

INTRODUCTION TO



January 16, 2018

Andris Gulans
Humboldt-Universität zu Berlin

Outline

- What is **exciting** and what can it do?
- LAPW+lo basis
- **exciting** input

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- What is **exciting** and what can it do?
- LAPW+lo basis
- **exciting** input

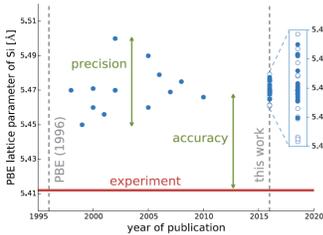
exciting code

- Full-potential all-electron code
- Flexible (L)APW+lo basis
- Broad functionality:
 - DFT
 - GW
 - TDDFT
 - Bethe-Salpeter equation
- Open-source code distributed under the GPL license



Gulans et al., JPCM 26, 363202 (2014)
exciting-code.org

Benchmarking DFT calculations



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

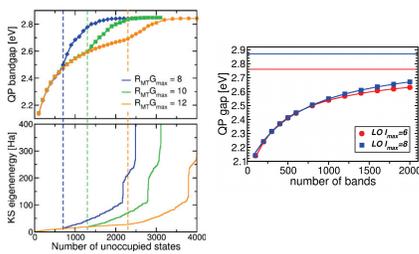
RESEARCH ARTICLE

DFT METHODS

Reproducibility in density functional theory calculations of solids

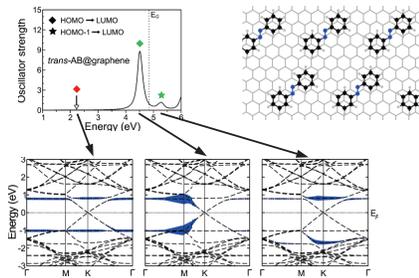
Kurt Lejaeghere,¹ Gustav Bihlmayer,² Torbjörn Björkman,^{3,4} Peter Blaha,⁵ Stefan Blügel,⁶ Volker Blum,⁷ Damien Caliste,^{7,8} Ivano E. Castelli,⁹ Stewart J. Clark,¹⁰ Andrea Dal Corso,¹¹ Stefano de Gironcoli,¹² Thierry Deutsch,^{7,8} John Kay Dewhurst,¹² Igor Di Marco,¹³ Claudia Draxl,^{14,15} Marcin Dulak,¹⁶ Olle Eriksson,¹³ José A. Flores-Livas,¹⁷ Kevin F. Garrity,¹⁷ Luigi Genovese,^{7,8} Paolo Giannozzi,¹⁸ Matteo Giantomassi,¹⁹ Stefan Goedecker,²⁰ Xavier Gonze,¹⁹ Oscar Grünis,^{19,21} E. K. U. Gross,¹⁹ Andris Gulans,^{14,15} François Gygi,^{7,8} D. R. Hamann,^{22,24} Phl J. Hasnip,²⁵ N. A. W. Holzwarth,²⁶ Diana Isyan,²⁷ Dominik B. Jochym,²⁷ François Jollet,²⁸ Daniel Jones,²⁹ Georg Kresse,³⁰ Klaus Koepernik,^{31,32} Emine Küçükbenli,³³ Yaroslav O. Kvashnin,³⁴ Inka L. M. Loch,^{35,36} Sven Lubeck,¹⁴ Martin Marsman,³⁰ Nicola Marzari,¹ Ulrike Niemoche,³⁷ Lars Nordström,³⁸ Tamas Ozaki,³⁴ Lorenzo Paulatto,³⁹ Chris J. Pickard,⁴⁰ Ward Poelmans,^{4,37} Matt L. J. Probert,⁴¹ Keith Refson,^{42,43} Manuel Richter,⁴⁴ Gian-Marco Rignanese,¹⁹ Santanu Saha,⁴⁵ Matthias Scheffler,^{46,47} Martin Schlipf,⁴⁸ Kartheinz Schwarz,⁴⁹ Sangeeta Sharma,⁵⁰ Francesca Tavazza,⁵¹ Patrik Thunström,⁵² Alexandre Tkatchenko,^{35,42} Marc Torrent,³⁸ David Vanderbilt,⁵³ Michiel J. van Setten,⁴⁹ Veronique Van Speybroeck,¹ John M. Willis,⁴⁴ Jonathan R. Yates,²⁹ Guo-Xu Zhang,⁴⁴ Steffan Cottenier,^{1,45,54}

