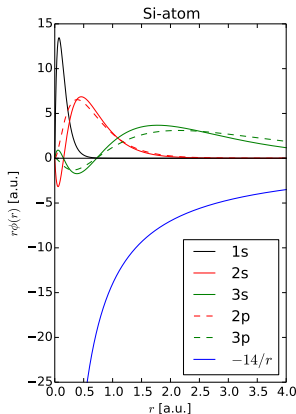




- Pseudo-potentials
- Projector Augmented Wave method
  - The theory
  - Approximations
- GPAW
  - Running calculations with ASE and GPAW
  - Finite-difference, LCAO and plane waves
  - Iterative diagonalization
  - Scaling with system size

# Pseudo-potentials

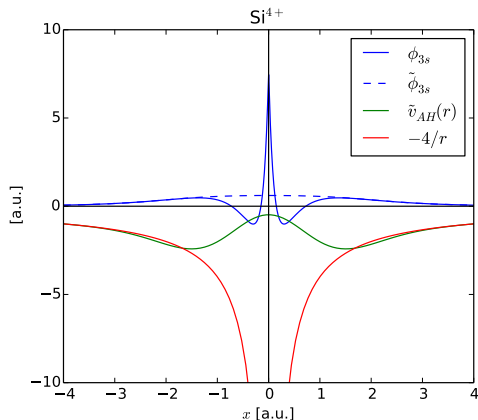
- Chemical properties are determined largely by valence electrons
- Strong Coulomb potential of nuclei leads to sharply varying wave functions
- Replace the real potential with a pseudo-potential reproducing the correct wave functions outside chosen radius



# Local pseudo-potential for silicon

Appelbaum-Hamann<sup>1</sup> potential ( $v_1 = 3.042$ ,  $v_2 = -1.372$ ,  $\alpha = 0.6102$ ):

$$\tilde{v}_{AH}(r) = (v_1 + v_2 r^2) e^{-\alpha r^2} - 4\text{erf}(\sqrt{\alpha}r)/r$$



<sup>1</sup>Joel A. Appelbaum and D. R. Hamann, PRB 8, 1777 (1973)

- Kleinman-Bylander<sup>2</sup> separable form:

$$\hat{V} = \hat{V}_{\text{local}} + \sum_{\ell m} |\delta v_{\ell m}\rangle \langle \delta v_{\ell m}|$$

- Ultra-soft PP's<sup>3</sup>: Pseudo wave functions need not be normalized - this allows for ultra-soft wave functions

---

<sup>2</sup>Leonard Kleinman and D. M. Bylander. Efficacious form for model pseudo-potentials. Phys. Rev. Lett. 48 (20), 1425 (May 1982).

<sup>3</sup>David Vanderbilt. Soft self-consistent pseudo-potentials in a generalized eigenvalue formalism. Phys. Rev. B 41 (11), 7892 (April 1990).

- Access to full all-electron wave-functions, density and potential
- An exact all-electron formalism
- *Pseudo-potentials done right*: PAW contains USPP and NCPP theory

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)

# The PAW transformation

The PAW transformation maps nice and smooth wave functions to all-electron wave functions with cusps and nasty oscillatory behavior near the nucleus:

$$\psi_n(\vec{r}) = \hat{\tau} \tilde{\psi}_n(\vec{r})$$

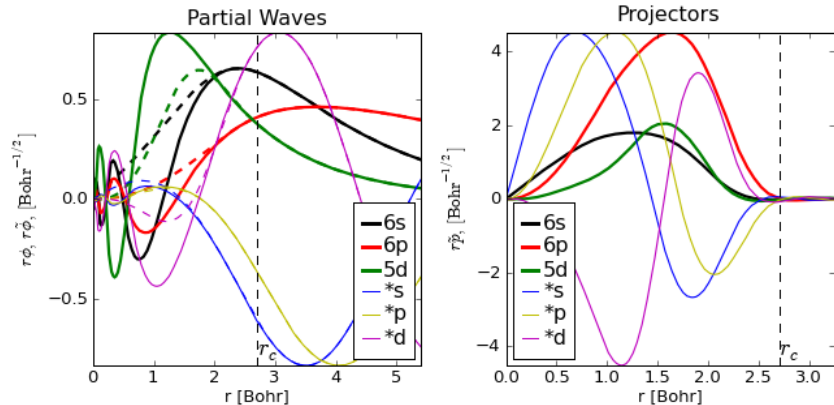
$$\hat{\tau} = \hat{1} + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a|.$$

