Claudia Draxl

Augmented - planewave methods

Kohn-Sham equation

$$\left[-\nabla^2 + V_{eff}(\mathbf{r})\right]\Psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r})$$

- Ritz variational principle

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G})\phi_{\mathbf{k}+\mathbf{G}}(\mathbf{r})$$

- Matrix form

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

Kohn-Sham equation

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

- Hamiltonian matrix

$$H_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \equiv \left\langle \phi_{\mathbf{k}+\mathbf{G}} \right| -\nabla^2 + V_{eff} \left| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{\Omega}$$

- Overlap matrix

$$S_{\mathbf{k}+\mathbf{G},\mathbf{k}+\mathbf{G}'} \equiv \left\langle \phi_{\mathbf{k}+\mathbf{G}} \middle| \phi_{\mathbf{k}+\mathbf{G}'} \right\rangle_{\Omega}$$

Augmented-planewave methods ….

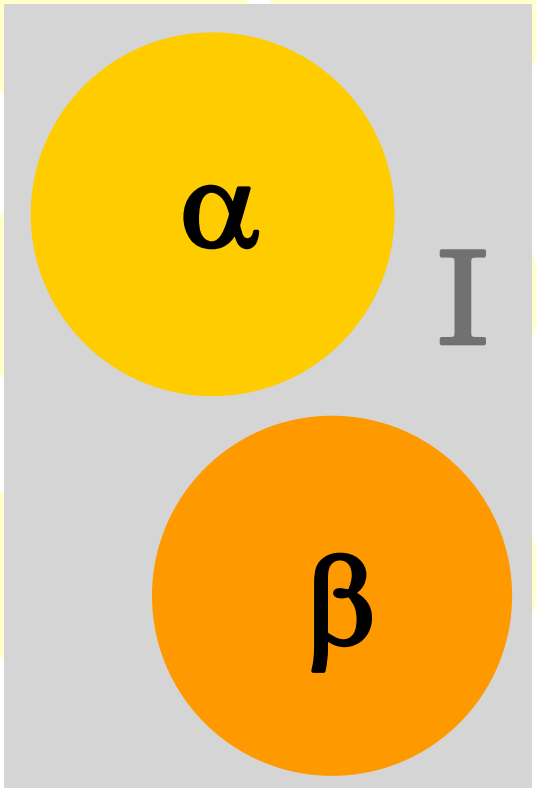
- APW
- LAPW
- SLAPW(3), SLAPW(4), …
- LAPW+LO
- APW+lo
- APW+lo+LO

"LAPW"

All these methods linearize the eigenvalue problem

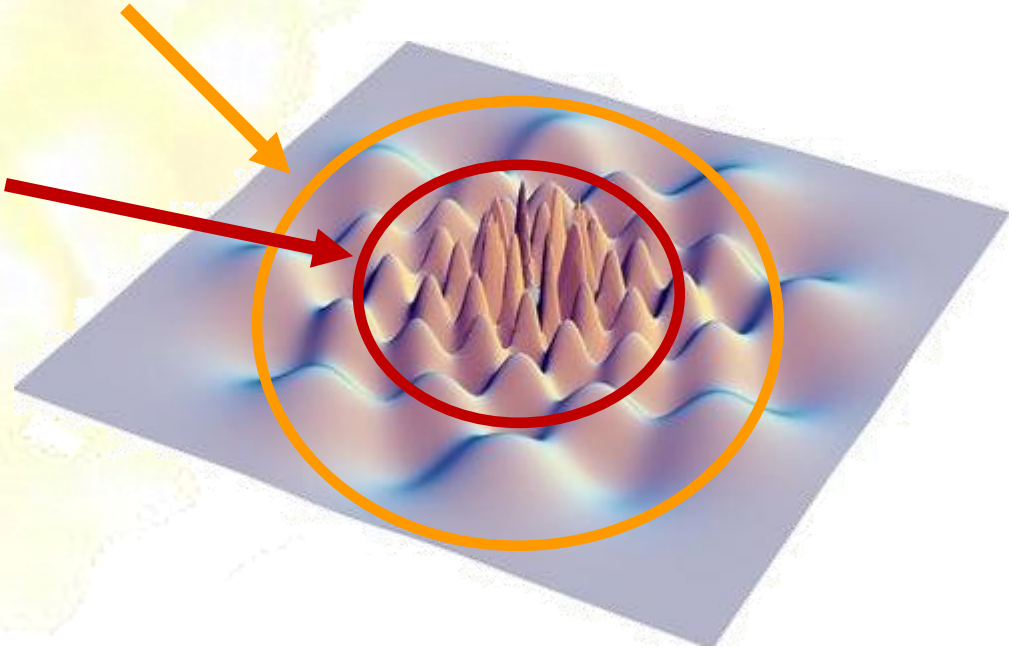
Dual basis for WF, density, potential, …

- Atomic spheres α, β
  - Atomic-like basis functions
- Interstitial
  - Planewave basis
- All-electron method
  - Can handle strong variations
  - Can explore the core region



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



Potential and density: dual basis

- The 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

- The density

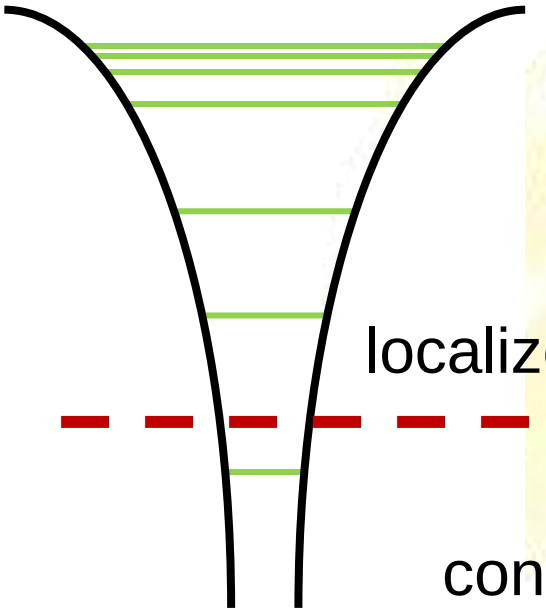
$$\rho_{eff}(\mathbf{r}) = \sum_{\mathbf{K}} \rho_{\mathbf{K}} e^{i\mathbf{K}\mathbf{r}}$$

I

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

α

All-electron description



valence

delocalized

scalar-relativistic
SO in second variation

semi-core

localized, but not confined in MT sphere

core

confined in the sphere

atom-like

Dirac equation

The APW basis set

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

- **Augmented Plane Waves**

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

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

APW: advantages & drawbacks

- *E* has to be the exact KS eigenvalue
  - *E* is a variational parameter
- Energy-dependent basis set
- Non-linear eigenvalue problem
- Search for zeros of the determinant
  - No single diagonalizaion
  - Time-consuming
- No full-potential method
- **BUT** a true all-electron method!

