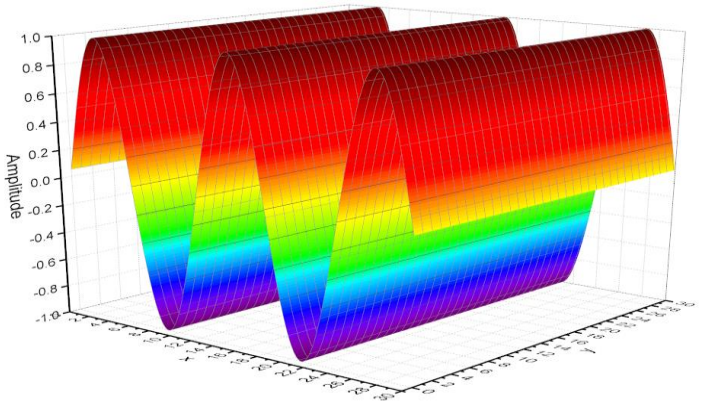
Convergence
-
Plane Wave Basis

Plane-Wave Basis Functions

Core Concept:

Fill space with solutions for free electron

All basis functions are orthogonal: $S = E$



Important Features:

Trivally only for periodic systems

Number of basis functions **independent** of

- *Number of atoms*
- *Number of electrons*

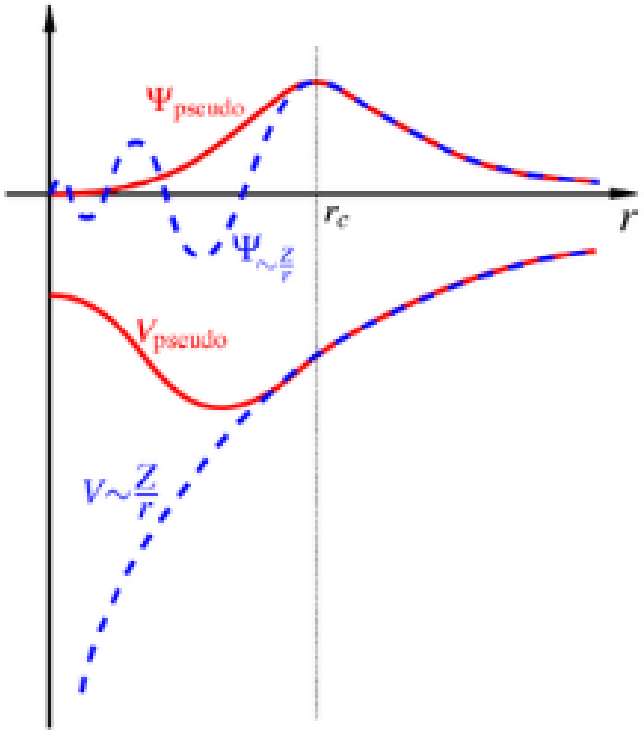
No BSSE!

Basis Set

Large number of plane-waves required to describe varying electron density (>10.000)

Even then, plane-waves cannot capture cusp of core-electrons

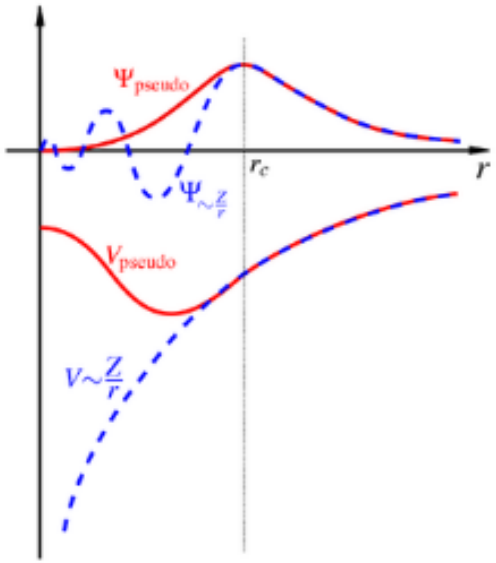
- **Pseudopotentials**
- **Plane-augmented waves**
- **Muffin-tin**



Describing the core

… is an art!