- Projector functions:  $\tilde{p}_{nlm}^a(\vec{r}) = 0$  for  $r > r_c^a$ .
- All-electron partial waves:  $\phi_{nlm}^a(\vec{r})$ .
- Pseudo partial waves:  $\tilde{\phi}_{nlm}^a(\vec{r}) = \phi_{nlm}^a(\vec{r})$  for  $r > r_c^a$ .
- $\langle \tilde{\phi}_{nlm}^a | \tilde{p}_{n'l'm'}^a \rangle = \delta_{nn'} \delta_{\ell\ell'} \delta_{mm'}$
- $\sum_{nlm} |\tilde{\phi}_{nlm}^a\rangle \langle \tilde{p}_{nlm}^a| = \hat{1}$  for  $r < r_c^a$  (completeness relation)

Fixed points for the transformation:

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

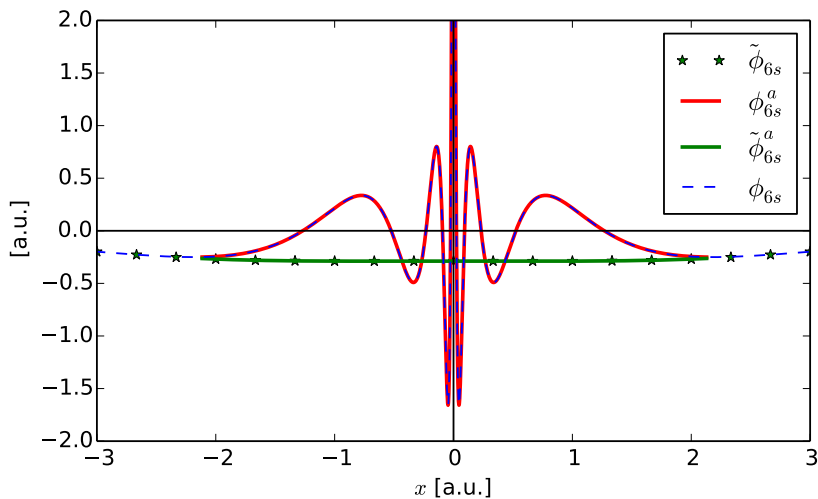
# Platinum dataset



## Note

The pseudo 5d is not normalized

# Platinum 6s orbital



$$\phi_{6s} = \tilde{\phi}_{6s} + \phi_{6s}^a - \tilde{\phi}_{6s}^a$$



$$|\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle$$

Take any local or semi-local operator  $\hat{O}$  (the kinetic energy, a local potential, the electron density ...):

$$\langle \psi_n | \hat{O} | \psi_n \rangle = \langle \tilde{\psi}_n | \hat{O} | \tilde{\psi}_n \rangle + \sum_{abij} \langle \tilde{\psi}_n | \tilde{p}_i^a \rangle (\langle \phi_i^a | - \langle \tilde{\phi}_i^a |) \hat{O} (|\phi_j^b\rangle - |\tilde{\phi}_j^b\rangle) \langle \tilde{p}_j^b | \tilde{\psi}_n \rangle +$$

$$\sum_{ai} (\langle \tilde{\psi}_n | \hat{O} (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle) \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle + \text{c.c.})$$

Use that  $\langle \phi_i^a | - \langle \tilde{\phi}_i^a | = 0$  outside the augmentation sphere of atom  $a$  and use this expansion inside the spheres:  $|\tilde{\psi}_n\rangle = \sum_i |\tilde{\phi}_i^a\rangle \langle \tilde{p}_i^a | \tilde{\psi}_n \rangle$ :

$$\langle \psi_n | \hat{O} | \psi_n \rangle = \langle \tilde{\psi}_n | \hat{O} | \tilde{\psi}_n \rangle + \sum_{aij} \langle \tilde{\psi}_n | \tilde{p}_i^a \rangle (\langle \phi_i^a | \hat{O} | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \hat{O} | \tilde{\phi}_j^a \rangle) \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle.$$

# Atomic density matrix

From last slide:

$$\langle \psi_n | \hat{O} | \psi_n \rangle = \langle \tilde{\psi}_n | \hat{O} | \tilde{\psi}_n \rangle + \sum_{aij} \langle \tilde{\psi}_n | \tilde{p}_i^a \rangle (\langle \phi_i^a | \hat{O} | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \hat{O} | \tilde{\phi}_j^a \rangle) \langle \tilde{p}_j^a | \tilde{\psi}_n \rangle.$$

