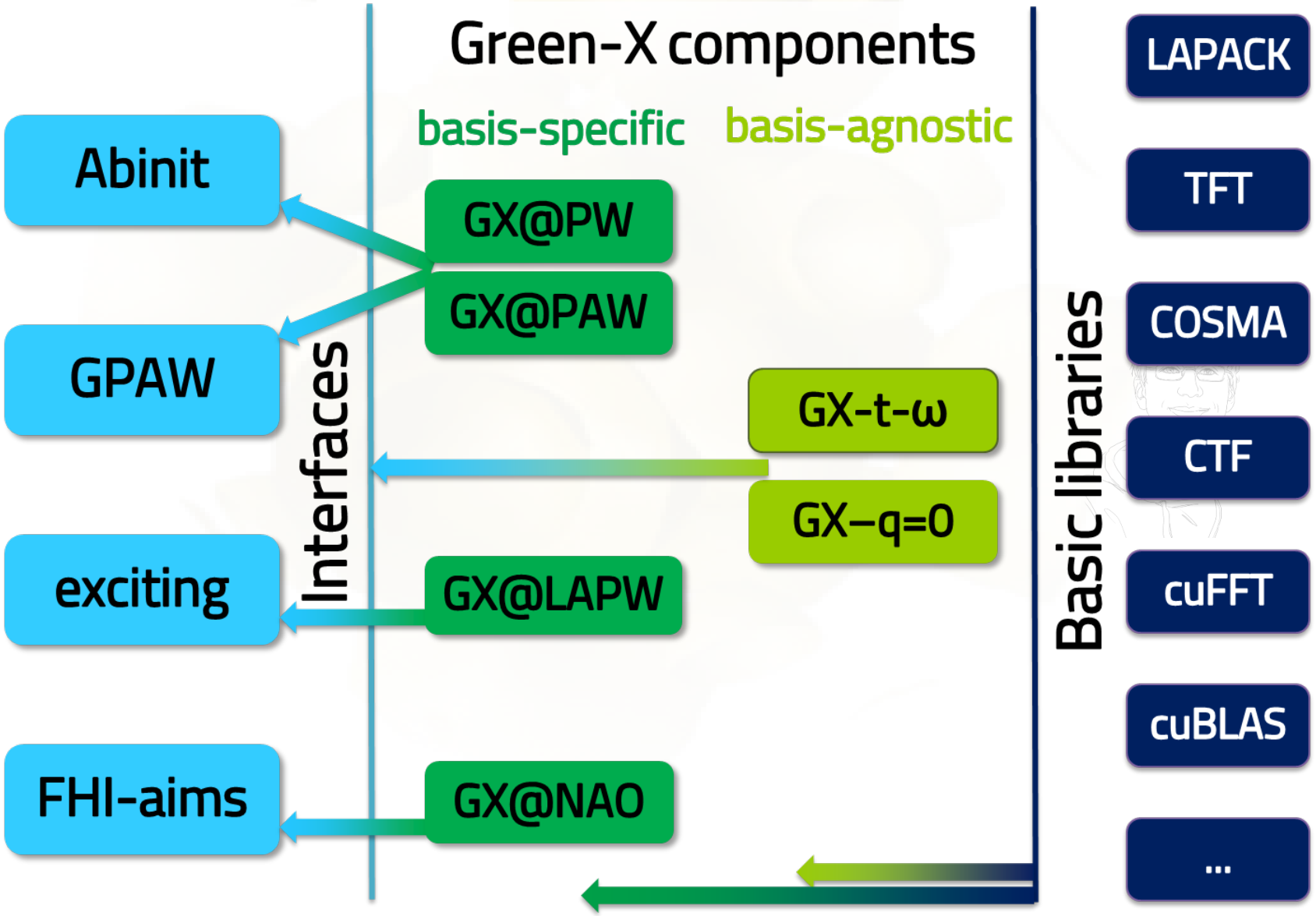
LEARN MORE

NOMAD CoE receives funding from the European Union's Horizon program under the grant agreement Nº 951786.

Our libraries

Example

Green-X



Our demonstrator codes

Representative for code families

Abinit

Pseudopotential

Planewave basis

exciting

All-electron

LAPW+lo basis

FHI-aims

The ab initio materials simulation package

All-electron

Atom-centered orbital basis

GPAW!

Pseudopotential / PAW

Real-space grid

Main developers in the team

The most exciting code

Kohn-Sham equation

$$\left[-\nabla^2 + V_{eff}(\mathbf{r})\right]\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

Ritz variational principle

$$\psi(\mathbf{r}) = \sum_n c_n \phi_n(\mathbf{r})$$

Matrix form

$$\boxed{\sum_{n'} \left(H_{n,n'} - \varepsilon_n S_{n,n'}\right) c_{n'} = 0}$$

$$H_{n,n'} \equiv \langle \phi_n | -\nabla^2 + V_{eff} | \phi_{n'} \rangle \qquad S_{n,n'} \equiv \langle \phi_n | \phi_{n'} \rangle$$

Augmented-planewave methods ....

APW

LAPW

SLAPW-3, SLAPW-4, ...