- **Describes correctly the potential/ wave function outside the core**
- **Depends on the method/functional used**
- **Gives rise to „Ghost states“**
- **„Freezes“ the core electrons**
- **Implicitly accounts for relativistic effects**



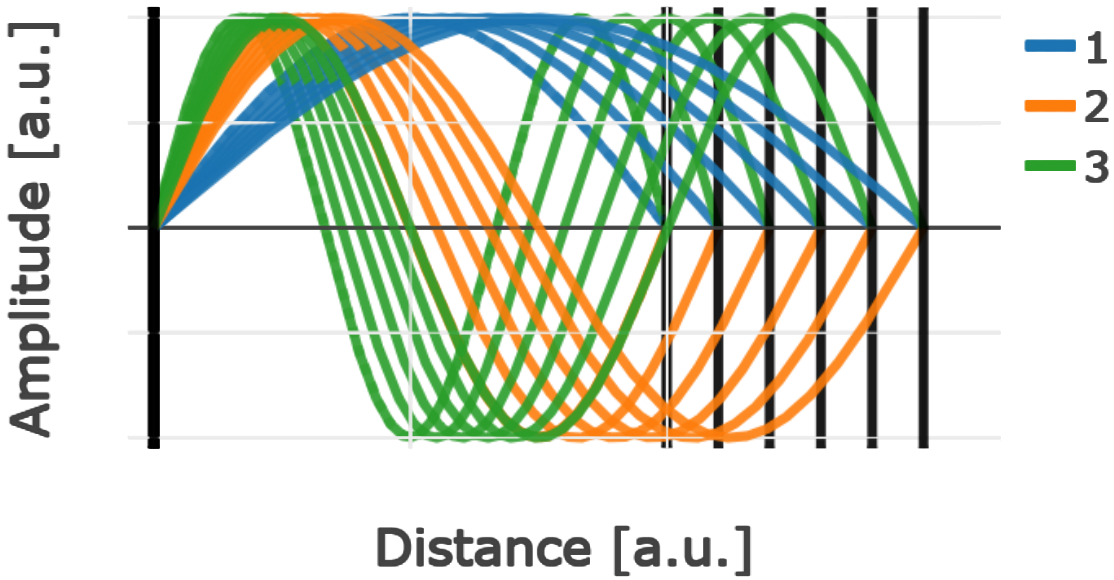
Particularly challenging for correlated methods

