

# The Projector Augmented Wave method

- Advantages of PAW.
- The theory.
- Approximations.
- Convergence.

# What is PAW?

The PAW method is ...

- A technique for doing DFT calculations efficiently and accurately.
- An all-electron method with easy-to-control approximations.
- An elegant theory.
- A method that works with smooth pseudo wave-functions that can be expanded in a few plane waves (or expressed on coarse grids).
- Ultra-soft pseudopotentials done right!

# Literature

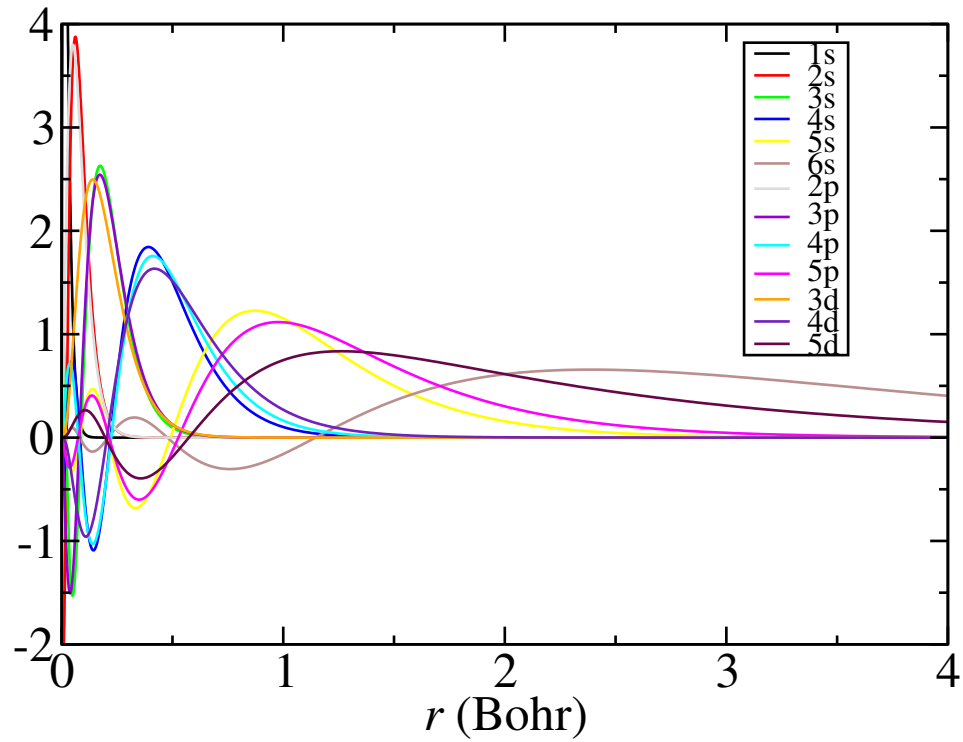
The PAW method was invented by Peter Blöchl in 1994:

- "Projector augmented-wave method", P. E. Blöchl, Phys. Rev. B 50, 17953 (1994)
- "Projector augmented wave method: *ab initio* molecular dynamics with full wave functions", P. E. Blöchl, C. J. Först and J. Schimpl, Bull. Mater. Sci, 26, 33 (2003)
- "Real-space grid implementation of the projector augmented wave method", J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, Phys. Rev. B, 71 035109 (2005)

# Advantages of PAW

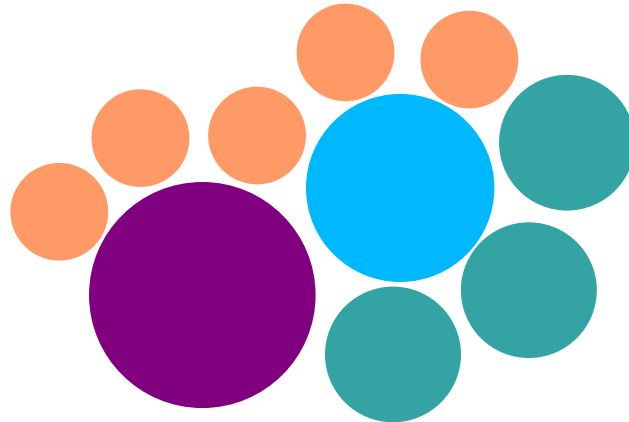
- No need to deal with inert core electrons.
- Valence pseudo wave functions are smooth and without nodes inside the augmentation spheres.
- Access to full all-electron wave functions and density. Useful for orbital-dependent XC-functionals.