LAPW + LO

APW + lo

APW + lo + LO

"LAPW"

All these methods linearize the eigenvalue problem

$$\sum_{n'} \left(H_{n,n'} - \varepsilon_n S_{n,n'} \right) c_{n'} = 0$$

The best of two worlds …

The best of two worlds

Dual basis

Atomic spheres α, β

Atomic-like basis functions

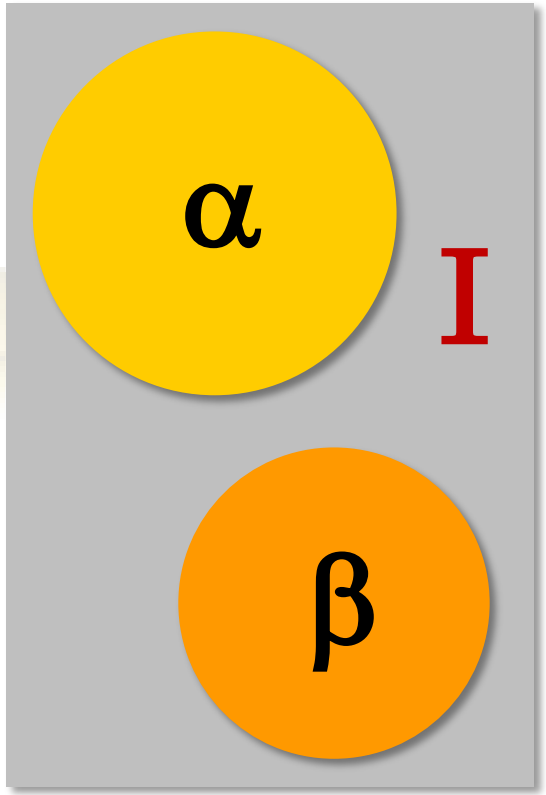
Interstitial I

Planewave basis

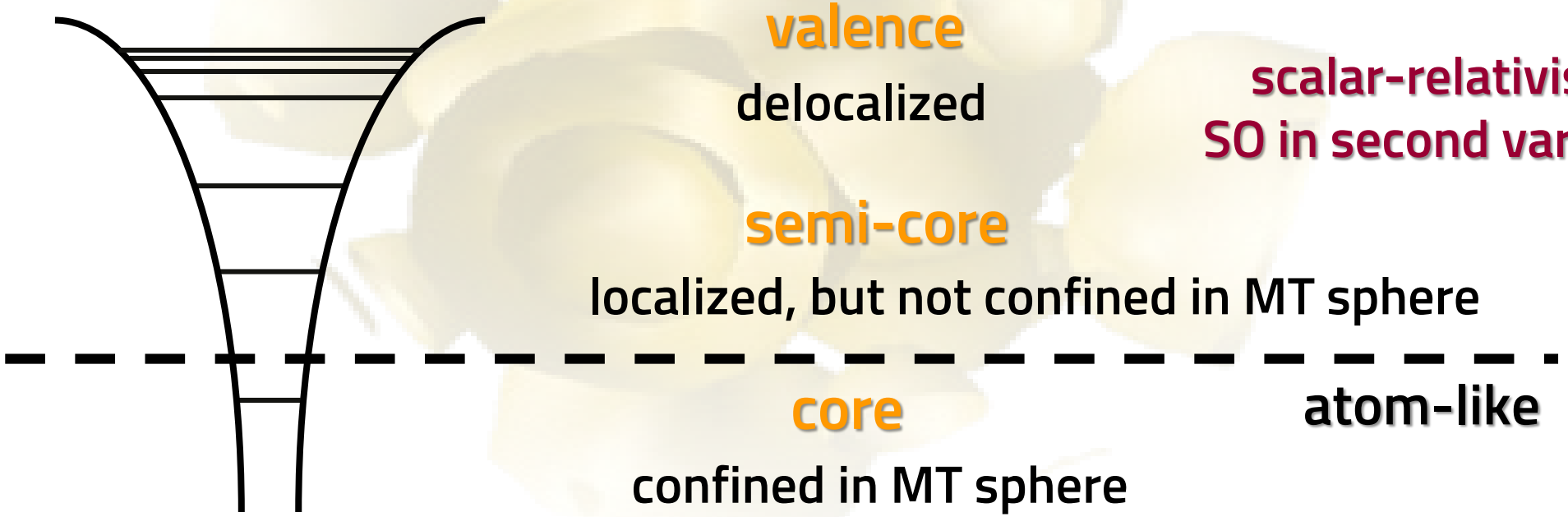
All-electron method

Can handle strong variations

Can explore the core region



All-electron description



valence

delocalized

scalar-relativistic
SO in second variation

semi-core

localized, but not confined in MT sphere

core

confined in MT sphere

atom-like

Dirac equation

A bit of history …

The APW basis set

J. C. Slater, Phys. Rev. 51, 834 (1937).
Adv. Quant. Chem. 1, 35 (1964).

Augmented planewaves

I

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

basis continuous
at sphere boundary R_{MT}

α

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{lm} A^\alpha_{lm}(\mathbf{k}+\mathbf{G}) u^\alpha_l(r, E) Y_{lm}(\hat{\mathbf{r}})$$

solutions of the radial Schrödinger equation

$$\left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V^\alpha(r) - E \right\} r\, u^\alpha_l(r, E) = 0$$

What determines the size of the basis?