The LAPW basis set

- **Linearized Augmented Plane Waves**

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

I

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

α

basis continuous in value and slope at R_{MT}

energy derivative

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

energy parameter

LAPW: advantages & drawbacks

- E_l is a fixed parameter
- Energy-independent basis set
- Linear eigenvalue problem

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

- No true all-electron method!

  Only one principle quantum number per *l*

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 ….

SLAPW Method

- **SLAPW-3**

α

basis continuous up to 2nd derivative

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

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 continuos

  No surface terms needed

- Costly: more basis functions needed

  Roughly 50% larger basis set

  Why?

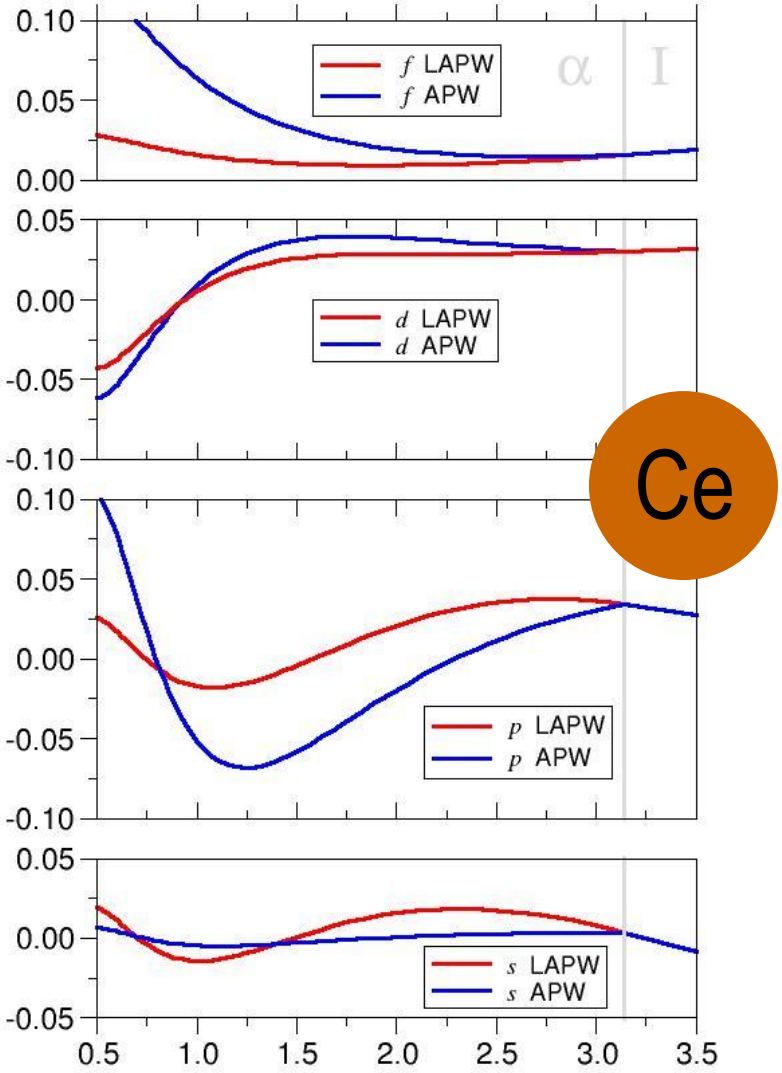
The radial functions in APW & LAPW

- They get distorted by boundary conditions

  More basis functions needed in LAPW to describe the same behavior as in APW

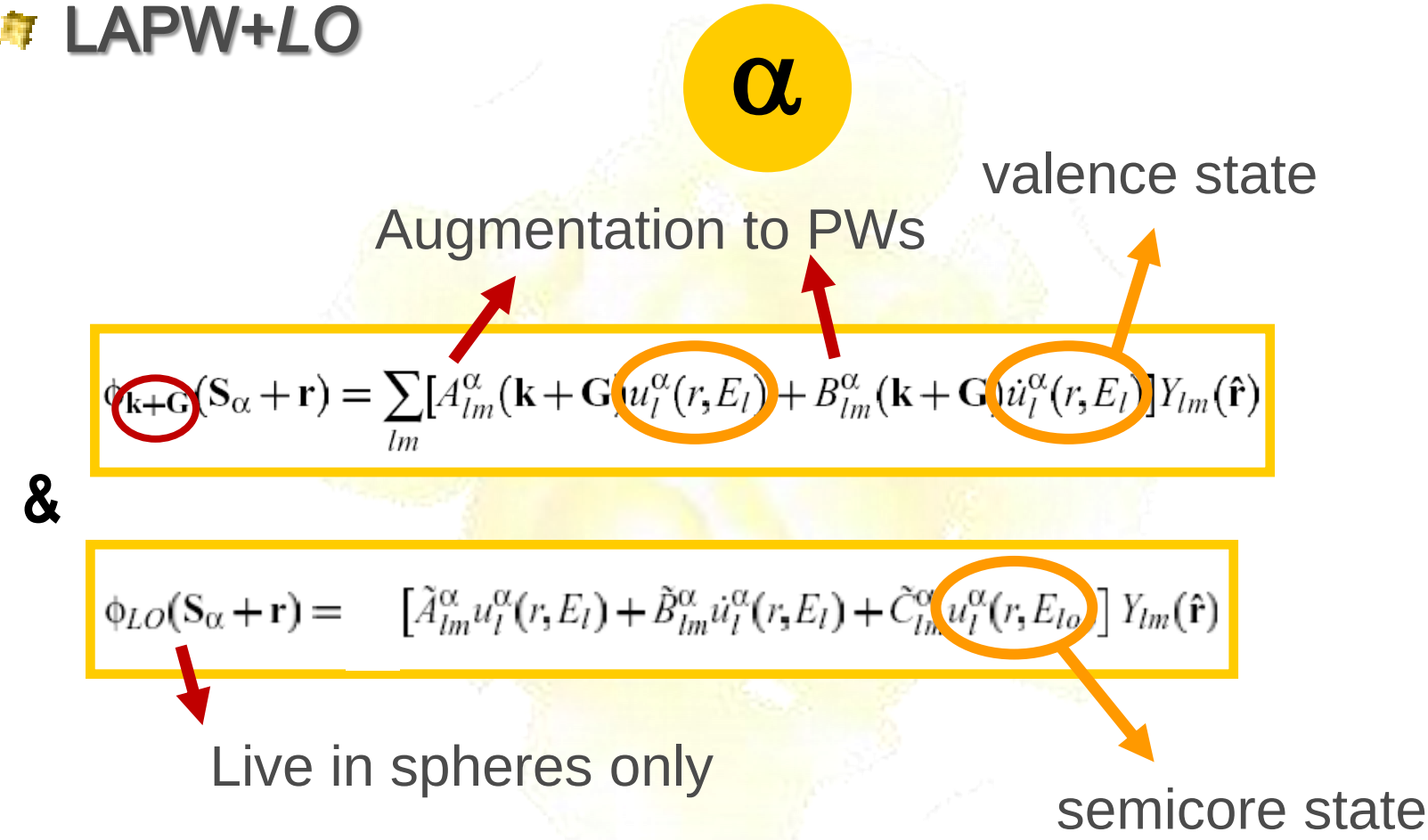
- Same effect in SLAPW

  Even more pronounced



The concept of local orbitals

- **LAPW+*LO***



Nearly no extra cost!