# Platinum atom

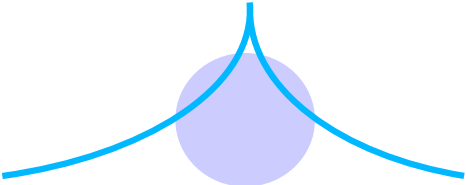
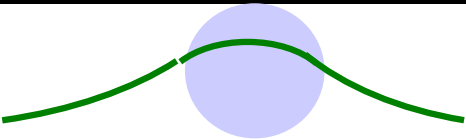
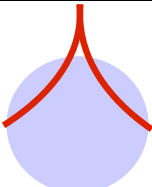
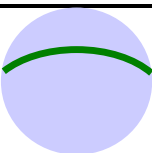


# Augmentation Spheres

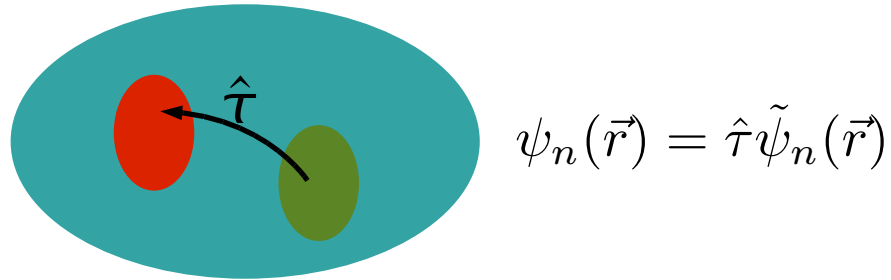
One cutoff radius for each type of atom. Spheres should not overlap:



# Electron density

$n$		
$= \tilde{n}$		plane waves/coarse grid
$+ \sum_a n^a$		logarithmic radial grids
$- \sum_a \tilde{n}^a$		logarithmic radial grids

# The PAW transformation



$$\hat{\tau} = 1 + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a|,$$

where  $\tilde{p}_i^a(\vec{r}) = 0$  and  $\tilde{\phi}_i^a(\vec{r}) = \phi_i^a(\vec{r})$  for  $r > r_c^a$ , and  $\langle \tilde{p}_i^a | \tilde{\phi}_j^a \rangle = \delta_{ij}$ .

$$|\tilde{p}_i^a\rangle = \tilde{p}_{n\ell m}^a(\vec{r} - \vec{R}^a) = \tilde{p}_{n\ell}^a(r) Y_{\ell m}(\widehat{\vec{r} - \vec{R}^a})$$

$$\hat{\tau} \tilde{\phi}_i^a = \phi_i^a$$



# Completeness relations

For  $|\vec{r} - \vec{R}^a| < r_c^a$  we must have:

$$\sum_i |\tilde{\phi}_i^a\rangle \langle \tilde{p}_i^a| = 1$$

From this follows that inside the augmentation spheres,  $\psi_n$  and  $\tilde{\psi}_n$  can be expanded in partial waves and pseudo partial waves respectively:

$$|\tilde{\psi}_n\rangle = \sum_i |\tilde{\phi}_i^a\rangle \langle \tilde{p}_i^a | \tilde{\psi}_n\rangle.$$

$$|\psi_n\rangle = \sum_i |\phi_i^a\rangle \langle \tilde{p}_i^a | \tilde{\psi}_n\rangle,$$

In the interstitial region, we have  $\psi_n = \tilde{\psi}_n$ .