Each planewave living in the interstitial is augmented

by atomic-like functions inside each sphere

Large muffin-tin sphere

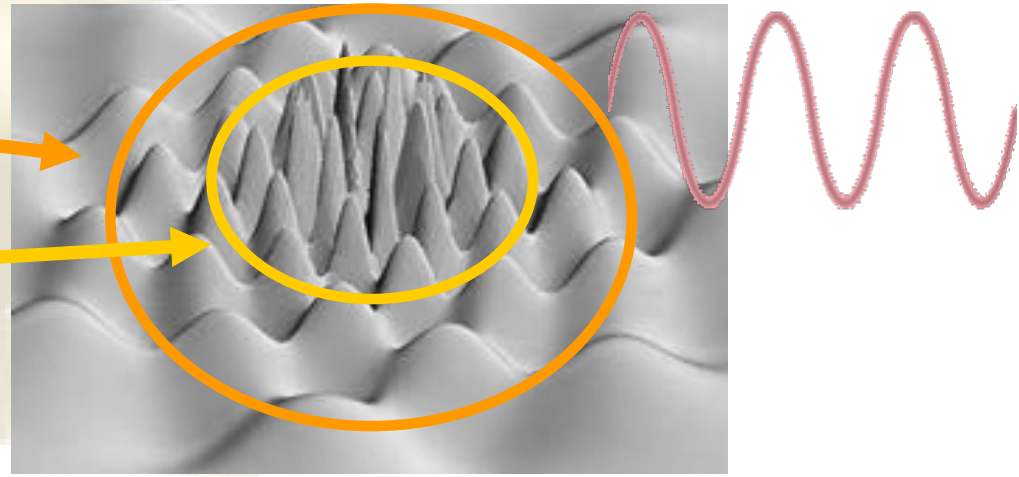
few planewaves

Small sphere size

many planewaves

The product $R_{MT}G_{max}$

is a good measure for a converged basis



APW: advantages & drawbacks

E has to be the exact KS eigenvalue

E is a variational parameter

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{lm} A^\alpha_{lm}(\mathbf{k}+\mathbf{G}) u^\alpha_l(r,E) Y_{lm}(\hat{\mathbf{r}})$$

Energy-dependent basis

Non-linear eigenvalue problem

$$\sum_{n'} \left(H_{n,n'} - \varepsilon_n S_{n,n'}\right) c_{n'} = 0$$

Search for zeros of the determinant

No single diagonalization

Time-consuming

No full-potential method

BUT a true all-electron method!

Potential and density: dual basis

Potential

$$V_{eff}(\mathbf{r}) = \sum_{\mathbf{K}} V_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}}$$

I

$$V_{eff}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{LM} V^{\alpha}_{LM}(r) Y_{LM}(\hat{\mathbf{r}})$$

α

Density

$$\rho(\mathbf{r}) = \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}}$$

I

$$\rho(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{LM} \rho^{\alpha}_{LM}(r) Y_{LM}(\hat{\mathbf{r}})$$

α

The LAPW basis set

Linearized augmented planewave method

O. K. Andersen, Phys. Rev. B 12, 3060 (1975).
D. D. Kölling and G. O. Arbman, J. Phys. F 5, 2041 (1975).

I

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

basis continuous in value and slope at R_{MT}

energy derivative

α

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha+\mathbf{r}) = \sum_{lm} [A^\alpha_{lm}(\mathbf{k}+\mathbf{G}) u^\alpha_l(r, E_l) \qquad Y_{lm}(\hat{\mathbf{r}})$$

energy parameter

LAPW: advantages & drawbacks

E_l is a fixed parameter

Energy-independent basis set

Linear eigenvalue problem

$$\boxed{\sum_{\mathbf{G}'} (H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} - \varepsilon_{n\mathbf{k}} S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'}) c_{n\mathbf{k}}(\mathbf{G}') = 0}$$

No true all-electron method!

Only one principal quantum number per l

Radial SG does not depend on principal quantum number

$$\left\{ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V^{\alpha}(r) - E \right\} r\, u_l^{\alpha}(r, E) = 0$$

The problem ...

Example: Cu: $3p^6 3d^{10} 4s^1$

- 3p states not confined in the muffin-tin sphere
- 4p states needed to have a flexible basis set

Ways out

Two-window calculation

- Orthogonality problems

A better basis set

- Super LAPW (SLAPW)
- or better ...

The Super LAPW method

SLAPW-3

basis continuous up to 2nd derivative

α

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha+\mathbf{r}) = \sum_{lm}[A^\alpha_{lm}(\mathbf{k}+\mathbf{G})u^\alpha_l(r,E_l)+B^\alpha_{lm}(\mathbf{k}+\mathbf{G})\dot{u}^\alpha_l(r,E_l)+C^\alpha_{lm}(\mathbf{k}+\mathbf{G})u^\alpha_l(r,E_{lo})]Y_{lm}(\hat{\mathbf{r}})$$

different energy parameters

SLAPW-4

....

D. J. Singh and H. Krakauer, Phys. Rev. B 43, 1441 (1991).

SLAPW: advantages & drawbacks

All-electron method

Kinetic energy continuous

No surface terms needed

Costly: more basis functions needed

Roughly 50% larger basis set

Why?

Radial functions in APW & LAPW

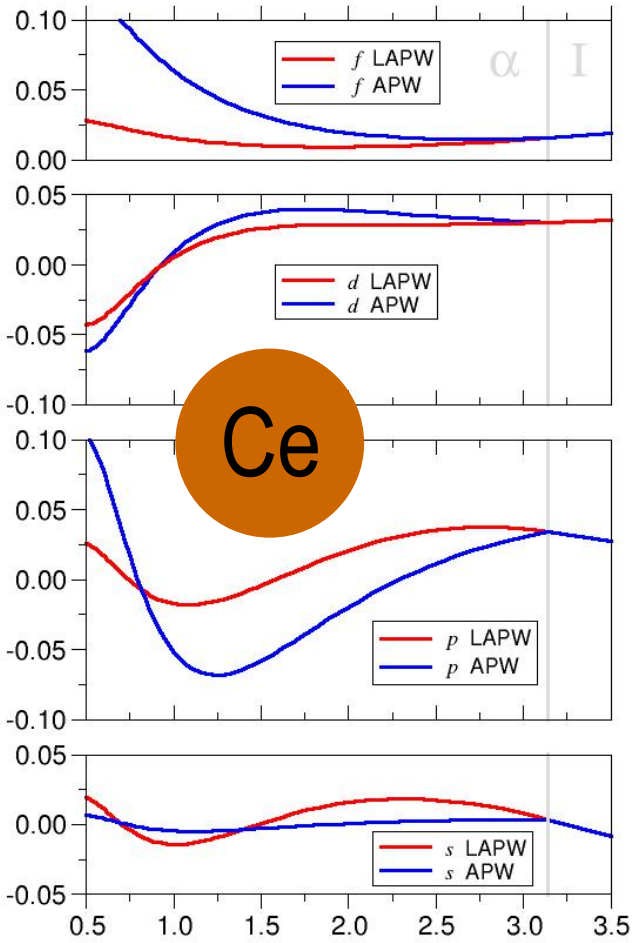
Radial functions get distorted by boundary conditions