Often, we are interested in  $\sum_n f_n \langle \psi_n | \hat{O} | \psi_n \rangle$ . We introduce the atomic density matrix:

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

We now have:

$$\sum_n f_n \langle \psi_n | \hat{O} | \psi_n \rangle = \sum_n f_n \langle \tilde{\psi}_n | \hat{O} | \tilde{\psi}_n \rangle + \sum_{aij} D_{ij}^a (\langle \phi_i^a | \hat{O} | \phi_j^a \rangle - \langle \tilde{\phi}_i^a | \hat{O} | \tilde{\phi}_j^a \rangle).$$

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

where

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

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

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

With frozen core density  $n_c^a(a)$  and pseudo core density  $\tilde{n}_c^a(r) = n_c^a(r)$  for  $r < r_c^a$  we have:

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

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

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

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

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

# Exchange-correlation energy

From semi-local functionals:

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

where

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

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

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

## Note

The densities  $n^a$  and  $\tilde{n}^a$  are not necessarily spherically symmetric!

## Note

No non-linear core correction needed - PAW does the right thing!

# The Coulomb energy

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

$$\begin{aligned} E_C &= \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{(n(\vec{r}) + \sum_a Z^a(\vec{r} - \vec{R}^a)) (n(\vec{r}') + \sum_a Z^a(\vec{r}' - \vec{R}^a))}{|\vec{r} - \vec{r}'|} \\ &= (n + \sum_a Z^a)^2 \\ &= (\tilde{n} + \sum_a [n^a - \tilde{n}^a + Z^a])^2 \end{aligned}$$

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

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

# The Coulomb energy (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:

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

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:

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

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

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



$$E_C = \tilde{\rho}^2 + \sum_a (\rho^a)^2 - \sum_a (\tilde{\rho}^a)^2 = \tilde{E}_C + \sum_a (E_C^a - \tilde{E}_C^a)$$

$$\tilde{E}_C = \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\tilde{\rho}(\vec{r})\tilde{\rho}(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

1) Solve Poisson equation:

$$\nabla^2 \tilde{v}_H = -4\pi\tilde{\rho}$$

$$\tilde{E}_C = \frac{1}{2} \int d\vec{r} \tilde{v}_H \tilde{\rho}$$

2) Fourier transform:

$$\tilde{E}_C = \frac{1}{2} \sum_{\mathbf{G}} |\tilde{\rho}(\mathbf{G})|^2 / G^2$$

Total energy:

$$E = \tilde{E}_{\text{kin}} + \tilde{E}_C + \tilde{E}_{\text{xc}} + \sum_a \Delta E^a(D_{ij}^a) = \tilde{E}[\{\tilde{\psi}_n\}] + \sum_a \Delta E^a(D_{ij}^a)$$

Hamiltonian ( $\delta E / \delta \tilde{\psi}_n^* = f_n \hat{H} \tilde{\psi}_n$ ):

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

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

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

(the PAW method is a generalized Kleinman-Bylander non-local pseudo-potential that adapts to the current environment)

Keep the wave functions orthogonal:

$$\delta_{nm} = \langle \psi_n | \psi_m \rangle = \langle \tilde{\psi}_n | \hat{\tau}^T \hat{\tau} | \tilde{\psi}_m \rangle = \langle \tilde{\psi}_n | \hat{S} | \tilde{\psi}_m \rangle,$$

where

$$\hat{S} = \hat{\tau}^T \hat{\tau} = \hat{1} + \sum_a \sum_{ij} |\tilde{p}_i^a\rangle \Delta S_{ij}^a \langle \tilde{p}_j^a|$$

and

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

We need to solve:

$$\hat{H} \tilde{\psi}_n = \varepsilon_n \hat{S} \tilde{\psi}_n$$

# Summary of approximations

- Frozen core states
- Finite number of projectors, partial waves and pseudo partial waves
- Overlapping augmentation spheres
- Standard DFT stuff:
  - Occupation number smearing
  - $\vec{k}$ -point sampling.
  - XC-functional

# Running a calculations with ASE and GPAW

```
from ase import Atoms
h2 = Atoms(...)
from ase.calculators.emt import EMT
h2.calc = EMT()
h2.get_potential_energy()
from ase.optimize import BFGS
opt = BFGS(h2)
opt.run(fmax=0.05)
h2.get_forces()
from gpaw import GPAW, PW
h2.calc = GPAW(mode=PW(300), txt='h2.txt')
h2.center(vacuum=2)
h2.cell
h2.get_forces()
from ase.visualize import view
view(h2)
```

Alternative to `Atoms(...)`:

```
from ase.structure import molecule
h2 = molecule('H2')
```

or:

```
from ase.io import read
h2 = read('H2.xyz')
```

- There is also a `bulk()` function and, and, and ...
- Use ASE's GUI called `ase-gui`. It understands the same file-formats as ASE's `read()` function: GPAW's text output, `.gpw` files, ASE's `.traj` files and many more.