Benchmarking GW: ZnO gap



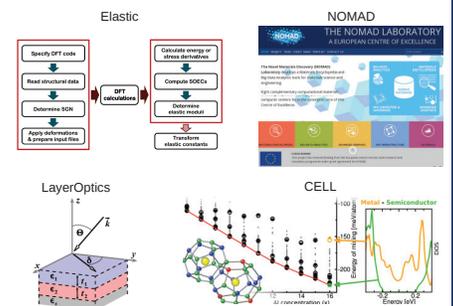
Dmitrii Nabok, Andris Gulans, and Claudia Draxl, Phys. Rev. B 94, 035118 (2016)

Optical properties: azobenzene on graphene

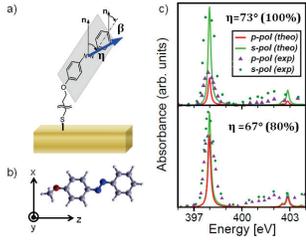


Fu, Cocchi, Nabok, Gulans, Draxl, Phys. Chem. Chem. Phys. 19, 6196 (2017)

Tools



LayerOptics



C. Vorwerk, C. Cocchi, C. Draxl, Comp. Phys. Comm. **201**, 119 (2016)

Outline

- What is exciting and what can it do?
- **LAPW+lo basis**
- exciting input

Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r})\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$v_{\text{KS}}(\mathbf{r}) = v_{\text{n}}(\mathbf{r}) + v_{\text{h}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

Potential due to nuclei
Exchange-correlation potential

Potential due to electron repulsion, or simply Hartree potential

Mapping onto a linear algebra problem

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r})\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i(\mathbf{G}+\mathbf{k})} \phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r})$$

Basis functions

Hamiltonian matrix elements

$$H_{\mathbf{G}\mathbf{G}'}^{\mathbf{k}} = \langle \phi_{\mathbf{G}+\mathbf{k}} | \hat{H} | \phi_{\mathbf{G}'+\mathbf{k}} \rangle$$

Overlap matrix elements

$$S_{\mathbf{G}\mathbf{G}'}^{\mathbf{k}} = \langle \phi_{\mathbf{G}+\mathbf{k}} | \phi_{\mathbf{G}'+\mathbf{k}} \rangle$$

Linear generalized eigenvalue problem

$$Hc = \varepsilon Sc$$

Mapping onto a linear algebra problem

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{KS}}(\mathbf{r})\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$\psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i(\mathbf{G}+\mathbf{k})} \phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r})$$

Basis functions

Hamiltonian matrix elements

$$H_{\mathbf{G}\mathbf{G}'}^{\mathbf{k}} = \langle \phi_{\mathbf{G}+\mathbf{k}} | \hat{H} | \phi_{\mathbf{G}'+\mathbf{k}} \rangle$$

Overlap matrix elements

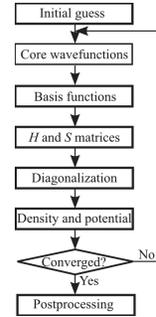
$$S_{\mathbf{G}\mathbf{G}'}^{\mathbf{k}} = \langle \phi_{\mathbf{G}+\mathbf{k}} | \phi_{\mathbf{G}'+\mathbf{k}} \rangle$$

Linear generalized eigenvalue problem

$$Hc = \varepsilon Sc$$

But the potential depends on the electron density, which depends on the wavefunctions...

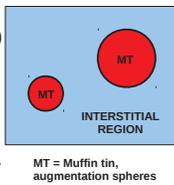
Workflow



(L)APW basis

- LAPW stands for (linearized) augmented plane waves.

- We have some *a priori* knowledge what to expect from wavefunctions close to nuclei and far away from them.

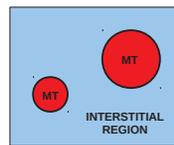
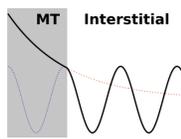


- Close to nucleus → atom-like WFs. Use “atomic orbitals”!

- Away from nucleus → smooth, slowly varying WFs. Use plane waves!