More basis functions needed in LAPW

to describe the same behavior as in APW

Same effect in SLAPW

Even more pronounced



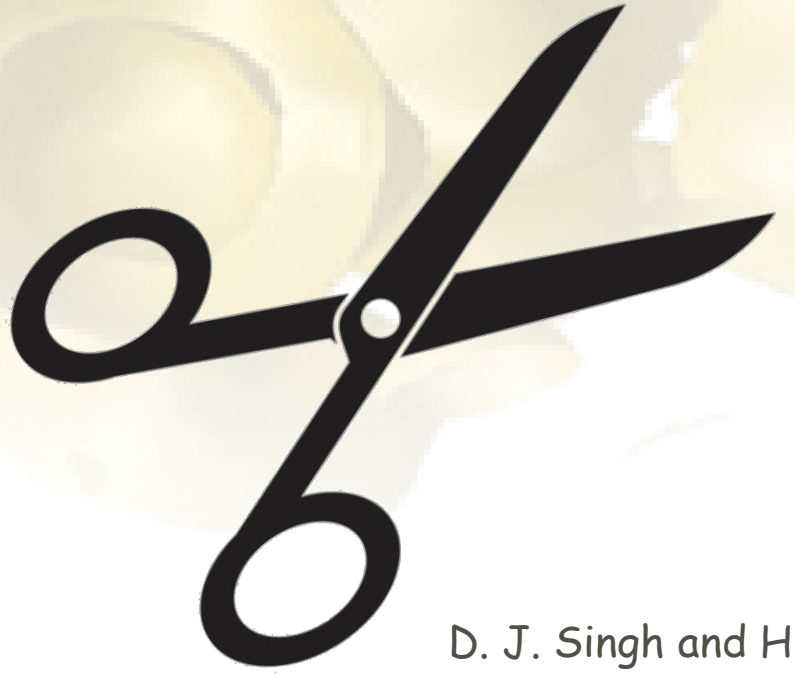
The Super LAPW method

SLAPW-3

basis continuous up to 2nd derivative

α

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha+\mathbf{r}) = \sum_{lm}[A^\alpha_{lm}(\mathbf{k}+\mathbf{G})u^\alpha_l(r,E_l)+B^\alpha_{lm}(\mathbf{k}+\mathbf{G})\dot{u}^\alpha_l(r,E_l)+C^\alpha_{lm}(\mathbf{k}+\mathbf{G})u^\alpha_l(r,E_{lo})]Y_{lm}(\hat{\mathbf{r}})$$



D. J. Singh and H. Krakauer, Phys. Rev. B 43, 1441 (1991).

The concept of local orbitals

LAPW+LO

D. J. Singh, Phys. Rev. B 43, 6388 (1991).

augmentation to PWs

valence state

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha + \mathbf{r}) = \sum_{lm} [A^\alpha_{lm}(\mathbf{k}+\mathbf{G}) u^\alpha_l(r, E_l) + B^\alpha_{lm}(\mathbf{k}+\mathbf{G}) \dot{u}^\alpha_l(r, E_l)$$

α

&

$$\phi^{lm}_{LO}(\mathbf{S}_\alpha + \mathbf{r}) = \left[\tilde{A}^\alpha_{lm} u^\alpha_l(r, E_l) + \tilde{B}^\alpha_{lm} \dot{u}^\alpha_l(r, E_l) + \tilde{C}^\alpha_{lm} u^\alpha_l(r, E_{lo})\right] Y_{lm}(\hat{\mathbf{r}})$$

lives in spheres only

semicore state

Nearly no extra cost!

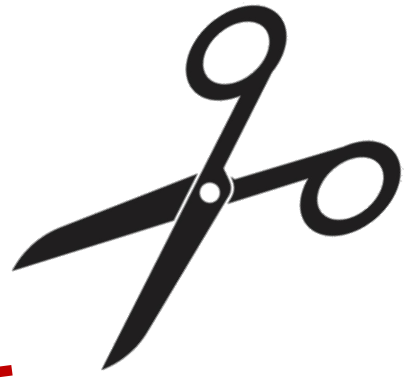
Can we do better?

Yes !!

… Is it possible to combine the advantages of the LAPW and the APW methods, i.e., to find an energy-independent basis that does not demand a noticeable higher planewave cutoff than the original APW functions? ...