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

Can we do better?

- *… 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? …*

- **YES !!**

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

The APW+*lo* basis set

- Forget *classic* LAPW

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

- Use APW & *local orbital* at the same energy

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

fixed

&

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

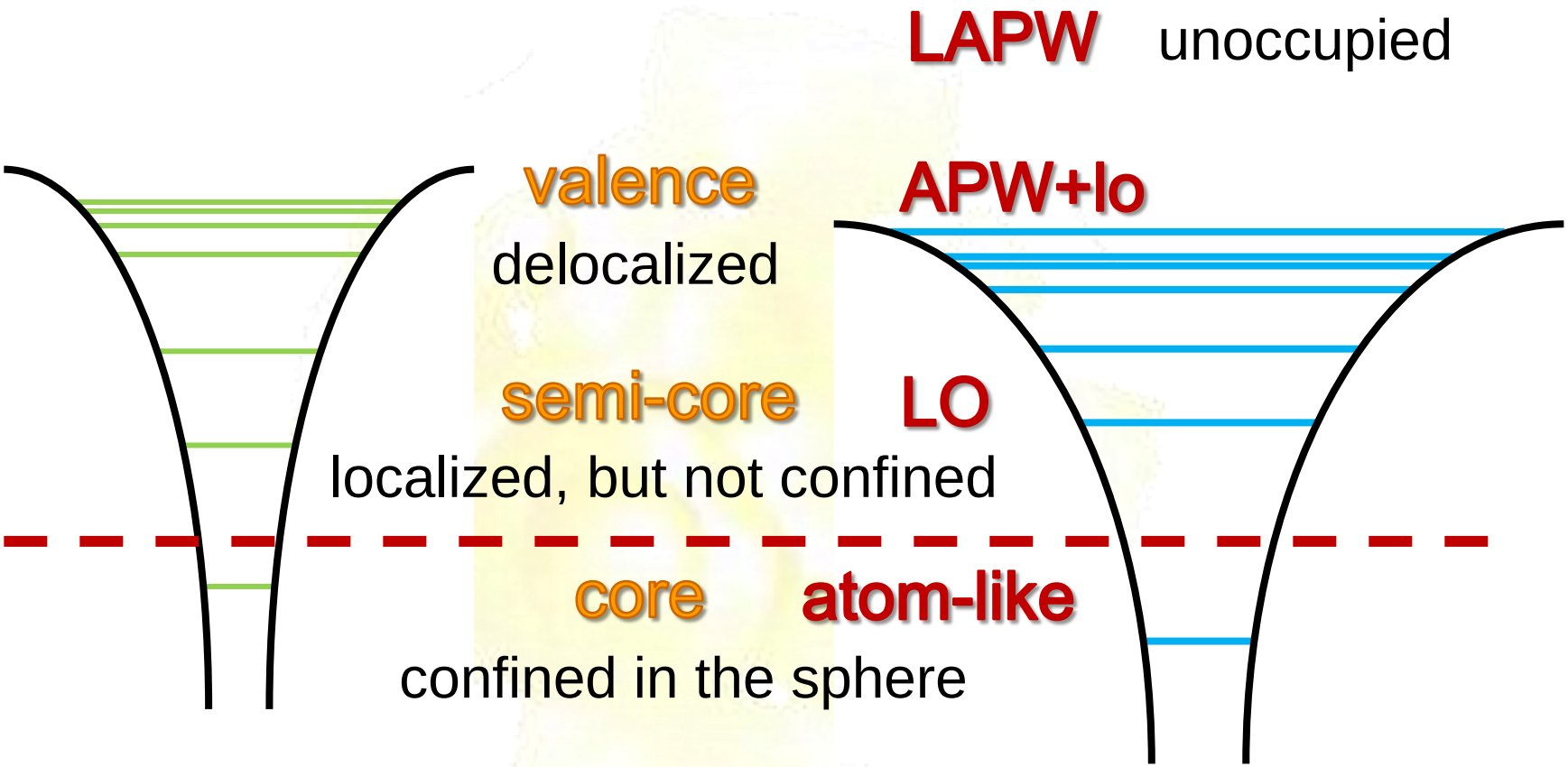
Alternative way of linearizetion

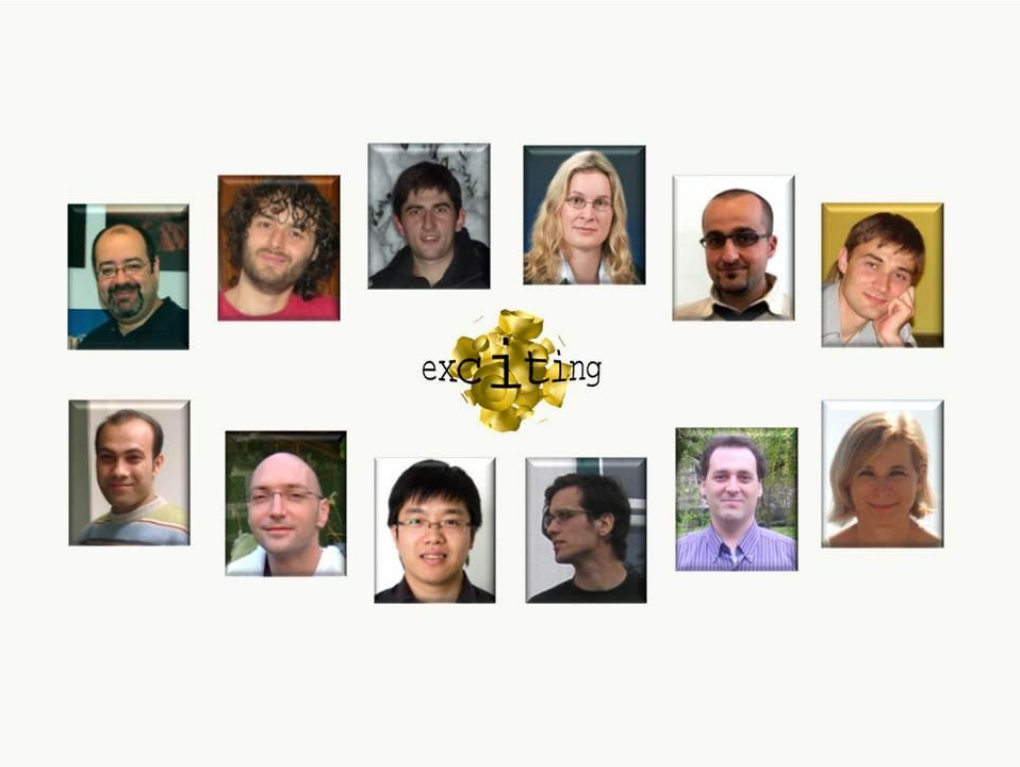
APW+*lo*: only advantages - **NO** drawbacks