# What is GPAW?

- An implementation of the PAW method
- Wave functions are described using
  - 1) real-space uniform grids (fd)
  - 2) atom-centered numerical basis functions (lcao)
  - 3) plane-waves (pw)
- It's written in a combination of the Python and C languages
- It's based on ASE and NumPy (a Python library for manipulating N-dimensional arrays of numbers)
- It uses these libraries for the hard work:
  - BLAS (GPAW does a lot of matrix-matrix multiplications)
  - LAPACK and optionally ScaLAPACK and BLACS
  - MPI (if you want to run GPAW in parallel)
  - FFTW (if you want to do fast plane-wave based calculations)
  - LIBXC (for LDA's, GGA's and MGGA's)
- The license is GPLv3+

Describe wave functions, electron density and the effective potential in real-space on uniform grids:

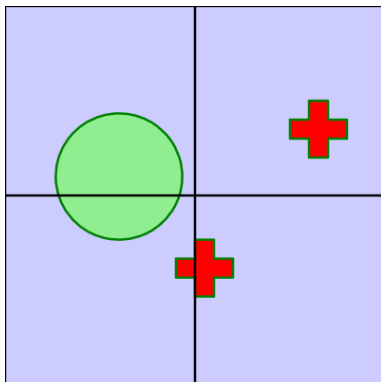
$$\vec{r}_{i_1 i_2 i_3} = (i_1/N_1)\vec{a}_1 + (i_2/N_2)\vec{a}_2 + (i_3/N_3)\vec{a}_3,$$

where  $\vec{a}_1$ ,  $\vec{a}_2$  and  $\vec{a}_3$  are the unit cell vectors and we use  $N_1 \times N_2 \times N_3$  grid points ( $i_\alpha = 0, 1, \dots, N_\alpha - 1$ ).

Use finite-difference approximation for  $\nabla^2$  and iterative multi-grid based solvers for the Poisson and Kohn-Sham equations.

$$\frac{\partial^2 f(x)}{\partial x^2} = \sum_{n=-N}^N C_n^N f(x + nh) + O(h^{2N+2})$$



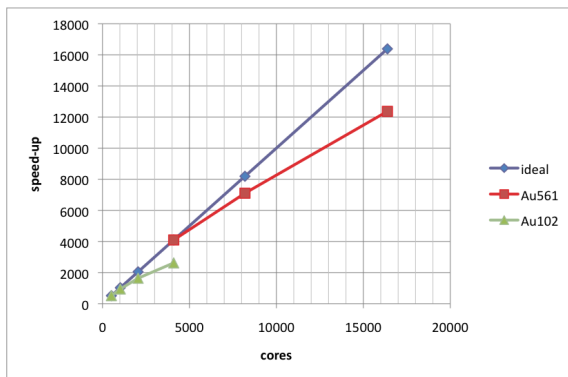


## Advantages:

- It's simple! Only one parameter (grid-spacing).
- No FFT's. Easy to parallelize using domain decomposition - only neighbor-neighbor communication.

## Disadvantages:

- You need many grid-points.



Gold clusters:  $\text{Au}_{561}$  and  $\text{Au}_{102}\text{S}_{44}\text{O}_{88}\text{C}_{308}\text{H}_{220}$ . Important to parallelize ( $N_e \times N_e$ ) matrix operations (ScaLAPACK) and parallelize over states.

**Note**

Don't use this many cores for the exercises!