E. Sjöstedt, L. Nordström, and D. J. Singh, Solid State Commun. 114, 15 (2000).

The APW+lo basis



Forget *classic* LAPW

α

$$\cancel{\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha+\mathbf{r}) = \sum_{lm}[A^\alpha_{lm}(\mathbf{k}+\mathbf{G})u^\alpha_l(r,E_l)+B^\alpha_{lm}(\mathbf{k}+\mathbf{G})\dot{u}^\alpha_l(r,E_l)]\,Y_{lm}(\hat{\mathbf{r}})}$$

Use APW & a local orbital at the same energy

$$\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{S}_\alpha+\mathbf{r}) = \sum_{lm} A^\alpha_{lm}(\mathbf{k}+\mathbf{G})u^\alpha_l(r,E_l)Y_{lm}(\hat{\mathbf{r}})$$

&

$$\phi^{lm}_{lo}(\mathbf{S}_\alpha+\mathbf{r}) = \left[\tilde{A}^\alpha_{lm}u^\alpha_l(r,E_l)+\tilde{C}^\alpha_{lm}\dot{u}^\alpha_l(r,E_l)\right]Y_{lm}(\hat{\mathbf{r}})$$

fixed

Alternative way of linearizetion

APW+lo: only advantages - NO drawbacks

All-electron method

As accurate as LAPW

Can be supplemented by LOs

Very efficient

- 50% less basis functions compared to LAPW
- Saves a factor of ~5 for large cells

Different augmentations can be combined

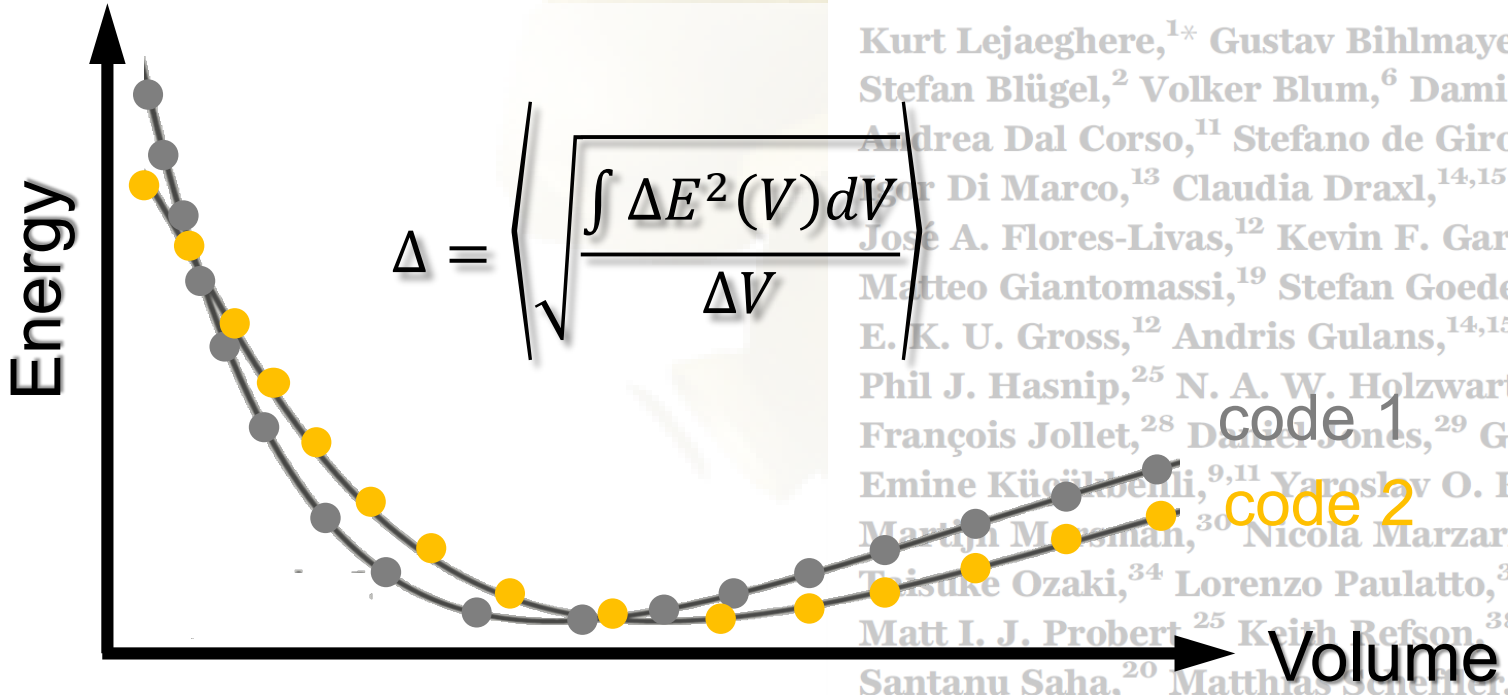
- APW+lo for *relevant* valence states only
- LAPW-like augmentation for all other /states

G. Madsen et al., PRB 64, 195134 (2001).

Benchmark quality ...

Precision

Quality factor



$$\Delta = \left\langle \sqrt{\frac{\int \Delta E^2(V)\,dV}{\Delta V}} \right\rangle$$

Kurt Lejaeghere *et al.*
Science **351**, aad3000 (2016).