- All-electron method
- As accurate as LAPW
- Can be supplemented by *LO*s
- 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 *l* states

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

Our LAPW flavor of choice





http://exciting-code.org

Most general implementation in exciting

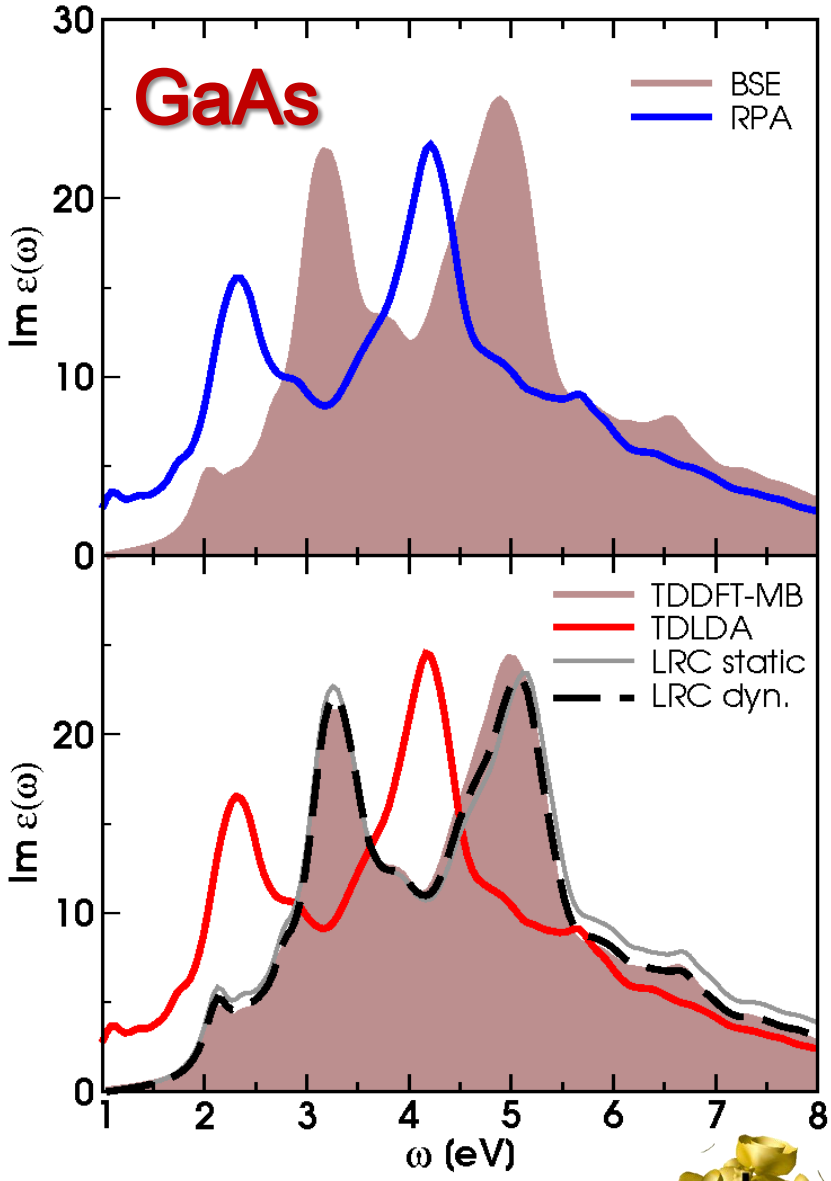
- Species generator
  - All types of augmentation possible
  - Allows for an individual setup
  - Default basis: APW+lo
- Species file for each atom
  - Written in XML
  - Defines
    - $R_{MT,}$ radial mesh
      core / semicore / valence
      matching order

Features

- Sate-of-the-art *ground-state package*
  - Band structure, DOS
  - Structure optimization
  - Various functionals (& libxc), including EXX
  - Phonons (supercell approach)
  - Thermodynamic properties
  - Link to cluster expansion: ATAT@`exciting`
- Excitation spectra
  - Time-dependent DFT
  - Many-body perturbation theory
    - *GW* & Bethe Salpeter equation (BSE)

Excitation spectra

- BSE & TDDFT
  - For Solids
- Allows comparison on equal footing
  - Same KS states, potential, density, matrix elements, …

