

Lecture on First-principles Computations (14): The Linear Combination of Atomic Orbitals (LCAO) Method

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Recall: the plane wave basis set

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}_I) \quad \text{Periodic crystal potential}$$

$$\left(-\frac{\nabla^2}{2m} + V(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}(\mathbf{r})$$

Ritz variational principle: expanding $\psi_{n\mathbf{k}}(\mathbf{r})$ in terms of basis functions:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mu} c_{\mu,n}(\mathbf{k}) \chi_{\mu\mathbf{k}}(\mathbf{r}) \quad \Rightarrow$$

$$\sum_{\nu} H_{\mu\nu}(\mathbf{k}) c_{\nu,n}(\mathbf{k}) = \epsilon_{n\mathbf{k}} c_{\mu,n}(\mathbf{k})$$

Basis-type I -- Plane waves :

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

$(\mu \rightarrow \mathbf{G})$

Linear combination of atomic orbitals (LCAO)

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}_I) \quad \text{Periodic crystal potential}$$

$$\left(-\frac{\nabla^2}{2m} + V(\mathbf{r}) \right) \psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}(\mathbf{r})$$

Expanding $\psi_{n\mathbf{k}}(\mathbf{r})$ in terms of basis functions:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mu} c_{\mu,n}(\mathbf{k}) \chi_{\mu\mathbf{k}}(\mathbf{r})$$

Basis-type II – localized atom-centered orbitals:

$$\chi_{\mu\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \chi_{a,j,l,m}(\mathbf{r} - \mathbf{R} - \mathbf{r}_a) e^{i\mathbf{k} \cdot \mathbf{R}}$$

$$(\mu = (a, j, l, m))$$

Atomic position within the unit cell

The LCAO method

General features of local orbitals

$$\chi_{a,j,l,m}(\mathbf{r} - \mathbf{r}_a) = R_{a,j,l}(|\mathbf{r} - \mathbf{r}_a|)Y_{lm}(\widehat{\mathbf{r} - \mathbf{r}_a})$$

- Centered at atomic positions. The angular part $Y_{lm}(\hat{\mathbf{r}})$ are spherical harmonics, while the radial functions $R_{a,j,l}(r)$ are flexible -- they can be analytical functions (Gaussians, Slater-type orbitals), or completely numerical.
- j denotes different radial functions with the same angular momentum, and hence controls the size of the basis set (from tight-binding to full quantitative calculations).
 - Single- ζ (SZ): $1s1p$ for O, C, N, etc. (minimal basis)
 - Double- ζ (DZ): $2s2p$ for O, C, N, etc.
 - Double- ζ plus polarization function (DZP): $2s2p1d$ for O, C, N, etc.
- Compact in size (efficient), and suitable for local symmetry analysis
- Constructing “systematically converging” atomic basis set is a highly nontrivial task, and needs special attention.

The Hamiltonian and overlap matrices

$$\begin{aligned} \hat{H}\psi_{nk}(\mathbf{r}) &= \epsilon_{nk}\psi_{nk}(\mathbf{r}) \\ \psi_{nk}(\mathbf{r}) &= \sum_{\mu} c_{\nu,n}(\mathbf{k})\chi_{\nu,k}(\mathbf{r}) \end{aligned} \quad \left. \vphantom{\begin{aligned} \hat{H}\psi_{nk}(\mathbf{r}) &= \epsilon_{nk}\psi_{nk}(\mathbf{r}) \\ \psi_{nk}(\mathbf{r}) &= \sum_{\mu} c_{\nu,n}(\mathbf{k})\chi_{\nu,k}(\mathbf{r}) \end{aligned}} \right\} \Rightarrow$$

$$\sum_{\nu} H_{\mu\nu}(\mathbf{k})c_{\nu,n}(\mathbf{k}) = \epsilon_{nk} \sum_{\nu} S_{\mu\nu}(\mathbf{k})c_{\nu,n}(\mathbf{k})$$

$$H_{\mu\nu}(\mathbf{k}) = \langle \chi_{\mu k} | \hat{H} | \chi_{\nu k} \rangle$$