Expand wave function in numerical atom-centered atomic-like orbitals with finite support:

$$\tilde{\psi} = \sum_a \sum_{nlm} c_{nlm}^a \Phi_{nlm}^a(\vec{r} - \vec{R}^a).$$

- The atomic orbitals are obtained from a free atom in a confining potential well
- Extra basis functions with the same angular momentum
- Polarization functions
- Same PAW approximation as with real-space grids

Advantages:

- $\langle \tilde{p}_i^a | \Phi_{n'l'm'}^a \rangle$ ,  $\langle \Phi_{nlm}^a | \Phi_{n'l'm'}^a \rangle$  and  $\langle \Phi_{nlm}^a | \nabla^2 | \Phi_{n'l'm'}^a \rangle$  can be calculated exactly
- One can do quick'n'dirty calculations

Disadvantages:

- Hard to reach complete basis-set limit.

$$\tilde{\psi}(\mathbf{r}) = \sum_{G < G_c} c_G e^{i\mathbf{G}\cdot\mathbf{r}}.$$

$$E_{\text{cut}} = \frac{1}{2} G_c^2$$

It's based on FFT and does the projector wave function overlaps in reciprocal space with ZGEMM.

Advantages:

- Fast for not too large systems
- Fast convergence with respect to number of plane-waves

Disadvantages:

- not so flexible boundary conditions
- delocalized basis functions

$$\hat{H}\tilde{\psi}_n = \varepsilon_n \hat{S}\tilde{\psi}_n$$

- 1) Initial guess for wave functions from LCAO ( $\tilde{\psi}_n$ )
- 2) Orthogonalize wave functions (make sure  $\langle \tilde{\psi}_n | \hat{S} | \tilde{\psi}_m \rangle = \delta_{nm}$ )
- 3) Calculate density, mix<sup>4</sup> and interpolate to finer grid ( $\tilde{n}$ ,  $D_{ij}^a$ )
- 4) Calculate potential ( $\tilde{v}$ ,  $\Delta H_{ij}^a$ )
- 5) Apply Hamiltonian ( $\hat{H}\tilde{\psi}_n$ )
- 6) Subspace diagonalization (rotate  $\tilde{\psi}_n$  so that  $\langle \tilde{\psi}_n | \hat{H} | \tilde{\psi}_m \rangle = \delta_{nm}\varepsilon_n$ )
- 7) Calculate residuals ( $R_n = \hat{H}\tilde{\psi}_n - \varepsilon_n \hat{S}\tilde{\psi}_n$ )
- 8) Improve wave functions<sup>4</sup> ( $\tilde{\psi}_n + \lambda \hat{P}R_n \rightarrow \tilde{\psi}_n$ )
- 9) Back to (2)

---

<sup>4</sup>G. Kresse, J. Furthmüller: Phys. Rev. B 54, 11169 - 11186 (1996) "Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set"

# Scaling with system size $N$ : FD-mode and PW-mode

- Number of atoms:  $N_a \sim 100$
- Number of electrons:  $N_e \sim 500$
- Number of grid points or plane waves:  $N_g \sim 100,000$

Linearly scaling parts of the code:

- Coulomb energy:
  - FD: (Poisson equation)  $N_g$
  - PW: (direct method)  $N_g \log N_g$
- Exchange-correlation energy and potential:  $N_g$
- Density mixing:  $N_g$

# Scaling with system size $N$ (continued)

## Quadratic:

- Evaluation of projections  $\langle \tilde{p}_i^a | \tilde{\psi}_n \rangle$ :
  - FD:  $N_a N_e$
  - PW:  $N_a N_e N_g$
- Calculation of  $-\frac{1}{2} \nabla^2 \tilde{\psi}_n$  and  $\tilde{v} \tilde{\psi}_n$ :
  - FD:  $N_e N_g$
  - PW:  $N_e N_g \log N_g$
- Pseudo density  $\tilde{n} = \sum_n f_n |\tilde{\psi}_n|^a + \sum_a \tilde{n}_c^a$ :  $N_e N_g$

## Cubic:

- Orthogonalization of wave functions:  $N_e^2 N_g$  ( $S_{nn'}$ )
- Subspace diagonalization:  $N_e^2 N_g$  ( $H_{nn'}$ )
- $(N_e \times N_e)$ -matrix operations:  $N_e^3$

We have generated datasets  $(\phi_i^a, \tilde{\phi}_i^a, \tilde{p}_i^a, n_c^a, \tilde{n}_c^a, \bar{v}^a)$  for most elements, but:

## Important

it's up to you to test them!