Plane Wave Basis set

Plane wave can be described by its energy: $E = \frac{1}{2}k^2$

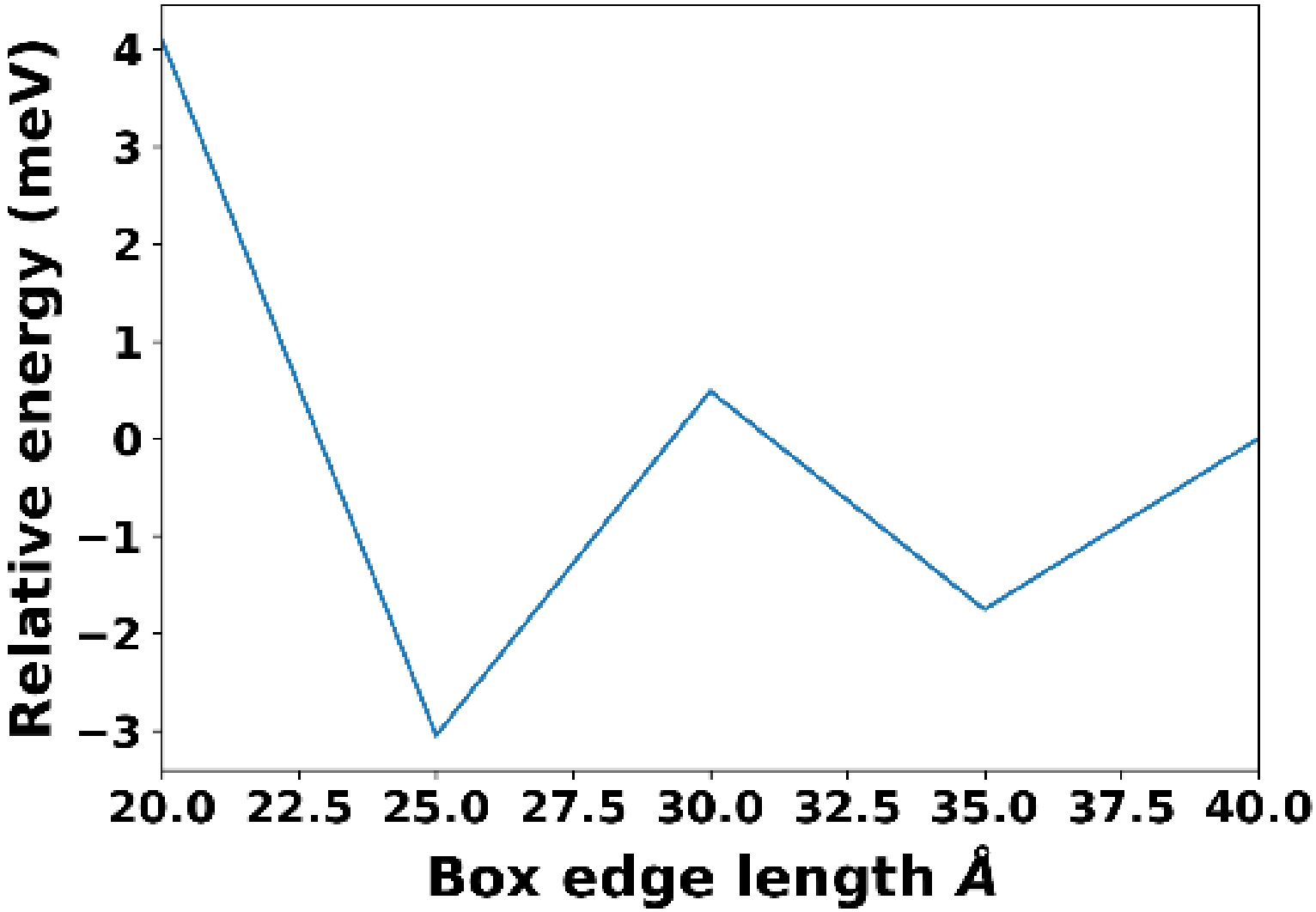
Quasi-systematic basis set, determined by:

- **cutoff** E_{cut}
- **Size and shape of the unit cell**

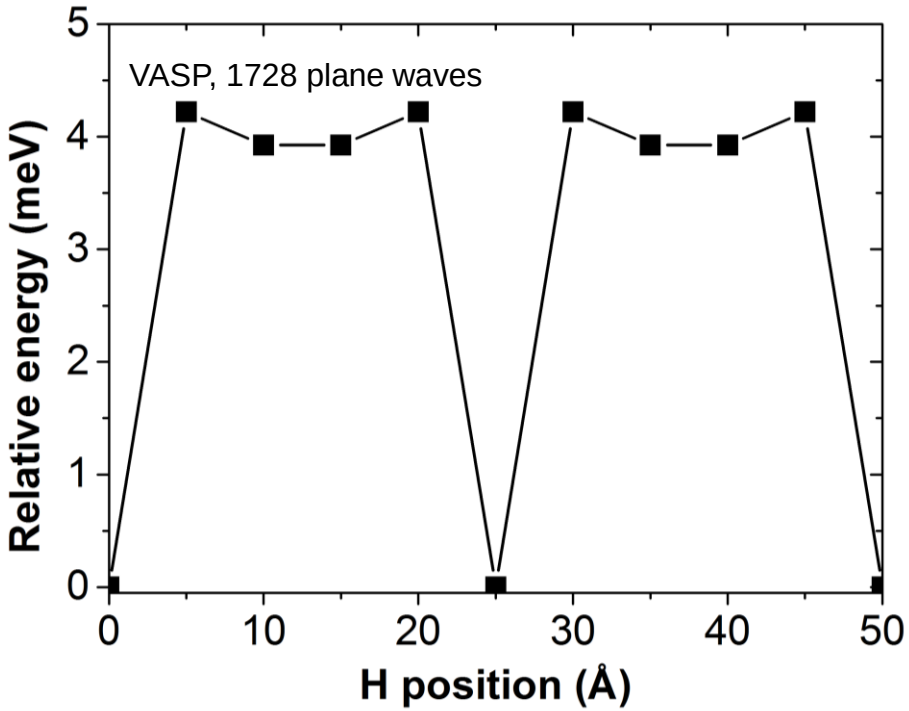


The first three plane waves in a cell with various lengths

Describing molecules



Aliasing Error: H atom in a unit cell



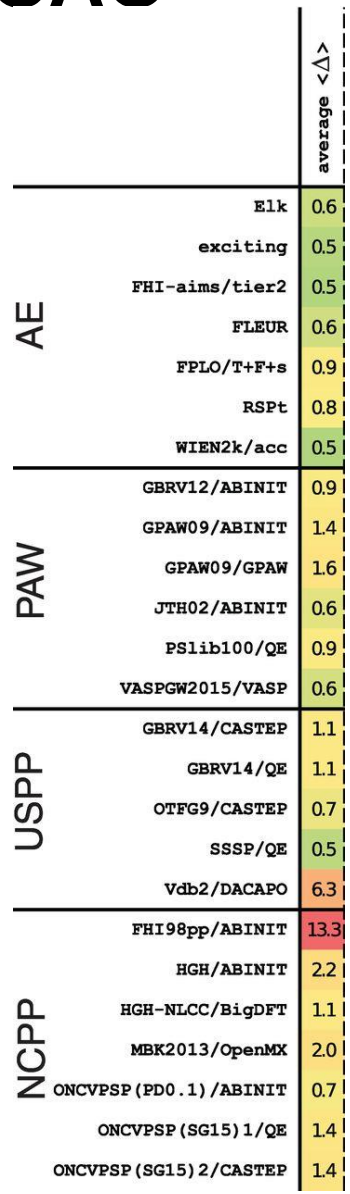
Aliasing error can yield spurious energies / gradients depending on position within the unit cell

Plane Waves vs. LCAO

Both LCAO (all electron) and Plane Wave can be accurate

Earlier calculations less reliable, mostly due to bad pseudopotentials (pre-2010)

	Year	$\langle\Delta\rangle_{\text{versus AE}}$
JTH01/ABINIT	2013	1.1
JTH02/ABINIT	2014	0.6
Vdb/CASTEP	1998	6.5
OTFG7/CASTEP	2013	2.6
OTFG9/CASTEP	2015	0.7
GPAW06/GPAW	2010	3.6
GPAW09/GPAW	2012	1.6
PSlib031/QE	2013	1.7
PSlib100/QE	2013	1.0
VASP2007/VASP	2007	2.0
VASP2012/VASP	2012	0.8
VASPGW2015/VASP	2015	0.6



All-electron

Plane-augmented waves

Ultra-soft Pseudo-potential

Norm-conserving pseudo-potentials

Lejaeghere et al., *Science* 25 Mar 2016:

Plane Waves vs. LCAO

Plane Wave	LCAO
Slowly varying electron density	Strongly varying electron density
Highly Systematic	Limited systematic
Densely packed systems	Loosly packed systems
Periodic	Non-periodic and periodic
Limited chemical insight	Insight through projection schemes
	Extrapolation schemes exist

„best“ choice of basis set depends on
system in question
quality of the implementations (code)
Scientific quesion