## Electron density (again)

$$\begin{aligned}
 n(\vec{r}) &= \sum_a n_c^a (|\vec{r} - \vec{R}^a|) + \sum_n f_n |\psi_n(\vec{r})|^2 \\
 &= \sum_a n_c^a + \sum_n f_n \left| \tilde{\psi}_n + \sum_{ai} \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle (\phi_i^a - \tilde{\phi}_i^a) \right|^2 \\
 &= \sum_a n_c^a + \sum_n f_n |\tilde{\psi}_n|^2 \\
 &\quad + \sum_n f_n \sum_{aij} \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle (\phi_i^a - \tilde{\phi}_i^a) \langle \tilde{\psi}_n | \tilde{p}_j^a \rangle (\phi_j^a - \tilde{\phi}_j^a) \\
 &\quad + 2\text{Re} \left\{ \sum_n f_n \sum_a \underbrace{\sum_i \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle \tilde{\phi}_i^a}_{\tilde{\psi}_n} \sum_j \langle \tilde{\psi}_n | \tilde{p}_j^a \rangle (\phi_j^a - \tilde{\phi}_j^a) \right\}
 \end{aligned}$$

## Electron density (continued)

$$n = \sum_n f_n |\tilde{\psi}_n|^2 + \sum_{aij} D_{ij}^a (\phi_i^a \phi_j^a - \tilde{\phi}_i^a \tilde{\phi}_j^a) + \sum_a n_c^a,$$

where we have defined atomic density matrices as:

$$D_{ij}^a = \sum_n \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle f_n \langle \tilde{\psi}_n | \tilde{p}_j^a \rangle$$

# Electron density (continued)

With these definitions:

$$n^a = \sum_{ij} D_{ij}^a \phi_i^a \phi_j^a + n_c^a,$$

$$\tilde{n}^a = \sum_{ij} D_{ij}^a \tilde{\phi}_i^a \tilde{\phi}_j^a + \tilde{n}_c^a,$$

$$\tilde{n} = \sum_n f_n |\tilde{\psi}_n|^2 + \sum_a \tilde{n}_c^a,$$

we get a very simple expression for the all-electron density:

$$n = \tilde{n} + \sum_a (n^a - \tilde{n}^a)$$

# Compensation charges

Let  $Z^a(\vec{r})$  be the nuclear charge for atom  $a$ . The Coulomb energy is:

$$\begin{aligned} E_C &= \int d\vec{r}d\vec{r}' \frac{\left(n(\vec{r}) + \sum_a Z^a(\vec{r} - \vec{R}^a)\right) \left(n(\vec{r}') + \sum_a Z^a(\vec{r}' - \vec{R}^a)\right)}{|\vec{r} - \vec{r}'|} \\ &= \left(n + \sum_a Z^a\right)^2 \\ &= \left(\tilde{n} + \sum_a [n^a - \tilde{n}^a + Z^a]\right)^2 \end{aligned}$$

We add and subtract compensation charges localized inside the augmentation spheres:

$$E_C = \left(\tilde{n} + \sum_a \tilde{Z}^a + \sum_a [n^a - \tilde{n}^a + Z^a - \tilde{Z}^a]\right)^2$$

# Compensation charges (continued)

The compensation charges are constructed like this:

$$\tilde{Z}^a(\vec{r}) = \sum_{\ell m} Q_{\ell m}^a \tilde{g}_{\ell m}^a(\vec{r}),$$

where  $\tilde{g}_{\ell m}^a(\vec{r}) = 0$  for  $r > r_c^a$ :

$$\tilde{g}_{\ell m}^a(\vec{r}) = C_{\ell} r^{\ell} \exp(-\alpha^a r^2) Y_{\ell m}(\hat{r}),$$

The  $Q_{\ell m}^a$ 's are chosen such that  $n^a - \tilde{n}^a + Z^a - \tilde{Z}^a$  has no multipole moments:

$$\int d\vec{r} r^{\ell} Y_{\ell m}(\hat{r}) (n^a - \tilde{n}^a + Z^a - \tilde{Z}^a) = 0$$