RESEARCH ARTICLE

Science
AAAS

DFT METHODS

Reproducibility in density functional theory calculations of solids

Kurt Lejaeghere,[1*] Gustav Bihlmayer,[2] Torbjörn Björkman,[3,4] Peter Blaha,[5] Stefan Blügel,[2] Volker Blum,[6] Damien Caliste,[7,8] Ivano E. Castelli,[9] Stewart J. Clark,[10] Andrea Dal Corso,[11] Stefano de Gironcoli,[11] Thierry Deutsch,[7,8] John Kay Dewhurst,[12] Igor Di Marco,[13] Claudia Draxl,[14,15] Marcin Dułak,[16] Olle Eriksson,[13] José A. Flores-Livas,[12] Kevin F. Garrity,[17] Luigi Genovese,[7,8] Paolo Giannozzi,[18] Matteo Giantomassi,[19] Stefan Goedecker,[20] Xavier Gonze,[19] Oscar Grånäs,[13,21] E. K. U. Gross,[12] Andris Gulans,[14,15] François Gygi,[22] D. R. Hamann,[23,24] Phil J. Hasnip,[25] N. A. W. Holzwarth,[26] Diana Iuşan,[13] Dominik B. Jochym,[27] François Jollet,[28] Daniel Jones,[29] Georg Kresse,[30] Klaus Koepernik,[31,32] Emine Küçükbenli,[9,11] Yaroslav O. Kvashnin,[13] Inka L. M. Locht,[13,33] Sven Lubeck,[14] Martijn Marsman,[30] Nicola Marzari,[9] Ulrike Nitzsche,[31] Lars Nordström,[13] Taisuke Ozaki,[34] Lorenzo Paulatto,[35] Chris J. Pickard,[36] Ward Poelmans,[1,37] Matt I. J. Probert,[25] Keith Refson,[38,39] Manuel Richter,[31,32] Gian-Marco Rignanese,[19] Santanu Saha,[20] Matthias Scheffler,[15,40] Martin Schlipf,[22] Karlheinz Schwarz,[5] Sangeeta Sharma,[12] Francesca Tavazza,[17] Patrik Thunström,[41] Alexandre Tkatchenko,[15,42] Marc Torrent,[28] David Vanderbilt,[23] Michiel J. van Setten,[19] Veronique Van Speybroeck,[1] John M. Wills,[43] Jonathan R. Yates,[29] Guo-Xu Zhang,[44] Stefaan Cottenier[1,45*]

Delta test

https://molmod.ugent.be/deltacodesdft

Code	Version	Basis	Electron treatment	Δ-value	Authors
Exciting	development version	LAPW+xlo	all-electron	0 meV/atom	Exciting [10,16]
FHI-aims	081213	tier2 numerical orbitals	all-electron (relativistic atomic_zora scalar)	0.1 meV/atom	ASE [2,16]
WIEN2k	13.1	LAPW/APW+lo	all-electron	0.2 meV/atom	S. Cottenier [16]
FHI-aims	081213	tier2 numerical orbitals	all-electron (relativistic zora scalar 1e-12)	0.3 meV/atom	ASE [2]
Quantum ESPRESSO	5.1	plane waves	SSSP Accuracy (mixed NC/US/PAW potential library)	0.3 meV/atom	QuantumESPRESSO [12,16]

Data quality

Excellent overall agreement between codes – great!

Larger discrepancies for certain elements

exciting vs Quantum Espresso

Δ [meV/atom]

H 0.05																	He 0.01
Li 0.04	Be 1.09											B 0.27	C 0.09	N 1.95	O 2.60	F 0.82	Ne 0.02
Na 0.03	Mg 0.02											Al 0.13	Si 0.03	P 0.40	S 0.21	Cl 1.43	Ar 0.01
K 0.04	Ca 0.04	Sc 0.03	Ti 0.18	V 0.06	Cr 3.70	Mn 1.24	Fe 1.06	Co 0.28	Ni 0.42	Cu 1.05	Zn 0.54	Ga 0.54	Ge 0.09	As 0.58	Se 0.04	Br 0.31	Kr 0.02
Rb 0.02	Sr 0.21	Y 0.03	Zr 0.19	Nb 0.88	Mo 0.16	Tc 0.13	Ru 0.53	Rh 0.55	Pd 0.09	Ag 0.49	Cd 0.07	In 0.25	Sn 0.18	Sb 0.17	Te 0.38	I 0.06	Xe 0.04
Cs 0.13	Ba 0.15	Lu	Hf 1.52	Ta 0.62	W 0.31	Re 0.60	Os 1.44	Ir 0.01	Pt 1.98	Au 0.36	Hg 0.48	Tl 0.37	Pb 0.45	Bi 0.32	Po 0.23	At	Rn 0.04

Average over 71 elemental solids: ~10 codes within 0.5 meV/atom

Data quality

Excellent overall agreement between codes – great!

Larger discrepancies for certain elements

exciting vs WIEN2k

Δ [meV/atom]

H 0.00																	He 0.00
Li 0.00	Be 0.17											B 0.08	C 0.24	N 1.26	O 0.61	F 0.29	Ne 0.02
Na 0.65	Mg 0.05											Al 0.18	Si 0.02	P 0.36	S 0.06	Cl 0.46	Ar 0.01
K 0.02	Ca 0.06	Sc 0.12	Ti 0.08	V 0.23	Cr 0.09	Mn 0.21	Fe 0.59	Co 0.72	Ni 0.36	Cu 0.25	Zn 0.13	Ga 0.03	Ge 0.23	As 0.02	Se 0.04	Br 0.02	Kr 0.05
Rb 0.09	Sr 0.22	Y 0.13	Zr 0.17	Nb 0.43	Mo 0.25	Tc 0.03	Ru 0.03	Rh 0.05	Pd 0.20	Ag 0.01	Cd 0.09	In 0.13	Sn 0.12	Sb 0.22	Te 0.06	I 0.03	Xe 0.04
Cs 0.06	Ba 0.21	Lu 0.10	Hf 0.07	Ta 0.23	W 0.14	Re 0.04	Os 0.06	Ir 0.14	Pt 0.07	Au 0.09	Hg 0.10	Tl 0.20	Pb 0.39	Bi 0.14	Po 0.20	At	Rn 0.05

What about other systems or quantities?