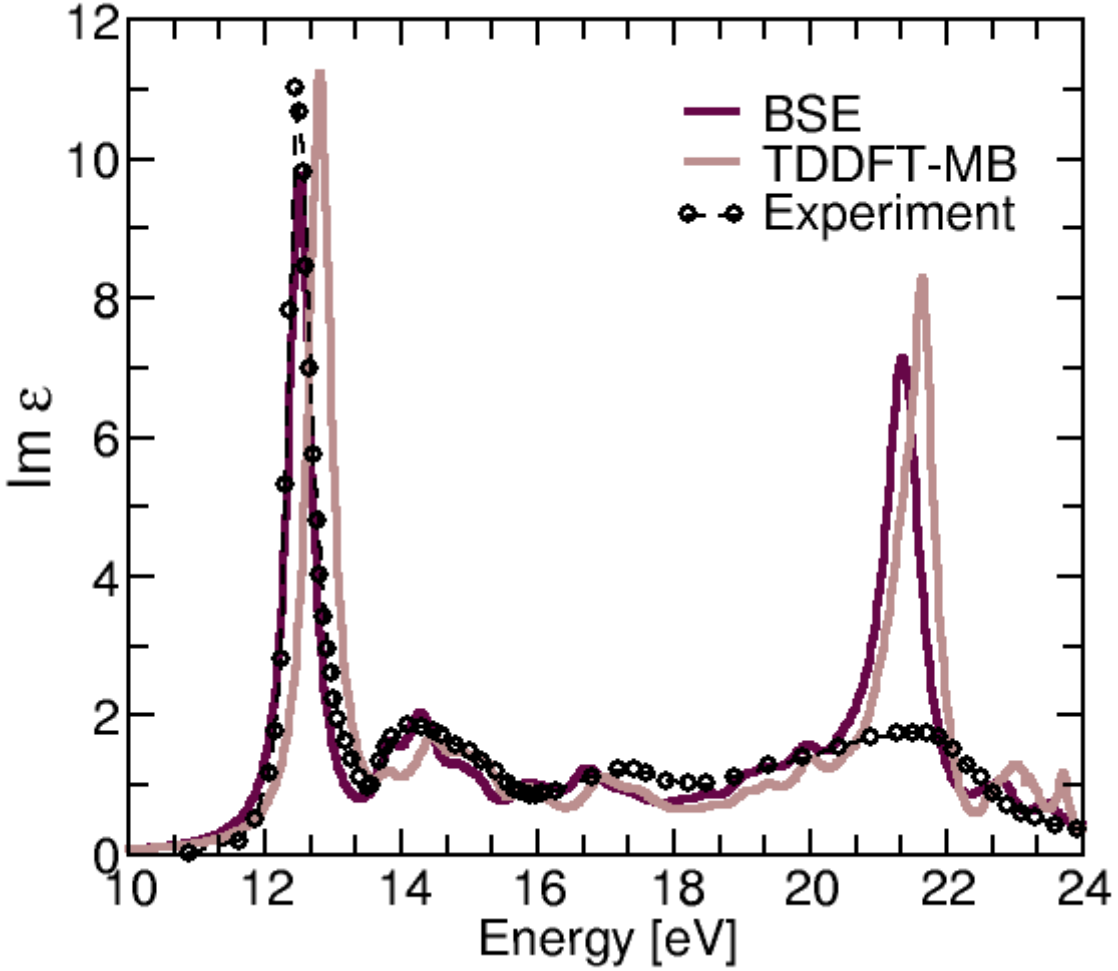


S. Sagmeister and CAD, PCCP 11, 4451 (2009).

exciting

Excitation spectra

LiF



Why all-electron methods?

- A striking example ….

  Results with the *FHI-gap* code: *GW*@WIEN2k

  Strongly improved version implemented in **exciting**

R. Gómez-Abal, X. Li, M. Scheffler, and CAD, PRL 101, 106404 (2008).

X. Li, R. Gómez-Abal, H. Jiang, CAD, and M. Scheffler, New J. Phys. 14, 023006 (2012).

The G_0W_0@LDA gap of Si

Si
$1s^2 2s^2 2p^6 3s^2 3p^2$
14

- **PP**
  1.19 – 1.29 eV
  M. S. Hybertsen and S. G. Louie, ...
- **PAW**
  1.00 eV
  B. Arnaud and M. Alouani, PRB 62, 4464 (2000).
- **AE-G_0W_0**
  0.85 eV - 0.95 eV
  W. Ku and A. G. Eguiluz, PRL 89, 126401 (2002).
  T. Kotani and M. van Schilfgaarde, Solid State Comm. 121, 461 (2002).
- **PP-G_0W_0** ***all-electron like***
  1.04 eV
  M. L. Tiago, S. Ismail-Beigi, and S. G. Louie, PRB 69, 125212 (2004).
- **LAPW**
  1. 00 – 1.05
  C. Friedrich, A. Schindlmayr, S. Blügel, and T. Kotani, PRB 74, 045104 (2006).
  R. Gomez-Abal, X. Z. Li, M. Scheffer, and C. Ambrosch-Draxl, PRL 101,106404 (2008).

The manybody concept

- **Quasiparticle equation**

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r})\right]\psi_i^{QP}(\mathbf{r}) + \int \boxed{\Sigma(\mathbf{r}, \mathbf{r}', \epsilon_i)}\psi_i^{QP}(\mathbf{r})d^3\mathbf{r}' = \epsilon_i^{QP}\psi_i^{QP}(\mathbf{r})$$

- **Kohn Sham equation**

$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \boxed{V_{xc}(\mathbf{r})}\right]\psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS}\psi_i^{KS}(\mathbf{r})$$

- **G_0W_0**

LDA

$$\epsilon_{n\mathbf{k}}^{\mathrm{QP}} = \epsilon_{n\mathbf{k}}^{\mathrm{KS}} + \left\langle n\mathbf{k}\middle|\Sigma(\epsilon_{n\mathbf{k}}^{QP}) - V_{xc}^{DFT}\middle|n\mathbf{k}\right\rangle$$

The G_0W_0@LDA band gap of Si …

- Why the big difference?

  Cancelation between vertex corrections
  & lack of self-consistency?

  W. Ku and A. G. Eguiluz, PRL 89, 126401 (2002).

  Cancelation between missing core electrons
  & lack of self-consistency?

  K. Delaney, P. Garca-Gonzalez, A. Rubio, P. Rinke, and R.W.Godby,
  PRL 93, 249701(2004).

  Bad convergence with unoccupied states?

- Remaining discrepancy small: 0.1 eV

- **Materials with semicore states** more problematic

Energy correction

$$\epsilon_{n\mathbf{k}}^{\mathrm{qp}} = \epsilon_{n\mathbf{k}}^{\mathrm{KS}} + \langle \varphi_{n\mathbf{k}} | \Re \left[\Sigma \left(\mathbf{r}, \mathbf{r}'; \epsilon_{n\mathbf{k}}^{\mathrm{qp}} \right) \right] - V^{\mathrm{xc}} \left(\mathbf{r} \right) | \varphi_{n\mathbf{k}} \rangle$$

- **Exact** $\Sigma \left(\{ \varphi_{n\mathbf{k}}, \varphi_{\mathrm{core}} \}, \epsilon_{n\mathbf{k}}^{\mathrm{qp}} \right)$ $V^{\mathrm{xc}} \left(n_{\mathrm{val}} + n_{\mathrm{core}} \right)$

- **Pseudo-potential approximation**

  Pseudoization of potential and KS wavefunctions

  Core-valence partitioning

  $$V^{\mathrm{xc}} \left[n(\mathbf{r}) \right] = V^{\mathrm{xc}} \left[n_{\mathrm{core}}(\mathbf{r}) \right] + V^{\mathrm{xc}} \left[n_{\mathrm{val}}(\mathbf{r}) \right]$$

  Frozen core

  $$\Sigma(\{ \tilde{\varphi}_{n\mathbf{k}} \}, \epsilon_{n\mathbf{k}}^{\mathrm{qp}}) \qquad V^{\mathrm{xc}} \left(\tilde{n}_{\mathrm{val}} \right)$$

Three levels of approximation

- **All electron (full potential)**

$$\Delta\epsilon_{n\mathbf{k}}^{\mathrm{AE}} = \Re\left(\left\langle\varphi_{n\mathbf{k}}\middle|\Sigma\left(\{\varphi_{n\mathbf{k}},\varphi_{\mathrm{core}}\},\epsilon_{n\mathbf{k}}^{\mathrm{qp}}\right)\middle|\varphi_{n\mathbf{k}}\right\rangle\right) - \left\langle\varphi_{n\mathbf{k}}\middle|V^{\mathrm{xc}}\left(n_{\mathrm{val}}+n_{\mathrm{core}}\right)\middle|\varphi_{n\mathbf{k}}\right\rangle$$

- **All electron – frozen core**

$$\Delta\epsilon_{n\mathbf{k}}^{\mathrm{AE\text{-}FC}} = \Re\left(\left\langle\varphi_{n\mathbf{k}}\middle|\Sigma\left(\left\{\varphi_{n\mathbf{k}}^{\mathrm{FC}},\varphi_{\mathrm{core}}^{\mathrm{FC}}\right\},\epsilon_{n\mathbf{k}}^{\mathrm{qp}}\right)\middle|\varphi_{n\mathbf{k}}\right\rangle\right) - \left\langle\varphi_{n\mathbf{k}}\middle|V^{\mathrm{xc}}\left(n_{\mathrm{val}}^{\mathrm{FC}}+n_{\mathrm{core}}^{\mathrm{FC}}\right)\middle|\varphi_{n\mathbf{k}}\right\rangle$$