APW basis

$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{G+k} u_l(r; \epsilon) Y_{lm}(\theta, \varphi), & \text{if } r \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \text{otherwise} \end{cases}$$



MT = Muffin tin, augmentation spheres

Kohn-Sham equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{KS}}(r)\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

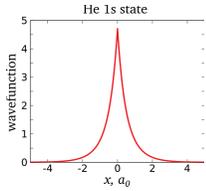
- If the potential is spherically symmetric, we could solve just the radial equation

$$\left[-\frac{1}{2r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r}\right) + \frac{l(l+1)}{2r^2} + v_{\text{KS}}(r)\right] u_l(r) = \varepsilon u_l(r)$$

Example: Helium atom

- 1s state can be solved for using just the radial equation

$$\left[-\frac{1}{2r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{l(l+1)}{2r^2} + v_{KS}(r) \right] u_l(r) = \epsilon u_l(r)$$

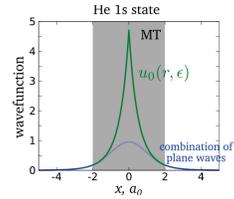


Example: Helium atom with APW

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}} \phi_{\mathbf{G}}(\mathbf{r})$$

Example: Helium atom with APW

$$\psi(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \sum_{lm} C_{\mathbf{G}} A_{lm}^{\mathbf{G}} u_l(r; \epsilon) Y_{lm}(\theta, \varphi), & \text{if } r \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, & \text{otherwise} \end{cases}$$

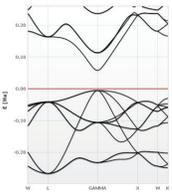


- 1s state is spherically symmetric, and only the $l=0$ component should be non-zero.

But how do we know the energy in advance?

Which energy would you take?

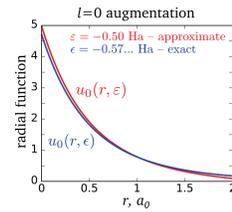
$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{\mathbf{G}+\mathbf{k}} u_l(r; \epsilon) Y_{lm}(\theta, \varphi), & \text{if } r \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \text{otherwise} \end{cases}$$



The energy parameter should match eigenenergies of a studied system.

The original APW method finds the energy parameters *automatically* by considering energy-dependent Hamiltonian. It is **too complicated!**

What if we just guess the energy?



Linearization

- Problem: we know how to compute $u(r, \epsilon)$, but we do not know which specific ϵ to take.
- A step towards solution: linearize u .

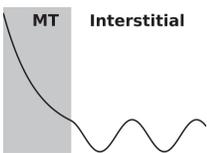
$$u_l(r, \epsilon) = u_l(r, \epsilon_l) + (\epsilon - \epsilon_l) \dot{u}_l(r, \epsilon_l) + O((\epsilon - \epsilon_l)^2)$$

Still depends on energy, but now we know the direction for the improvement

LAPW basis

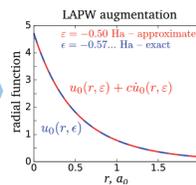
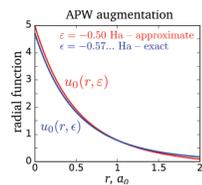
$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} [A_{lm}^{\mathbf{G}+\mathbf{k}} u_l(r; \epsilon_l) + B_{lm}^{\mathbf{G}+\mathbf{k}} \dot{u}_l(r; \epsilon_l)] Y_{lm}(\theta, \varphi), & \text{if } r \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \text{otherwise} \end{cases}$$

Smoothness condition



Example: Helium atom with LAPW

$$\psi(\mathbf{r}) = \begin{cases} \sum_{\mathbf{G}} \sum_{lm} C_{\mathbf{G}} [A_{lm}^{\mathbf{G}} u_l(r; \epsilon) + B_{lm}^{\mathbf{G}} \dot{u}_l(r; \epsilon)] Y_{lm}(\theta, \varphi), & \text{if } r \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}, & \text{otherwise} \end{cases}$$



Features of LAPW

- Improves upon APW with frozen energy parameters.
- Preserves the number of basis functions compared to APW.
- Is limited to description of valence electrons, since there can be only one energy parameter per l . Core states are treated differently than valence states.

