

Projector-Augmented Wave Method:

An introduction

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Why PAW

- all-electron wave functions (EFG's, etc.)
- ab-initio molecular dynamics (Fictitious Lagrangian)
- exact when converged (no transferability problems)
- computationally efficient
- provides theoretical basis for pseudopotentials

PAW unifies all-electron and pseudopotential approaches

PAW Transformation theory

Transform physical wave functions $\Psi(r)$ onto auxiliary wave functions $\tilde{\Psi}(r)$

$$\tilde{\Psi}(r) = \hat{\mathcal{U}}\Psi(r)$$

Goal: Smooth auxiliary wave functions $\tilde{\Psi}(r)$ that can be represented in a plane wave expansion

PAW Transformation theory

- start with **auxiliary wave functions** $\tilde{\Psi}_n(r)$
- define **transformation operator** $\hat{\mathcal{T}} = \hat{\mathcal{U}}^{-1}$

$$\Psi_n(r) = \hat{\mathcal{T}}\tilde{\Psi}_n(r) \iff \tilde{\Psi}_n(r) = \hat{\mathcal{U}}\Psi_n(r)$$

that maps the auxiliary wave functions $\tilde{\Psi}_n(r)$ onto true wave functions $\Psi_n(r)$

- express **total energy** by auxiliary wave functions

$$E = E[\Psi_n(r)] = E[\hat{\mathcal{T}}\tilde{\Psi}_n(r)]$$

- **Schrödinger-like equation** for auxiliary functions

$$\frac{\partial E}{\partial \tilde{\Psi}_n^*(r)} = \left(\mathcal{T}^\dagger H \mathcal{T} - \mathcal{T}^\dagger \mathcal{T} \epsilon_n \right) \tilde{\Psi}_n(r) = 0$$

- **Expectation values**

$$\langle A \rangle = \sum_n \langle \Psi_n | A | \Psi_n \rangle = \sum_n \langle \tilde{\Psi}_n | \mathcal{T}^\dagger A \mathcal{T} | \tilde{\Psi}_n \rangle$$

**Find a transformation $\hat{\mathcal{T}}$ so,
that the auxiliary wave function are well behaved**

Requirements for a suitable transformation operator

- the relevant wave functions shall be transformed onto numerically convenient auxiliary wave functions

$$\tilde{\Psi}_n(\vec{r}) = \sum_{\vec{G}} e^{i\vec{G}\vec{r}} \tilde{\Psi}_n(\vec{G})$$

- linear (algebraic operations)
- local (no interaction between sites)

$$\mathcal{T} = 1 + \sum_R \mathcal{S}_R$$

PAW Transformation operator I

How to define the operator \mathcal{T} ?

- define a complete set of initial and final states for the transformation

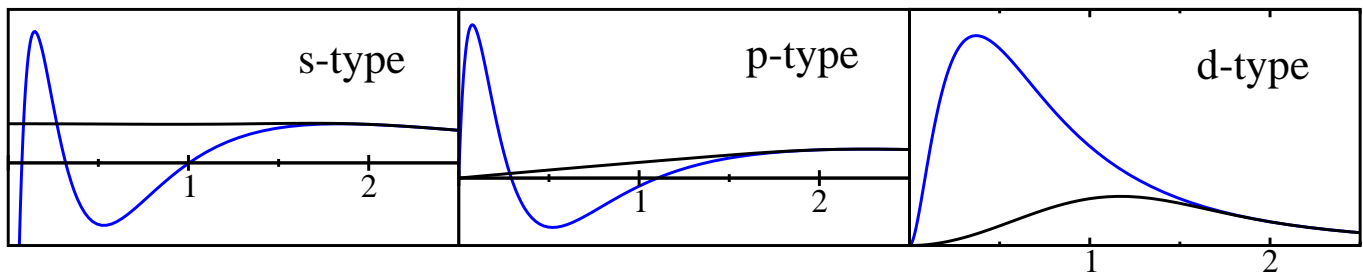
$$\forall_i \quad |\phi_i\rangle = \mathcal{T}|\tilde{\phi}_i\rangle \rightarrow \mathcal{T}$$

1. Final states: All-electron valence partial waves $|\phi_i\rangle$
 $i = \vec{R}, \ell, m, \alpha$
 - solve Schrödinger equation for the all-electron atomic potential for a set of energies