- **All electron – valence**

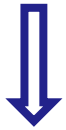
$$\Delta\epsilon_{n\mathbf{k}}^{\mathrm{AE\text{-}V}} = \Re\left(\left\langle\varphi_{n\mathbf{k}}\middle|\Sigma\left(\left\{\varphi_{n\mathbf{k}}^{\mathrm{FC}}\right\},\epsilon_{n\mathbf{k}}^{\mathrm{qp}}\right)\middle|\varphi_{n\mathbf{k}}\right\rangle\right) - \left\langle\varphi_{n\mathbf{k}}\middle|V^{\mathrm{xc}}\left(n_{\mathrm{val}}^{\mathrm{FC}}\right)\middle|\varphi_{n\mathbf{k}}\right\rangle$$

- **Pseudopotential**

$$\Delta\epsilon_{n\mathbf{k}}^{\mathrm{PP}} = \Re(<\tilde{\varphi}_{n\mathbf{k}}\left|\Sigma(\{\tilde{\varphi}_{n\mathbf{k}}\},\epsilon_{n\mathbf{k}}^{\mathrm{qp}})\right|\tilde{\varphi}_{n\mathbf{k}}>) - <\tilde{\varphi}_{n\mathbf{k}}\left|V^{\mathrm{xc}}\left(\tilde{n}_{\mathrm{val}}\right)\right|\tilde{\varphi}_{n\mathbf{k}}>$$

Three levels of approximation

- All electron



frozen-core approximation

- All electron – frozen core

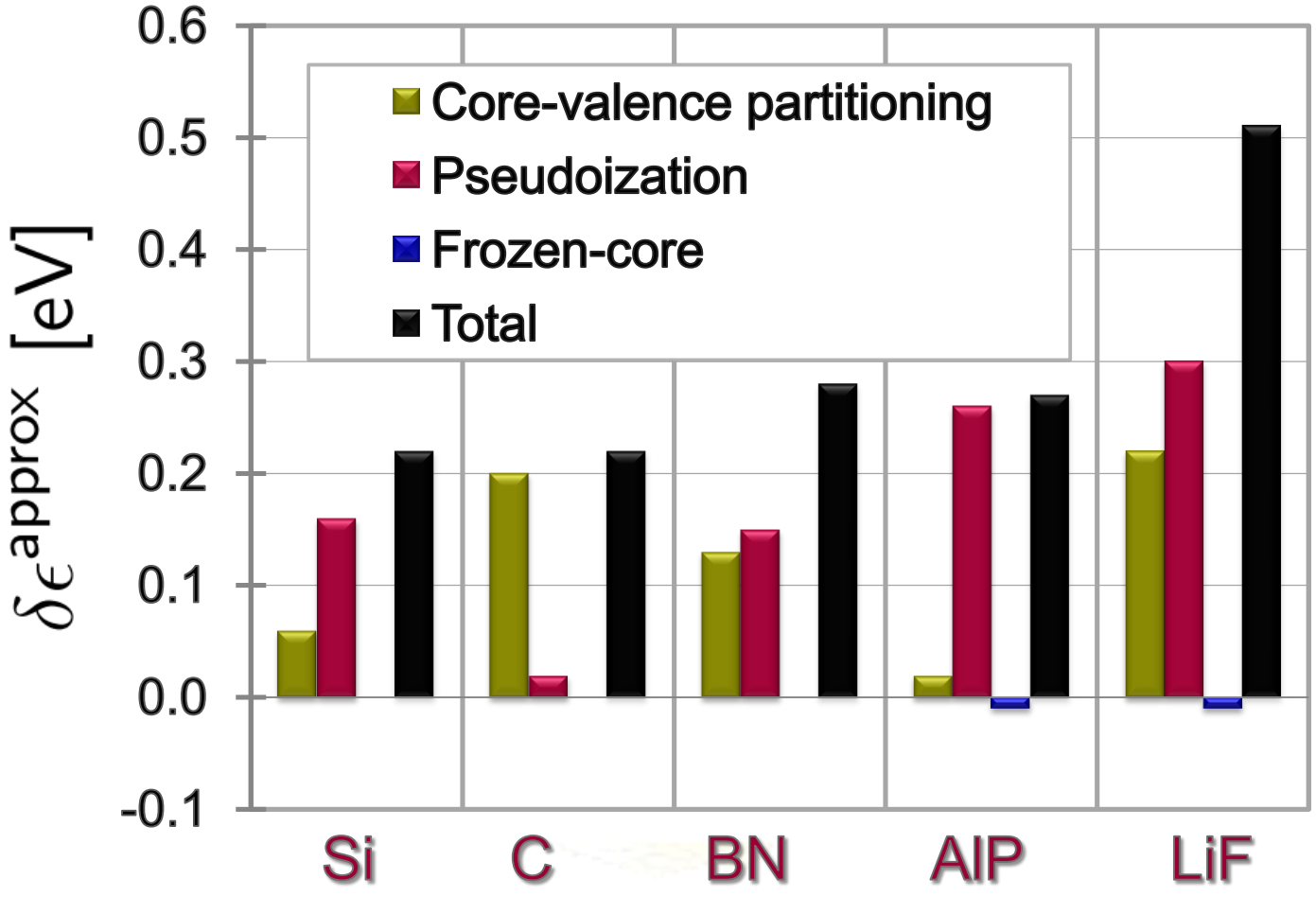
core-valence partitioning

- All electron – valence

pseudoization

- Pseudopotential

sp semiconductors



AIP

	ϵ^{gap}_{LDA}	Σ^c	Σ^x	V^{xc}	$\Sigma^x - V^{xc}$	$\Delta\epsilon^{gap}$	$\epsilon^{gap}_{G_0W_0}$
AE							
Γ_v		1.42	-16.08	-14.07	-2.01	-0.59	
X_c		-3.96	-5.27	-9.40	4.13	0.17	
Δ	1.44	-5.38	10.81	4.67	6.14	0.76	2.20
AE-FC							
Γ_v		1.42	-16.10	-14.07	-2.03	-0.61	
X_c		-3.95	-5.31	-9.40	4.09	0.14	
Δ	1.44	-5.37	10.79	4.67	6.12	0.75	2.19
AE-V							
Γ_v		1.40	-14.08	-12.03	-2.05	-0.65	
X_c		-3.94	-4.48	-8.54	4.06	0.12	
Δ	1.44	-5.34	9.60	3.49	6.11	0.77	2.21
PP							
				-11.82	-2.27	-0.93	
				-8.49	3.92	0.10	
Δ	1.47	-5.16	9.52	3.33	6.19	1.03	2.50

core-valence partitioning

GaN: 3 configurations

- **AE-V-1**

Ga	31	N	7
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$		$1s^2 2s^2 2p^3$	