$$S_{\mu\nu}(\mathbf{k}) = \langle \chi_{\mu k} | \chi_{\nu k} \rangle$$

The Hamiltonian and overlap matrices in the LCAO method

$$\sum_{\nu} H_{\mu\nu}(\mathbf{k}) c_{\nu,n}(\mathbf{k}) = \epsilon_{nk} \sum_{\nu} S_{\mu\nu}(\mathbf{k}) c_{\nu,n}(\mathbf{k})$$

$$H_{\mu\nu}(\mathbf{k}) = \langle \chi_{\mu\mathbf{k}} | \hat{H} | \chi_{\nu\mathbf{k}} \rangle, \quad S_{\mu\nu}(\mathbf{k}) = \langle \chi_{\mu\mathbf{k}} | \chi_{\nu\mathbf{k}} \rangle$$

Now

$$\chi_{\mu\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} \chi_{a,j,l,m}(\mathbf{r} - \mathbf{R} - \mathbf{r}_a) e^{i\mathbf{k}\cdot\mathbf{R}}$$

$$H_{\mu\nu}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} H_{\mu\nu}(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}, \quad S_{\mu\nu}(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} S_{\mu\nu}(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}$$

$$H_{\mu\nu}(\mathbf{R}) = \langle \chi_{a,j,l,m}(\mathbf{r} - \mathbf{r}_a) | \hat{H} | \chi_{a',j',l',m'}(\mathbf{r} - \mathbf{r}_{a'} - \mathbf{R}) \rangle$$

$$S_{\mu\nu}(\mathbf{R}) = \langle \chi_{a,j,l,m}(\mathbf{r} - \mathbf{r}_a) | \chi_{a',j',l',m'}(\mathbf{r} - \mathbf{r}_{a'} - \mathbf{R}) \rangle$$

Multi-center integrals

Two-center integrals:

$$S_{\mu\nu}(\mathbf{R}) = \langle \chi_{a,j,l,m}(\mathbf{r} - \mathbf{r}_a) | \chi_{a',j',l',m'}(\mathbf{r} - \mathbf{r}_{a'} - \mathbf{R}) \rangle$$

$$T_{\mu\nu}(\mathbf{R}) = \langle \chi_{a,j,l,m}(\mathbf{r} - \mathbf{r}_a) | -\frac{\nabla^2}{2m} | \chi_{a',j',l',m'}(\mathbf{r} - \mathbf{r}_{a'} - \mathbf{R}) \rangle$$

Can be computed efficiently in Fourier space.

Three-center integrals:

$$V_{\mu\nu}(\mathbf{R}) = \langle \chi_{a,j,l,m}(\mathbf{r} - \mathbf{r}_a) | \hat{V} | \chi_{a',j',l',m'}(\mathbf{r} - \mathbf{r}_{a'} - \mathbf{R}) \rangle$$

$$V(\mathbf{r}) = \sum_{a'', \mathbf{R}'} V_{a''}(\mathbf{r} - \mathbf{r}_{a''} - \mathbf{R}')$$



Three centers

For numerical orbitals, this is often evaluated by grid integration.

Slater-type orbitals (STO)

$$\chi_{abc}^{STO}(x, y, z) = N x^a y^b z^c e^{-\zeta r}$$



Normalization factor

- a, b, c control the angular momentum: $l = a + b + c$.
- ζ controls the spread of the orbital in space.
- These basis functions don't have nodes, and not pure spherical harmonics. For $1s$, it is hydrogen-like orbital.
Hydrogen $1s$ orbital: $\psi_{1s}(r) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$, a_0 : Bohr radius
- Long-range and short-range behaviors are correct.
 - ✓ Exponential decay at the long range
 - ✓ Kato's cusp condition at the short range

$$\text{Effective nuclear charge: } Z = \frac{a_0}{2n(\mathbf{r})} \left. \frac{dn(\mathbf{r})}{dr} \right|_{r \rightarrow R}$$