- Do test calculations and compare to reference numbers

```
$ gpaw-setup Si -f BLYP # dataset for BLYP-Si
$ gpaw-setup Si -r 2.0 # change cutoff
$ gpaw-setup -h # HELP!
```



- Surface energy, diffusion, band structure, Wannier functions, NEB, magnetism, DOS, STM, databases, vibrations, stress tensor, transport, TDDFT.
- EELS, GW and RPA correlation: For these exercises you need the density response function:  $\chi_{\mathbf{G}\mathbf{G}'}^0(\mathbf{q}, \omega)$ 
  1. Do a ground-state calculation
  2. Fixed potential and set up Hamiltonian and overlap matrices
  3. Find all eigenvectors using (Sca)Lapack

```
from gpaw import GPAW
calc = GPAW('abc.gpw', txt=None)
calc.diagonalize_full_hamiltonian(nbands=...)
calc.write('abc.all.gpw', 'all')
```

# Where is what?

`$GPAW_SETUP_PATH`:

*PAW-datasets (H.LDA.gz, He.LDA.gz, ...) also contains PBE, revPBE, RPBE, GLLBSC and LCAO basis functions.*

`$PYTHONPATH`:

- *The ASE code.*
- *The GPAW code.*
- *`_gpaw.so`: GPAW's C-extensions for Python.*

`$PATH`:

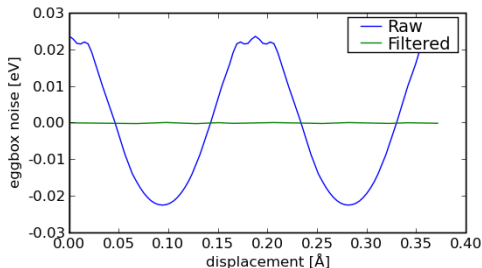
- *`gpaw-python`: MPI-enabled Python interpreter with GPAW's C-code inside.*

- Check out:
  - <http://wiki.fysik.dtu.dk/ase>
  - <http://wiki.fysik.dtu.dk/gpaw>
- *Thanks* to the GPAW-team:  
Andre, Ari, Arto, Ask, Carsten, Chris, Christian, David, Duncan, Elvar, Falco, Filip, Georg, George, Haiping, Heine, Henrik, Hildur, Ivano, Jakob, Janosch, Jeppe, Jess S.-M., Jess W. P., Jingzhe, Juan Maria, Jun, Jussi, Keld, Kirsten, Kristen, Kristian, Lara, Lauri, Mads, Marcin, Marco, Mathias, Mikael, Michael, Mikkel, Mohnish, Morten, Nick, Olga, Ondrej, Per, Peter, Poul Georg, Rolf, Samuli, Simone, Thomas, Torsten, Troels, Tuomas and Vivien
- Talk to us on the #gpaw channel on [irc.freenode.net](http://irc.freenode.net) or on our mailing lists: `gpaw-developers`, `ase-developers`, `gpaw-users` and `ase-users`.
- Thank you for your attention
- Questions?

...

# The egg-box effect

Translation of hydrogen in empty space with  $h = 0.19 \text{ \AA}$ :



Fourier filtering<sup>5</sup> of  $\tilde{p}_i$  and  $\tilde{v}$ :

- Fourier transform  $\tilde{p}_i(r)/m(r)$ , where  $m(r)$  is a mask function that goes smoothly to zero at a chosen cutoff radius.
- Cut off high frequency components.
- Transform back and multiply by  $m(r)$ .

---

<sup>5</sup>Mask-function real-space implementations of nonlocal pseudo-potentials, Phys. Rev. B 64, 201107(R) Published 6 November 2001, Lin-Wang Wang

# PAW atomic datasets in one slide

- Solve  $(-\frac{1}{2}\nabla + v - \epsilon_{nl})\phi_{nl} = 0$
- Construct  $\tilde{\phi}_{nl}$ : smooth continuation of  $\phi_{nl}$  for  $r < r_c$
- Construct  $\tilde{n}_c$ : smooth continuation of core density  $n_c$  for  $r < r_c$
- $\tilde{n} = \tilde{n}_c + \sum_{nl} f_{nl} \tilde{\phi}_{nl}^2$
- $\tilde{\rho} = \tilde{n} + Qe^{-\alpha r^2}$ ,  $\int d\mathbf{r} \tilde{\rho} = 0$
- Construct  $\tilde{v}$  somehow (several possibilities)
- Calculate projector functions:  $\tilde{p}_{nl} \propto (-\frac{1}{2}\nabla + \tilde{v} - \epsilon_{nl})\tilde{\phi}_{nl}$
- Unscreen:  $\bar{v} = \tilde{v} - \int d\mathbf{r}' \tilde{\rho}(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| - v_{xc}[\tilde{n}]$
- Add more projectors
- Check logarithmic derivatives and pseudo-atom eigenvalues