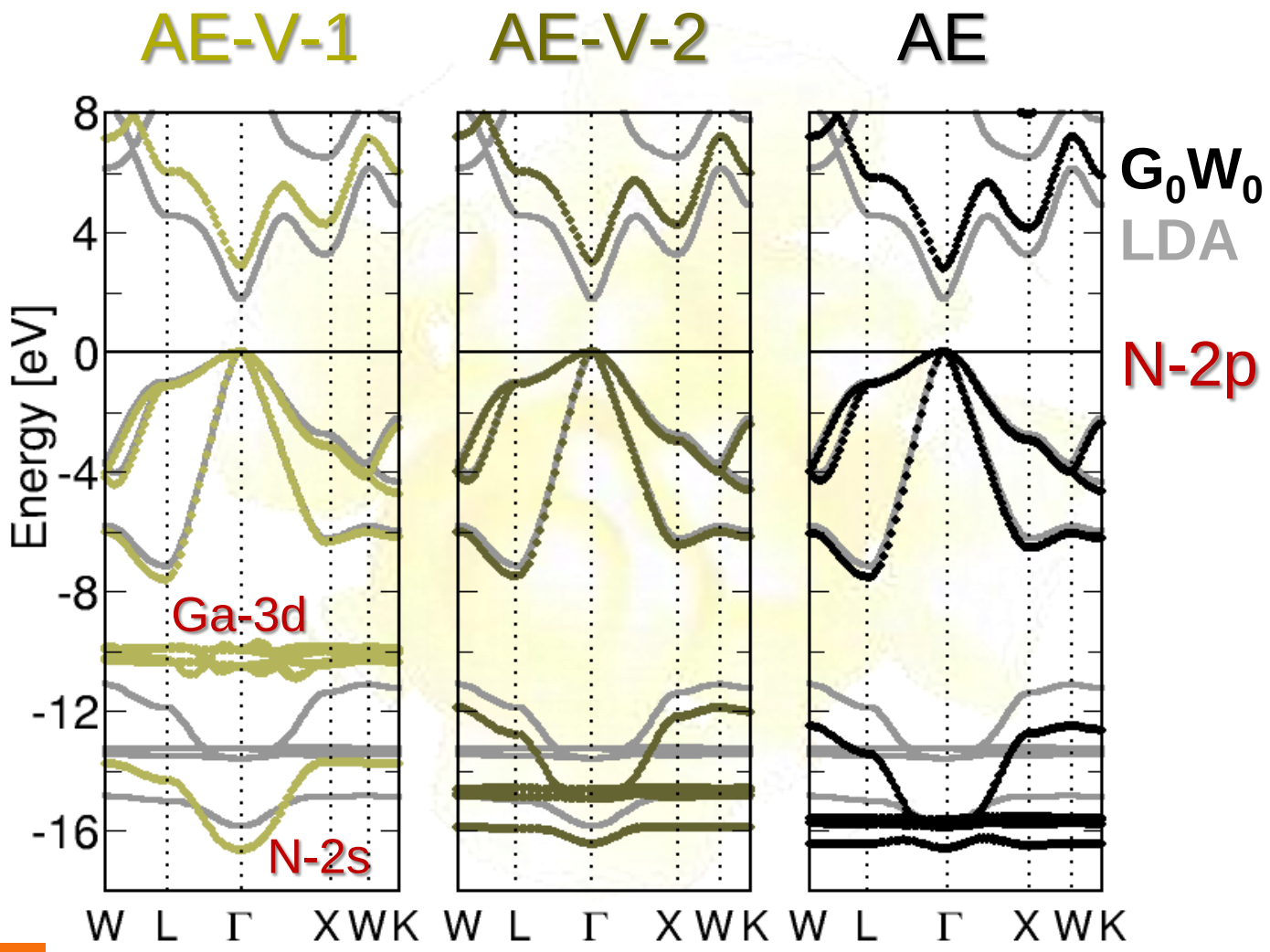
- **AE-V-2**

Ga	31
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	

- **AE**

Ga	31
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	

GaN: core-valence partitioning



Ga

$2s^2 2p^6 3s^2 3p^6 3d^{10}$

$2s^2 2p^6 3s^2 3p^6 3d^{10}$

$2s^2 2p^6 3s^2 3p^6 3d^{10}$

Core-valence partitioning

	$\Delta\epsilon^{VBM}_{LDA}$	Σ^c	Σ^x	V^{xc}	$\Sigma^x - V^{xc}$	$\Delta\epsilon^{corr}$	$\Delta^{VBM}_{G_0W_0}$
AE-V1	$2s^2 2p^6 3s^2 3p^6 3d^{10}$						
Γ_{VBM}		3.16	-21.60	-18.65	-2.95	0.21	
Γ_d		8.51	-38.28	-33.28	-5.00	3.51	
Δ	13.26	-5.35	16.68	14.63	2.05	-3.30	9.96
AE-V2	$2s^2 2p^6 3s^2 3p^6 3d^{10}$						
Γ_{VBM}		3.22	-22.62	-19.21	-3.41	-0.19	
Γ_d		10.23	-51.90	-40.11	-11.79	-1.56	
Δ	13.26	-7.01	29.28	20.90	8.38	1.37	14.63
AE	$2s^2 2p^6 3s^2 3p^6 3d^{10}$						
Γ_{VBM}		3.19	-23.88	-20.48	-3.40	-0.21	
Γ_d		10.50	-56.81	-43.76	-13.05	-2.55	
Δ	13.26	-7.31	32.93	23.28	9.65	2.34	15.60

All-electron G_0W_0 calculations reveal …

- Errors in matrix elements can be of the order of several eV
- Main problems in PP calculations due to
  - core-valence partitioning
  - pseudoization
- Cancelation effects on different levels
  - Σ^x and V^{xc}
  - exchange and correlation
  - valence and conduction states
- Cancelation incomplete for semicore
- AE calculations needed as benchmark
  - but be aware of issues concerning unoccupied states!