APW+lo basis

- APW

$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{G+k} u_l(r; \varepsilon_l) Y_{lm}(\theta, \varphi), & \text{if } r \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}, & \text{otherwise} \end{cases}$$

- Local orbital

$$\phi_{\mu}(\mathbf{r}) = [a_{\mu} u_l(r; \varepsilon_l) + b_{\mu} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\mu}} \delta_{mm_{\mu}}$$

Local orbital is normalized and turns to zero on the augmentation sphere

Size of the basis and Hamiltonian is defined by the number of plane-waves and local orbitals.

Linearization, quadratization etc.

$$u_l(r, \varepsilon) = u_l(r, \varepsilon_l) + (\varepsilon - \varepsilon_l) \dot{u}_l(r, \varepsilon_l) + \frac{(\varepsilon - \varepsilon_l)^2}{2} \ddot{u}_l(r, \varepsilon_l) + \frac{(\varepsilon - \varepsilon_l)^3}{6} \dddot{u}_l(r, \varepsilon_l) + \dots$$

- APW

$$\phi_{\mathbf{G}+\mathbf{k}}(\mathbf{r}) = \begin{cases} \sum_{lm} A_{lm}^{G+k} u_l(r; \varepsilon_l) Y_{lm}(\theta, \varphi), & \text{if } r \in \text{MT} \\ \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{G}+\mathbf{k})\mathbf{r}}, & \text{otherwise} \end{cases}$$

- Local orbitals

$$\phi_{\mu}(\mathbf{r}) = [a_{\mu} u_l(r; \varepsilon_l) + b_{\mu} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\mu}} \delta_{mm_{\mu}}$$

$$\phi_{\nu}(\mathbf{r}) = [a_{\nu} u_l(r; \varepsilon_l) + b_{\nu} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\nu}} \delta_{mm_{\nu}}$$

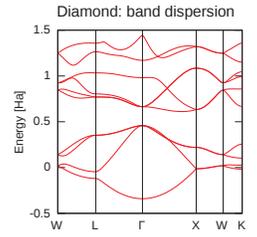
$$\phi_{\xi}(\mathbf{r}) = [a_{\xi} u_l(r; \varepsilon_l) + b_{\xi} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\xi}} \delta_{mm_{\xi}}$$

...

Example: diamond

- Consider $l=1$
 $\varepsilon_{2p} = 0.15$

method	E_{tot} , Ha
APW	-75.576230
LAPW	-75.590045
APW+lo	-75.590101
APW+2lo	-75.590103
APW+3lo	-75.590103



- rgkmax=8

Core electrons are considered separately using the 4-component Dirac equation

Example: diamond

- Consider $l=1$
 $\varepsilon_{2p} = 0.15$

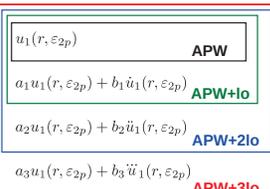
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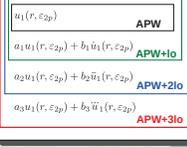
Diamond: band dispersion

Radial degrees of freedom for $l=1$



Species

Radial degrees of freedom for $l=1$



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Semicore states

- $u_l(r; \varepsilon_l), \dot{u}_l(r; \varepsilon_l), \dots$ have nodal structures that are not compatible with the semicore. We need a basis function that recovers the correct nodal structure.

- A choice that brings you to the "APW level":

$$\phi_{\mu}(\mathbf{r}) = [a_{\mu} u_l(r; \varepsilon_l) + b_{\mu} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\mu}} \delta_{mm_{\mu}}$$

- Use expansion in series to go beyond it!

$$\phi_{\mu}(\mathbf{r}) = [a_{\mu} u_l(r; \varepsilon_l) + b_{\mu} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\mu}} \delta_{mm_{\mu}}$$

$$\phi_{\nu}(\mathbf{r}) = [a_{\nu} u_l(r; \varepsilon_l) + b_{\nu} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\nu}} \delta_{mm_{\nu}}$$

$$\phi_{\xi}(\mathbf{r}) = [a_{\xi} u_l(r; \varepsilon_l) + b_{\xi} \dot{u}_l(r; \varepsilon_l)] Y_{lm}(\hat{\mathbf{r}}) \delta_{ll_{\xi}} \delta_{mm_{\xi}}$$

...