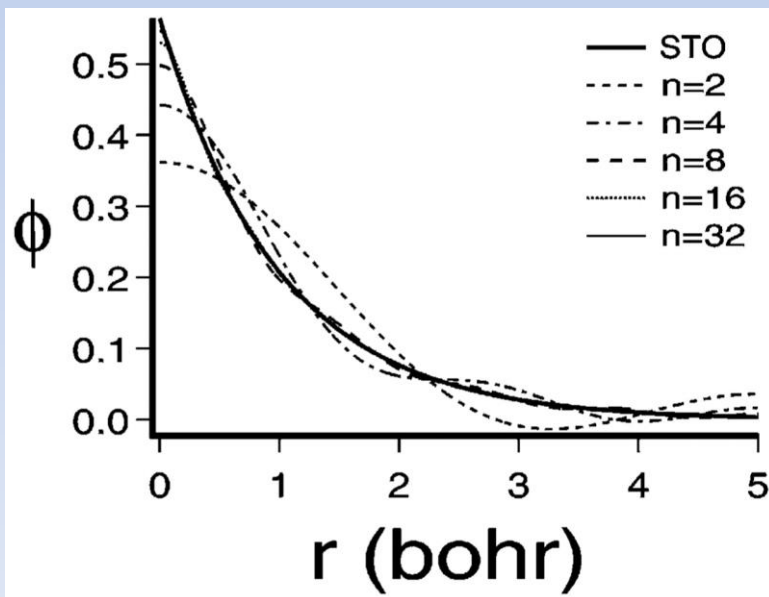
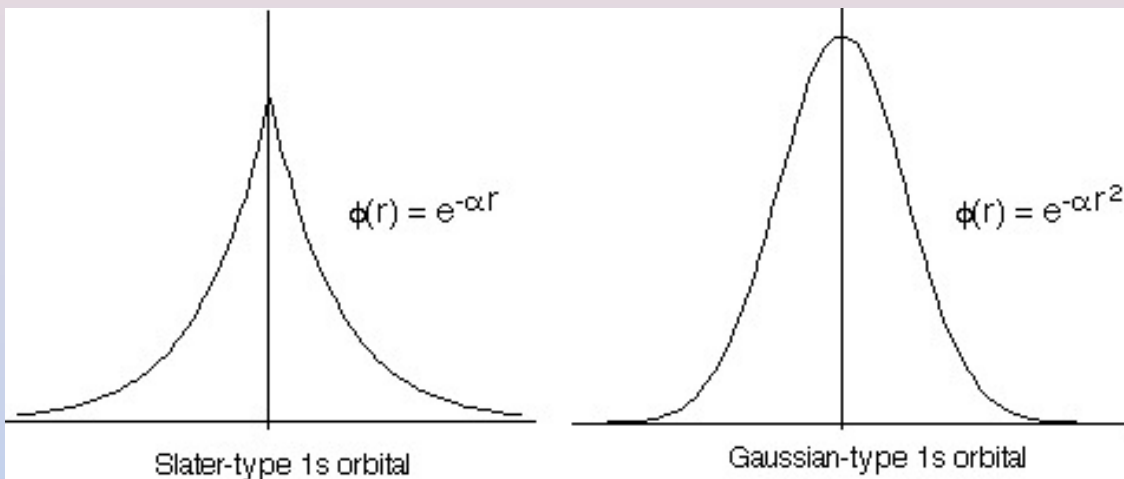
Gaussian-type orbitals (GTO)

$$\chi_{lmn}^{\text{GTO}}(x, y, z) = N x^a y^b z^c e^{-\zeta r^2}$$

Normalization factor $N = \sqrt{\frac{(2a-1)!! (2b-1)!! (2c-1)!! \pi^{3/2}}{(4\zeta)^{a+b+c} (2\zeta)^{3/2}}}$

- a, b, c control the angular momentum.
- ζ controls the width of the orbital.
- They are not hydrogen-like orbitals for $1s$.
- Long-range and short-range behaviors are incorrect.
- The Coulomb integrals involving GTOs can be easily computed