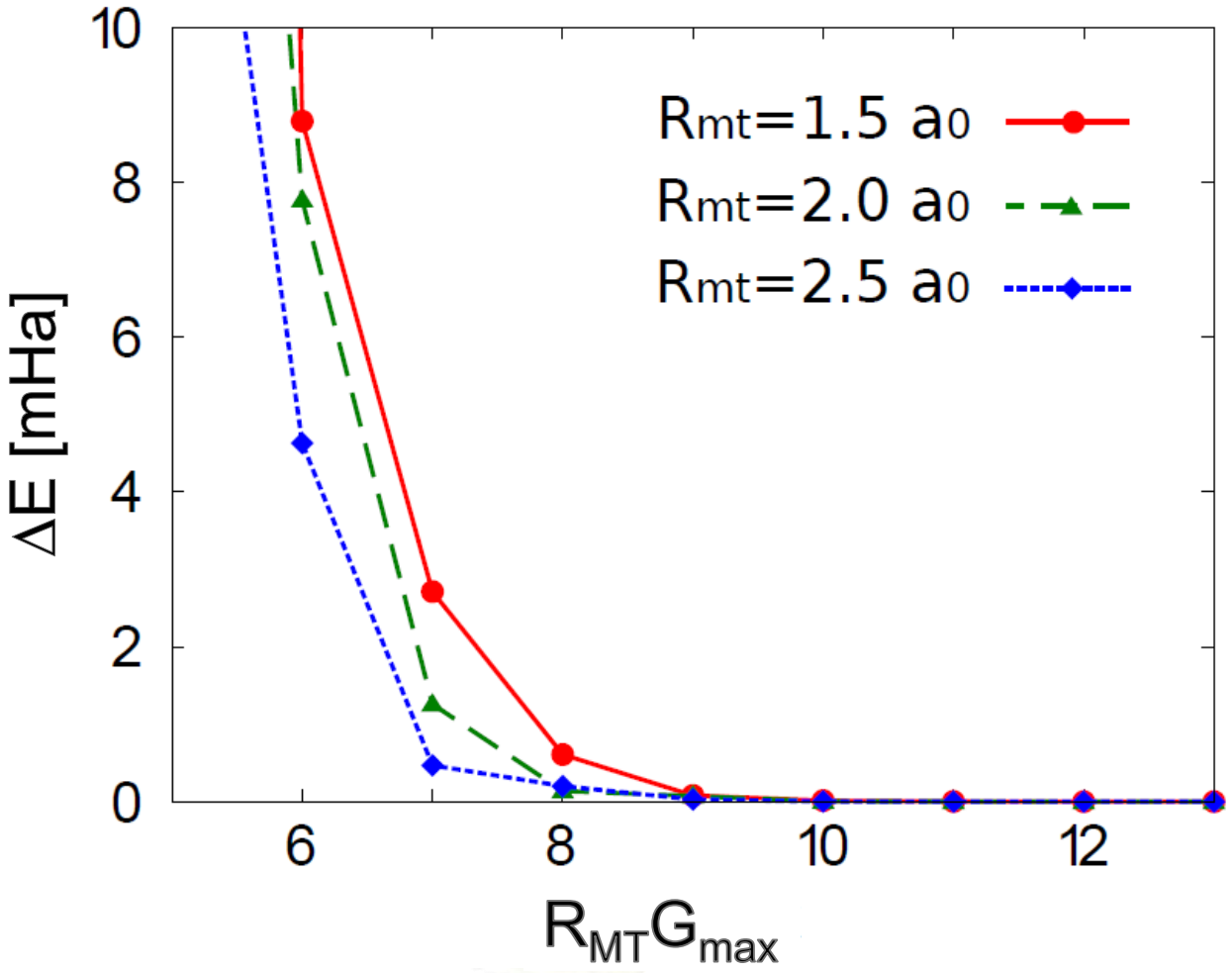
LAPW and related methods …

- are more complicated and more costly than many other methods
- but highly precise

  … if used properly!
- can handle any material

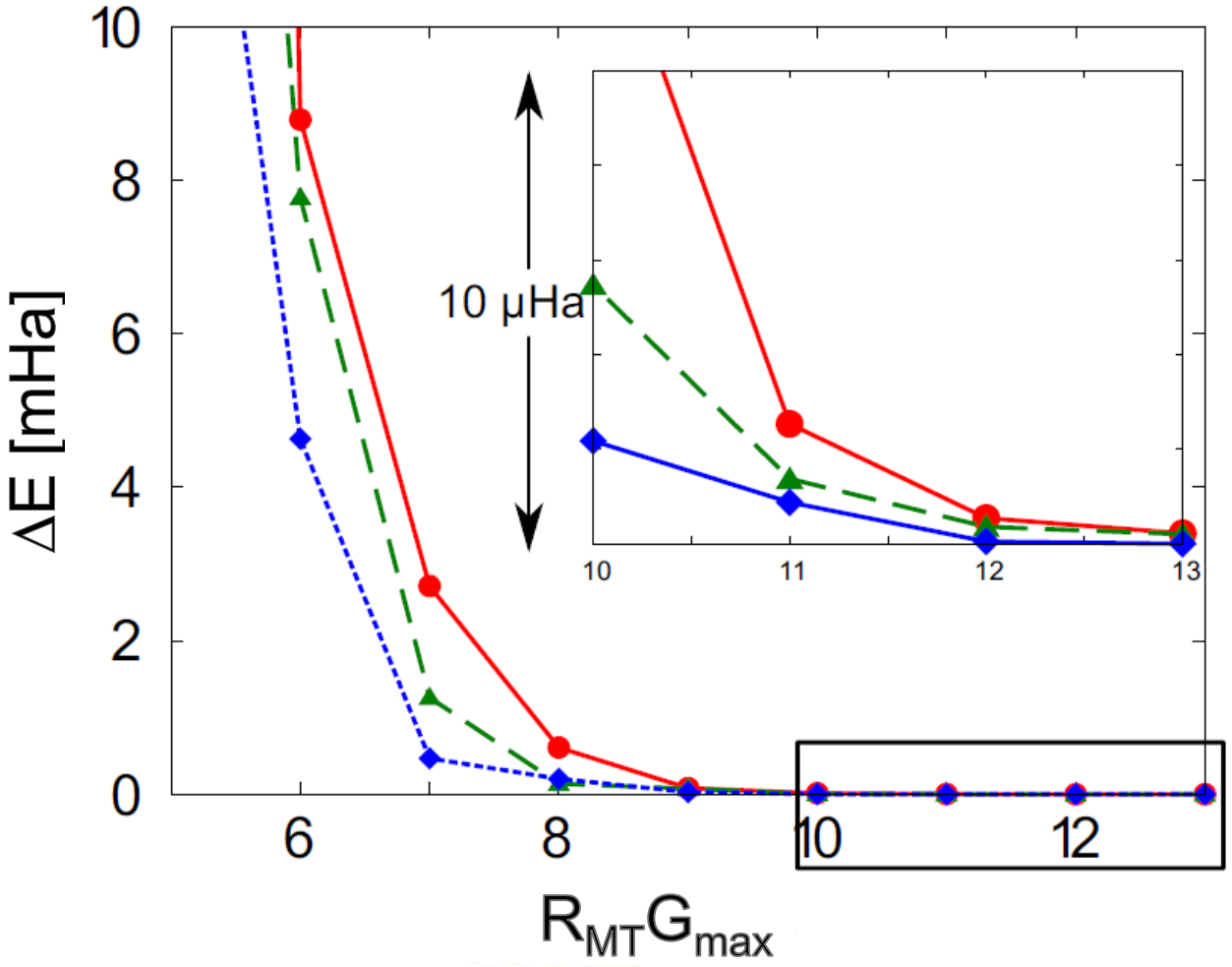
  irrespective of the atoms involved
- allow for exploring the core region
- can be regarded as benchmark for other methods

Example: Ar atom



- Same holds for diamond, GaN, …

Example: Ar atom



- Same holds for diamond, GaN, …

The `exciting` team

- in the excited state