# Compensation charges (continued)

Using  $\tilde{\rho} = \tilde{n} + \sum_a \tilde{Z}^a$ ,  $\tilde{\rho}^a = \tilde{n}^a + \tilde{Z}^a$  and  $\rho^a = n^a + Z^a$ , we get:

$$\begin{aligned} E_C &= \left( \tilde{n} + \sum_a \tilde{Z}^a + \sum_a [n^a - \tilde{n}^a + Z^a - \tilde{Z}^a] \right)^2 \\ &= \left( \tilde{\rho} + \sum_a [\rho^a - \tilde{\rho}^a] \right)^2 \\ &= \tilde{\rho}^2 + 2\tilde{\rho} \sum_a (\rho^a - \tilde{\rho}^a) + \sum_{ab} (\rho^a - \tilde{\rho}^a)(\rho^b - \tilde{\rho}^b) \end{aligned}$$

Since  $\rho^a - \tilde{\rho}^a$  has no multipole moments, we get:

$$\begin{aligned} E_C &= \tilde{\rho}^2 + 2 \sum_a \tilde{\rho}^a (\rho^a - \tilde{\rho}^a) + \sum_a (\rho^a - \tilde{\rho}^a)^2 \\ &= \tilde{\rho}^2 + \sum_a (\rho^a)^2 - \sum_a (\tilde{\rho}^a)^2 \end{aligned} \tag{1}$$

# Finally ...

... we have  $E_C = \tilde{E}_C + \sum_a (E_C^a - \tilde{E}_C^a)$ , where  $\tilde{E}_C$  has contributions from all of space:

$$\tilde{E}_C = \int d\vec{r}d\vec{r}' \frac{\left( \tilde{n}(\vec{r}) + \sum_a \tilde{Z}^a(\vec{r} - \vec{R}^a) \right) \left( \tilde{n}(\vec{r}') + \sum_a \tilde{Z}^a(\vec{r}' - \vec{R}^a) \right)}{|\vec{r} - \vec{r}'|},$$

and  $E_C^a - \tilde{E}_C^a$  is a correction from each augmentation sphere:

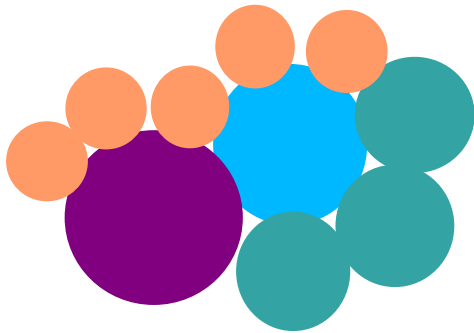
$$E_C^a = \int d\vec{r}d\vec{r}' \frac{\left( n^a(\vec{r}) + Z^a(\vec{r}) \right) \left( n^a(\vec{r}') + Z^a(\vec{r}') \right)}{|\vec{r} - \vec{r}'|},$$

$$\tilde{E}_C^a = \int d\vec{r}d\vec{r}' \frac{\left( \tilde{n}^a(\vec{r}) + \tilde{Z}^a(\vec{r}) \right) \left( \tilde{n}^a(\vec{r}') + Z^a(\vec{r}') \right)}{|\vec{r} - \vec{r}'|}$$



# Approximations

- Frozen core states.
- Truncated multipole expansion of compensation charges.
- Finite number of projectors, partial waves and pseudo partial waves:
  - Hydrogen: 2 *s*-type, 1 *p*-type.
  - Oxygen: 2 *s*-type, 2 *p*-type, 1 *d*-type.
  - Copper: 2 *s*-type, 2 *p*-type, 2 *d*-type.
- Overlapping augmentation spheres:



# Kinetic energy

$$E_{\text{kin}} = \tilde{E}_{\text{kin}} + \sum_a (E_{\text{kin}}^a - \tilde{E}_{\text{kin}}^a),$$

where

$$\tilde{E}_{\text{kin}} = -\frac{1}{2} \sum_n f_n \int d\vec{r} \tilde{\psi}_n^* \nabla^2 \tilde{\psi}_n$$

$$E_{\text{kin}}^a = -\frac{1}{2} \sum_{ij} D_{ij}^a \int d\vec{r} \phi_i^a \nabla^2 \phi_j^a - \frac{1}{2} \sum_c^{\text{core}} \int d\vec{r} \phi_c^a \nabla^2 \phi_c^a$$

$$\tilde{E}_{\text{kin}}^a = -\frac{1}{2} \sum_{ij} D_{ij}^a \int d\vec{r} \tilde{\phi}_i^a \nabla^2 \tilde{\phi}_j^a$$

# Exchange-correlation energy

$$E_{xc} = \tilde{E}_{xc} + \sum_a (E_{xc}^a - \tilde{E}_{xc}^a),$$

where

$$\tilde{E}_{xc} = \int d\vec{r} \tilde{n} \epsilon_{xc}[\tilde{n}]$$

$$E_{xc}^a = \int d\vec{r} n^a \epsilon_{xc}[n^a]$$

$$\tilde{E}_{xc}^a = \int d\vec{r} \tilde{n}^a \epsilon_{xc}[\tilde{n}^a]$$

# Hamiltonian

$$E = \tilde{E} + \sum_a \Delta E^a(D_{ij}^a), \quad \frac{\delta E}{\delta \tilde{\psi}_n^*} = f_n \hat{H} \tilde{\psi}_n$$

$$\hat{H} = -\frac{1}{2} \nabla^2 + \tilde{v} + \sum_a \sum_{ij} |\tilde{p}_i^a\rangle \Delta H_{ij}^a \langle \tilde{p}_j^a|,$$

where  $\tilde{v} = \delta \tilde{E} / \delta \tilde{n} = \tilde{v}^H + \tilde{v}_{xc}$  and

$$\Delta H_{ij}^a = \frac{\Delta E^a}{\partial D_{ij}^a} + \sum_{lm} \frac{\partial Q_{lm}^a}{\partial D_{ij}^a} \int d\vec{r} \tilde{v}^H \tilde{g}_{lm}^a$$

The PAW method is a generalized Kleinman-Bylander non-local pseudopotential that adapts to the current environment!

# Orthogonality

Keep the wave functions orthogonal:

$$\delta_{nm} = \langle \psi_n | \psi_m \rangle = \langle \tilde{\psi}_n | \hat{O} | \tilde{\psi}_m \rangle,$$

where

$$\hat{O} = 1 + \sum_a \sum_{ij} |\tilde{p}_i^a\rangle \Delta O_{ij}^a \langle \tilde{p}_j^a|$$

and

$$\Delta O_{ij}^a = \int d\vec{r} (\phi_i^a \phi_j^a - \tilde{\phi}_i^a \tilde{\phi}_j^a)$$

# PBE atomization energy of a nitrogen molecule

```
from ASE import Atom, ListOfAtoms
from gridpaw import Calculator

a = 8.0 # size of unit cell
h = 0.18 # grid spacing
N = ListOfAtoms([Atom('N', (0, 0, 0), magmom=3)],
                cell=(a, a, a), periodic=1)
calc = Calculator(nbands=4, xc='PBE', h=h)
N.SetCalculator(calc)
e1 = N.GetPotentialEnergy()

d = 1.1 # bond length
N2 = ListOfAtoms([Atom('N', [0, 0, 0]),
                 Atom('N', [0, 0, 1.1])],
                 cell=(a, a, a), periodic=1)
calc = Calculator(nbands=5, xc='PBE', h=h)
N2.SetCalculator(calc)
e2 = N2.GetPotentialEnergy()

print 2 * e1 - e2, 'eV'
```

# Convergence

$spd$	11	22	221	222	321	231
$\Delta E$ (eV)	10.016	10.141	10.520	10.519	10.519	10.514

$l_{\max}$	0	1	2
$\Delta E$ (eV)	10.520	10.574	10.560

	Dacapo	Blaha <i>et al.</i>	Experiment
$\Delta E$ (eV)	9.611	10.546	9.909