Comparison between STOs and GTOs



$$\phi^{STO}(r) = e^{-\alpha r} \approx \sum_i a_i e^{-\beta_i r^2}$$

The computation integrals among GTOs

Gaussian product theorem:

$$\chi_A^{GTO} = N_A x_A^{a_1} y_A^{b_1} z_A^{c_1} e^{-\zeta_1 |\mathbf{r} - \mathbf{R}_A|^2}, \quad \chi_B^{GTO} = N_B x_B^{a_2} y_B^{b_2} z_B^{c_2} e^{-\zeta_2 |\mathbf{r} - \mathbf{R}_B|^2}$$

$$\mathbf{r}_A = \mathbf{r} - \mathbf{R}_A = (x_A, y_A, z_A)$$

$$e^{-\zeta_1 |\mathbf{r} - \mathbf{R}_A|^2} e^{-\zeta_2 |\mathbf{r} - \mathbf{R}_B|^2} = e^{-\frac{\zeta_1 \zeta_2}{\zeta_1 + \zeta_2} |\mathbf{R}_A - \mathbf{R}_B|^2} e^{-(\zeta_1 + \zeta_2) \left| \mathbf{r} - \frac{\zeta_1 \mathbf{R}_A + \zeta_2 \mathbf{R}_B}{\zeta_1 + \zeta_2} \right|^2}$$

$$\chi_A^{GTO} \chi_B^{GTO} = e^{-\frac{\zeta_1 \zeta_2}{\zeta_1 + \zeta_2} |\mathbf{R}_A - \mathbf{R}_B|^2} \times$$

$$\left\{ \text{linear combination of Gaussians centered at } \frac{\zeta_1 \mathbf{R}_A + \zeta_2 \mathbf{R}_B}{\zeta_1 + \zeta_2} \right\}$$

Multi-centered integrals can be reduced to linear combination of two-centered integrals, that can be computed analytically.

STOs, GTOs, and NAOs

GTOs

STOs

NAOs

Accuracy of the basis functions



Number of basis functions at
a given level of accuracy



Number of integrals to be evaluated



Difficulty of evaluating the integrals



Symmetry analysis for two-center integrals

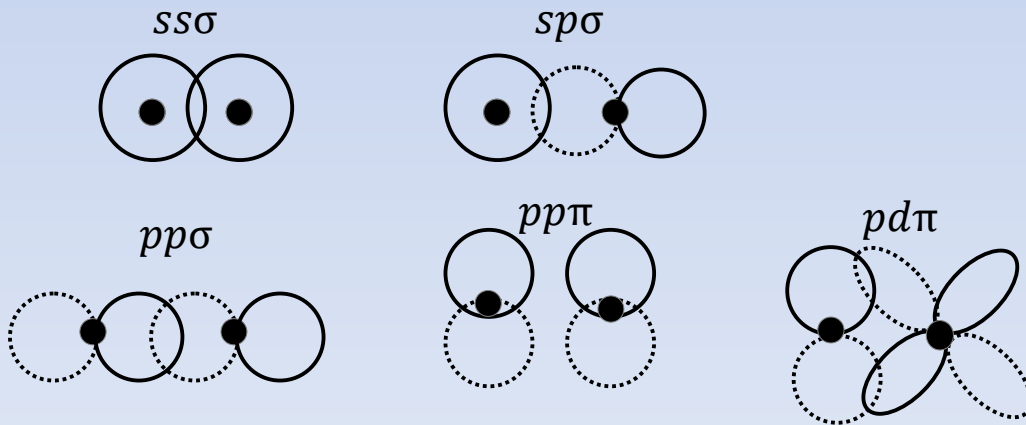
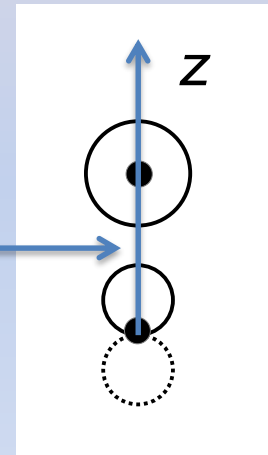
$$\langle \chi_{a,j,l,m} | \chi_{a',j',l',m'} \rangle = \int d^3 r R_{a,j,l}(|\mathbf{r} - \mathbf{r}_a|) Y_{lm}(\widehat{\mathbf{r} - \mathbf{r}_a}) R_{a',j',l'}(|\mathbf{r} - \mathbf{r}_{a'} - \mathbf{R}|) Y_{l'm'}(\widehat{\mathbf{r} - \mathbf{r}_{a'} - \mathbf{R}})$$