Surfaces, defects, molecules … barriers, band gaps, spectra, …

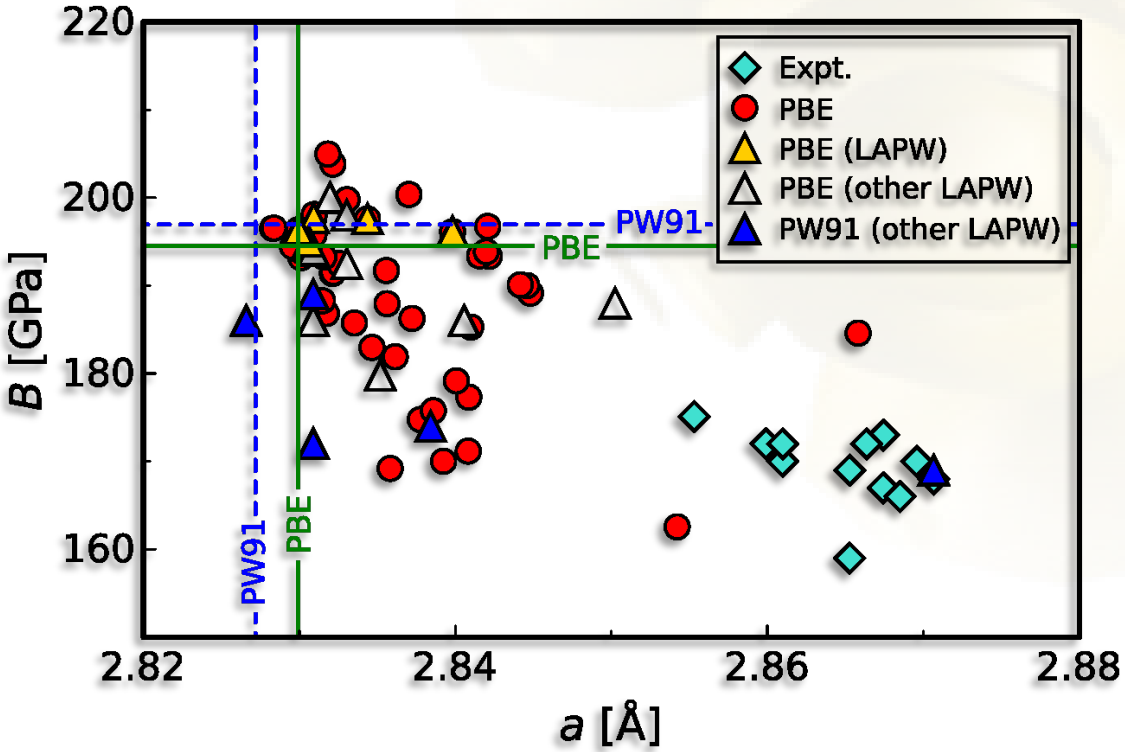
Accuracy vs precision

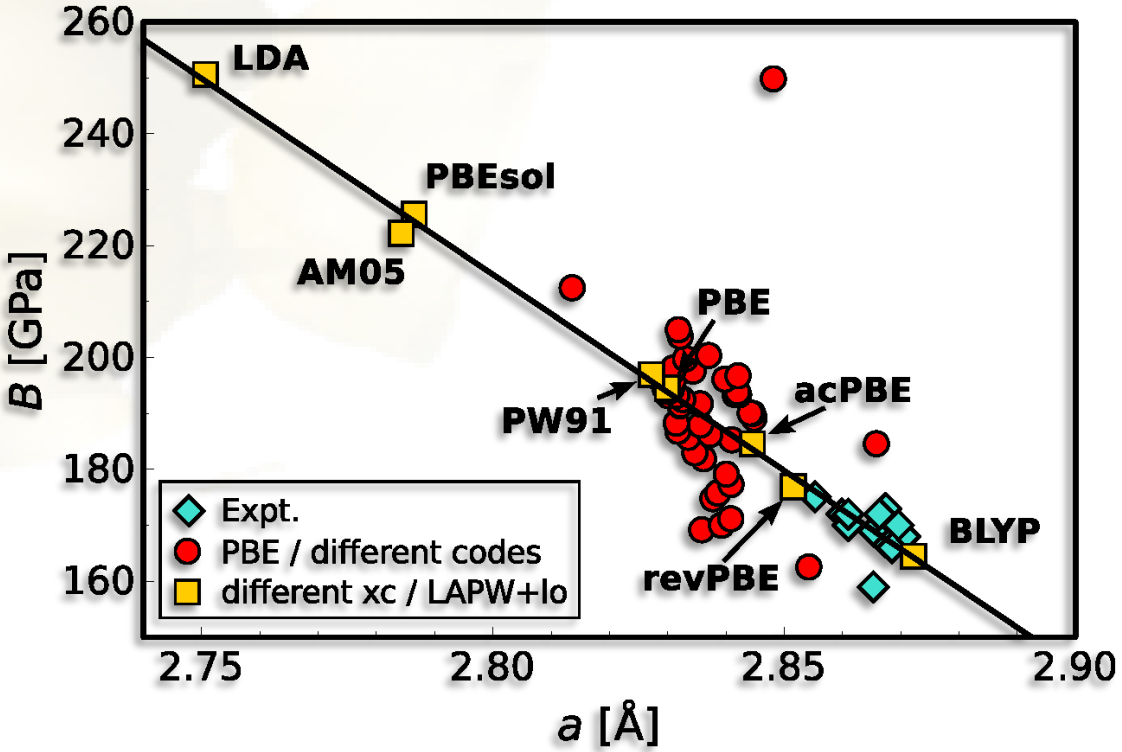
A. Gulans, A. Kozhevnikov, and C. Draxl
Phys. Rev. B **97**, 161105(R) (2018).

exciting

Example bcc Fe

Distinction between numerical precision of a calculation and accuracy of an xc funtional