Example: diamond

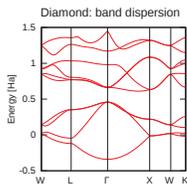
- Consider $l=0$ with 1s and 2s both considered as valence electrons

$$\varepsilon_{1s} = -9.20$$

$$\varepsilon_{2s} = 0.15$$

method	E_{tot} , Ha
APW	-29.678023
LAPW	-29.745748
APW+lo	-75.526692
APW+2lo	-75.589507
APW+3lo	-75.590142
APW+4lo	-75.590143

- rgkmax=8



Example: diamond

- Consider $l=0$ with 1s and 2s both considered as valence electrons

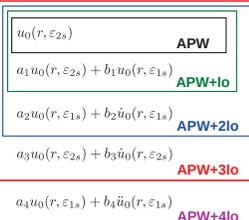
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APW+4lo	-75.590143

- rgkmax=8

Radial degrees of freedom for $l=0$



Features of APW+lo

- Improves upon APW with frozen energy parameters.

- Slightly increases the number of basis functions compared to APW.

- Can describe valence states, semicore states and even core states. But normally core states are treated differently than valence states.

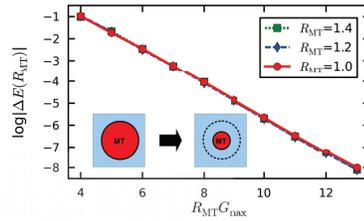
- Can be easily adjusted to yield any accuracy you like.

What about plane waves?

- Accuracy of the plane-wave part of the basis is controlled by their cut-off. However, the required cut-off strongly depends on the size of muffin tins. Hence the LAPW community uses $R_{MT}G_{max}$ as the dimensionless cut-off parameter.

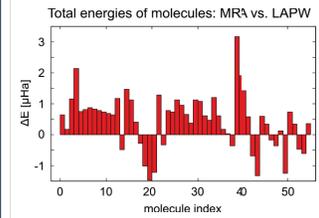
- Larger is $R_{MT}G_{max}$, more accurate is your calculation. But do not abuse it! By the value of ~12 you get ~1 μ Ha at a high expense. Beyond it, the basis becomes almost linearly dependent.

Example: diamond



Gulans *et al.*, JPCM 26, 363202 (2014)

Example: G2-1 molecule set



Gulans, Kozhevnikov, Draxl, submitted.

Outline

- What is **exciting** and what can it do?
- LAPW+lo basis
- exciting** input

exciting input

- Extensible Markup Language (XML)
- Input validation
 - Elements → actions
 - Attributes → parameters

input.xml

```

1 <input>
2 <title>Lithium Fluoride</title>
3 <structure speciespath=".">
4 <crystal>
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6 <basevect> 3.80402 0.00000 3.80402 </basevect>
7 <basevect> 0.00000 3.80402 3.80402 </basevect>
8 </crystal>
9 <species speciesfile="Li.xml">
10 <atom coord="0.0000 0.0000 0.0000"/>
11 </species>
12 <species speciesfile="F.xml">
13 <atom coord="0.5000 0.5000 0.5000"/>
14 </species>
15 </structure>
16 <groundstate>
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18 <lmxvr="8"
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20 <avidh="0.0001"/>
21 </groundstate>
22 </input>
    
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input.xml

```

<input>
...
</input>
    
```

input.xml

```

<input>
  <title> Title </title>
...
</input>
    
```

input.xml

```

<input>
  <title> Title </title>
  <structure ...> ... </structure>
...
</input>
    
```

input.xml

```
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<title> Title </title>

<structure speciespath='/path/species'>
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</structure>

...

</input>
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input.xml

```
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<structure ...> ... </structure>

<groundstate ...> ... </groundstate>

...

</input>
```

input.xml

```
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...
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input.xml

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<groundstate ...> ... </groundstate>

<relax ...>
</relax>

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</input>
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input.xml

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...
<phonon ...> ... </phonon>

</input>
```

HoW
exciting!
2018

July 31 - August 9, 2018
Berlin, Germany

<https://www2.physik.hu-berlin.de/how-exciting-2018/>

Acknowledgments



Summary

- Full-potential all-electron code
- Flexible (L)APW+lo basis
- Broad functionality:
 - DFT
 - GW
 - TDDFT
 - Bethe-Salpeter equation
- Open-source code distributed under the GPL license

exciting

Gulans et al., JPCM 26, 363202 (2014)
exciting-code.org