$$= S_{\mu,\nu} \delta_{m,m'} \sim S_{ll'm} \delta_{m,m'}$$

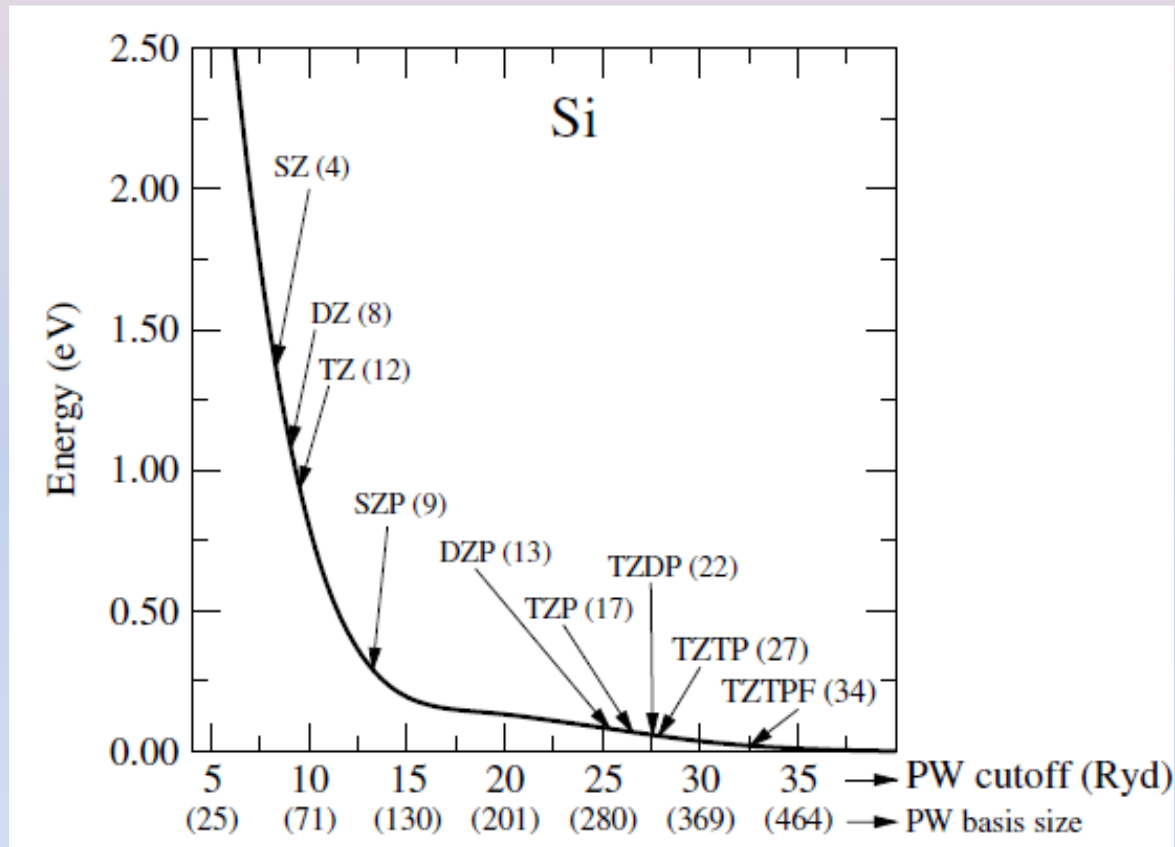
$l = s, p, d, f, \dots$

$m = \sigma, \pi, \delta, \dots$

$$D = R + r_{a'} - r_a$$



From tight-binding to full calculations



J. M. Soler et al, *J. Phys: Condens. Matter* **14**, 2745 (2002)

<http://departments.icmab.es/leem/siesta/>



Spanish Initiative for Electronic Simulations with Thousands of Atoms

[[About](#)] [[Access to the code](#)] [[Documentation](#)] [[Databases \(Pseudos and Bases\)](#)] [[The Team](#)]