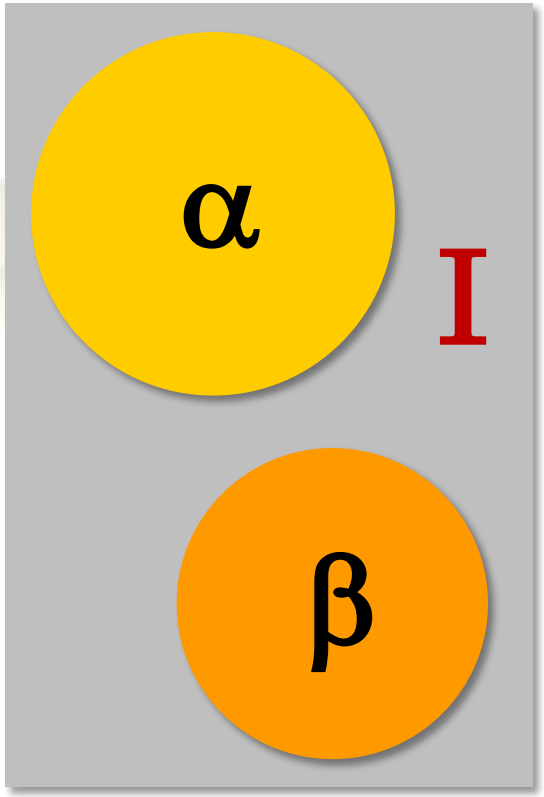
Can we claim 'exact' results?

exciting

Self-evaluation of results

Example: bcc Fe

R_{MT}	$R_{\mathrm{MT}}G_{\max}$	V_0	B_0	B'	ΔE^{tot} [μHa]
1.4	14	71.3298	236.296	4.5992	0.0
1.5	14	71.3299	236.297	4.5996	0.1
1.6	14	71.3299	236.295	4.5998	0.2
1.7	14	71.3299	236.294	4.5994	0.3
1.8	14	71.3299	236.295	4.5994	0.4
1.9	14	71.3300	236.295	4.5989	0.5
2.0	14	71.3301	236.296	4.5989	0.6
2.1	14	71.3302	236.295	4.5994	0.8



A. Gulans, A. Kozhevnikov, and CD, 97, 161105(R) 2018.

μHa precision

Comparison to 'exact' results for atoms and molecules from quantum-chemistry packages

G2-1 test set

exciting

	Total energy		Atomization energy	
	$\Delta E^{tot}_{\mathrm{MRA}}$	$\Delta E^{tot}_{\mathrm{LCAO}}$	$\Delta E^{at}_{\mathrm{MRA}}$	$\Delta E^{at}_{\mathrm{LCAO}}$
MD	$0.2 \cdot 10^{-6}$	$1.2 \cdot 10^{-3}$	$0.4 \cdot 10^{-6}$	$6.1 \cdot 10^{-5}$
MAD	$0.3 \cdot 10^{-6}$	$1.2 \cdot 10^{-3}$	$0.5 \cdot 10^{-6}$	$9.9 \cdot 10^{-5}$
MaxD	$1.1 \cdot 10^{-6}$	$7.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-6}$	$2.1 \cdot 10^{-3}$

	Ha	μHa
	$E^{\mathrm{LAPW+lo}}$	ΔE^{MRA}
H	−0.4787107	0.3
He	−2.8344552	0.2
Li	−7.3432843	1.6
Be	−14.4464735	0.6
B	−24.3548568	1.3
C	−37.4685404	0.9
N	−54.1343867	0.7
O	−74.5286993	0.2
F	−99.1118530	−0.3
Ne	−128.2299171	0.3
Na	−161.4436320	2.1
Mg	−199.1352882	0.7
Al	−241.3178300	2.3
Si	−288.2171655	1.6
P	−340.0000526	1.8
S	−396.7390648	0.7
Cl	−458.6643433	0.1
Ar	−525.9397933	0.8

A. Gulans, A. Kozhevnikov, and CD, 97, 161105(R) 2018.

The most exciting code

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone,
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J. Phys: Condens. Matter **26**, 363202 (2014).

exciting

a full-potential all-electron
package implementing
linearized augmente
planewave methods

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About exciting

exciting is a full-potential all-electron density-functional-theory package implementing linearized augmented planewave methods. It can be applied to all kinds of materials, irrespective of the atomic species involved and allows for exploring the physics of core electrons. As the name tells, **exciting** has a particular focus on excitations.

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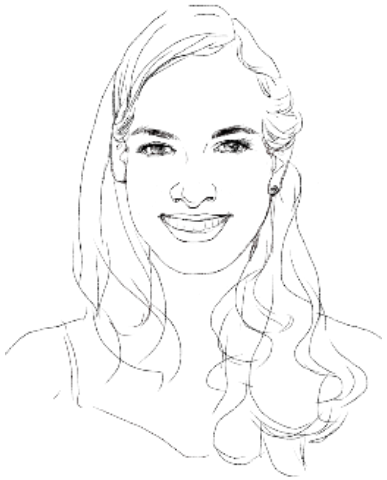

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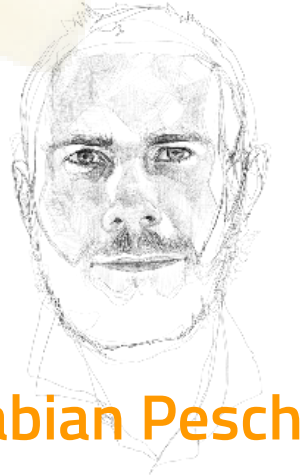

Fabian Peschel

More developers

Andris Gulans
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Ronaldo Rodriuges

Alex Buccheri

Teamwork