News

- [Release of Siesta-3.2](#)
 - [New development version snapshot \(OM method, Joblist suite\)](#)
 - [Enhancements to the TranSiesta/TBTrans code](#)
 - [New book on the electronic structure of solids](#)
-

SIESTA is both a method and its computer program implementation, to perform efficient electronic structure calculations and ab initio molecular dynamics simulations of molecules and solids. SIESTA's

FHI-aims (<https://aimsclub.fhi-berlin.mpg.de/>)



FHI-aims: Full-Potential, All-Electron Electronic Structure Theory with Numeric Atom-Centered Basis Functions

Methods and code development · Fritz-Haber-Institut der Max-Planck-Gesellschaft · Theory Department

FHI-aims

aimsclub

Stable Features at a glance:

FHI-aims is an all-electron electronic structure code based on numeric atom-centered orbitals.

We here provide a list of some of the functionality that is now available. If a specific item is missing that should be here, or if you would like to know about a specific (future) item, feel free to ask us directly.

Most of FHI-aims was developed within the group at FHI, but a growing number of important contributions is being made by other groups. Please see our "The people behind FHI-aims" page for proper attribution.

Physical functionality:

- Periodic geometries on equal footing with non-periodic systems for LDA, GGA, and hybrid functionals, including:
 - dipole corrections for surface slab calculations
 - well-converged large vacuum regions for surface slabs with practically no overhead
- Non-relativistic and scalar relativistic total energies (scalar relativistic energy differences match full-potential LAPW benchmark accuracy)
- Total energy gradients (forces) [LDA, GGA, and hybrid functionals]
- Efficient structure optimization (BFGS or Trust Radius optimization, tunable initial Hessian matrix including scheme by Lindh and coworkers)
- Stress tensor based unit cell optimization for periodic systems
- Born-Oppenheimer molecular dynamics:
 - *NVE* ensemble: Optional wave function extrapolation or higher-order integrator beyond Verlet

ABACUS (<https://abacus.ustc.edu.cn/>)



Today is: Wednesday the 11th of November,

2015

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News

15.10.1

ABACUS V1.0.0

ABACUS version 1.0.0 is available for download!

ABACUS (Atomic-orbital Based Ab-initio Computation at UStc) is an open-source computer code package aiming for large-scale electronic-structure simulations from first principles, developed at the Key Laboratory of Quantum Information, University of Science and Technology of China (USTC) - Computer Network and Information Center, Chinese of Academy (CNIC of CAS).

ABACUS currently provides the following features and functionalities:

1. Ground-state total energy calculations using Kohn-Sham (KS) density functional theory (DFT) with local-density or generalized gradient approximations (LDA/GGAs).
2. Brillouin zone sampling using the Monkhorst-Pack special k-points.
3. Geometry relaxation with both Conjugated Gradient (CG) and BFGS methods.
4. Semi-empirical van der Waals energy correction using the Grimme DFT-D2 scheme.
5. NVT molecular dynamics simulation using the Nose-Hoover thermostat.

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[user's guide](#)



[pseudopotential library](#)



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Other computer codes based on NAOs

- OpenMX (Open source package Material eXplorer)
www.openmx-square.org
- Dmol (Bernard Delley, Swiss, all-electron)
- FPLO (Full-potential local orbital, all-electron, Dresden)
www.fplo.de
- ADF (Amsterdam, Slater-type orbitals)
www.scm.com
- Crystal (Gaussian orbitals for solids)
www.crystal.unito.it
-

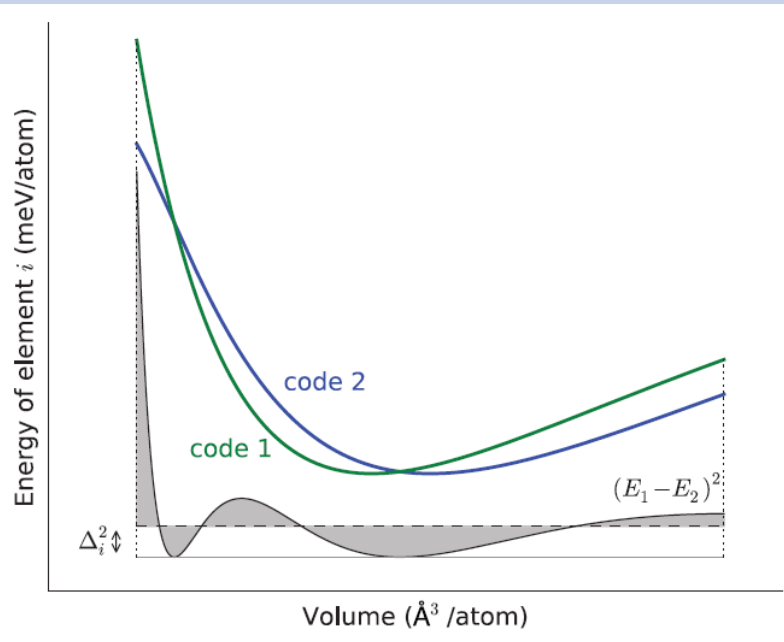
Quantum chemistry codes based on GTOs

- Gaussian (commercial code)
(www.gaussian.com)
- NWChem (free code)
(www.nwchem-sw.org)
- Q-CHEM (commercial code)
(www.q-chem.com)
- Turbomole
(www.turbomole.com)

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Δ -value project in materials science: reproducibility of density-functional theory calculations for solids.

$$\Delta_i(a, b) = \sqrt{\int_{0.94V_{0,i}}^{1.06V_{0,i}} \frac{(E_{b,i}(V) - E_{a,i}(V))^2}{0.12V_{0,i}} dV}$$



PERIODIC TABLE OF THE ELEMENTS
<http://www.periodict.com>

GROUP	1	2	13	14	15	16	17	18										
1	H	He																
2	Li	Be	B	C	N	O	F	Ne										
3	Na	Mg	Al	Si	P	S	Cl	Ar										
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

A set of 71 elemental solids.

Test accuracies of methods/codes
(basis sets, pseudopotentials,
relativistic treatment etc.)

K. Lejaeghere, S. Cottenier, et al.
Science **351**, 1415 (2016).

Comparing solid-state DFT codes, basis sets, and potentials

<https://molmod.ugent.be/deltacodesdft>

Code	Version	Basis	Electron treatment	Δ -value
WIEN2k	13.1	LAPW/APW+lo	all-electron	0 meV/atom
FHI-aims	081213	tier2 numerical orbitals	all-electron (relativistic atomic_zora scalar)	0.2 meV/atom
Exciting	development version	LAPW+xlo	all-electron	0.2 meV/atom
VASP	5.2.12	plane waves	PAW 2015 GW-ready (5.4)	0.3 meV/atom
FHI-aims	081213	tier2 numerical orbitals	all-electron (relativistic zora scalar 1e-12)	0.3 meV/atom
Quantum ESPRESSO	5.1	plane waves	SSSP Accuracy (link is external) (mixed NC/US/PAW potential library)	0.3 meV/atom
Elk	3.1.5	APW+lo	all-electron	0.3 meV/atom
ABINIT	7.8.2	plane waves	PAW JTH v1.0 (link is external)	0.4 meV/atom
FLEUR	0.26	LAPW (+lo)	all-electron	0.4 meV/atom
Quantum ESPRESSO	5.1	plane waves	SSSP Efficiency (link is external) (mixed NC/US/PAW potential library)	0.4 meV/atom
CASTEP	9.0	plane waves	OTFG CASTEP 9.0	0.5 meV/atom

Homework III

Please discuss and compare the following electronic structure methods to solve the KS equations:

1. Orthogonalized plane waves
2. Norm-conserving pseudopotential plane waves
3. Ultrasoft pseudopotential plane waves
4. Projector plane waves
5. Linearized augmented plane waves
6. Korringa-Kohn-Rostoker method
7. The linear combination of atomic orbital method

Emphasis should be placed on their advantages and limitations, and the connections (if they exist) between them.