2. Initial states: auxiliary partial waves $|\tilde{\phi}_i\rangle$

- true and auxiliary wave function are pairwise identical outside some augmentation radius r_c

$$\tilde{\phi}_i(\vec{r}) = \phi_i(\vec{r}) \text{ for } |\vec{r} - \vec{R}| > r_c$$



PAW Transformation operator II

Find a closed expression for the transformation operator

$$\mathcal{T} = 1 + \sum_R \mathcal{S}_R$$

Derivation:

$$\overbrace{|\phi_i\rangle}^{\text{true}} = \underbrace{\overbrace{|\tilde{\phi}_i\rangle}^{\text{aux.}} + \mathcal{S}_{R_i} \overbrace{|\tilde{\phi}_i\rangle}^{\text{aux.}}}_{\mathcal{T}|\tilde{\phi}_i}$$

$$\Rightarrow \mathcal{S}|\tilde{\phi}_i\rangle = |\phi_i\rangle - |\tilde{\phi}_i\rangle = \sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \underbrace{\langle \tilde{p}_j | \tilde{\phi}_i \rangle}_{\delta_{i,j}}$$

$$\Rightarrow \mathcal{T} = 1 + \underbrace{\sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \langle \tilde{p}_j |}_{\mathcal{S}_R}$$

Projector functions $\langle \tilde{p}_i |$

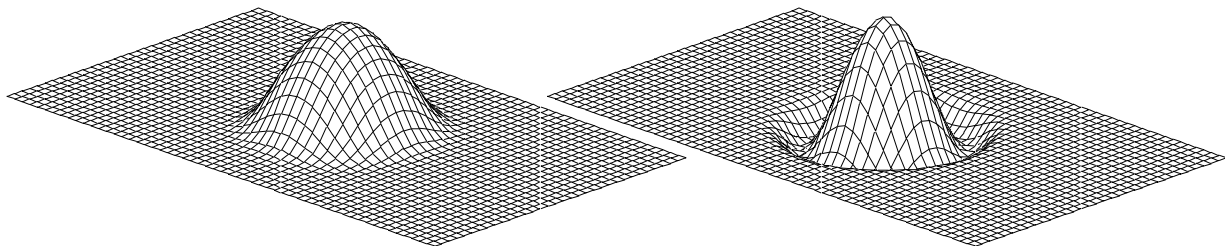
- must be localized within its own augmentation region
- obey bi-orthogonality condition

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{i,j}$$

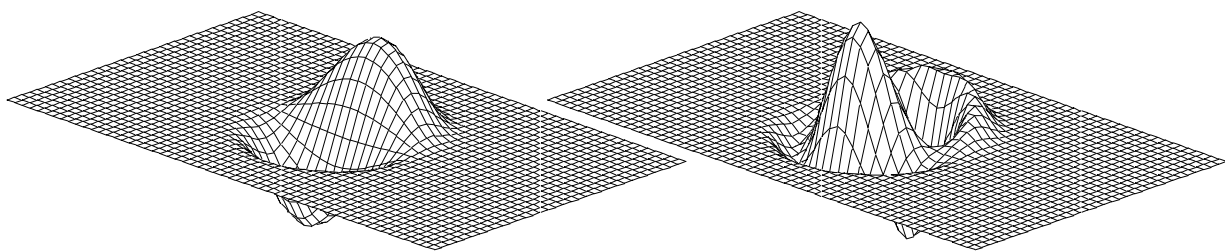
- projector functions $\langle \tilde{p} |$ are not yet uniquely determined: closure relation will be explained later

PAW Projector functions $\langle \tilde{p}_i |$

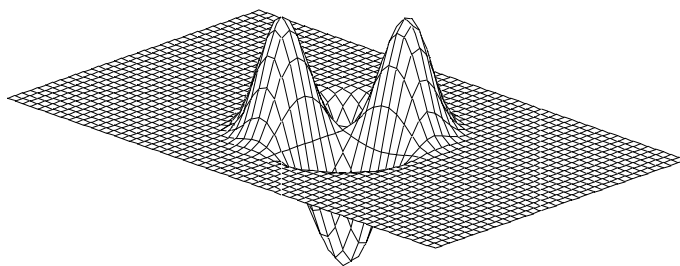
s-type projector functions



p-type projector functions



d-type projector function



Projector functions probe the character of the wave function

Reconstruction of the true wave function

Using the transformation operator

$$\mathcal{T} = 1 + \sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \langle \tilde{p}_j|,$$

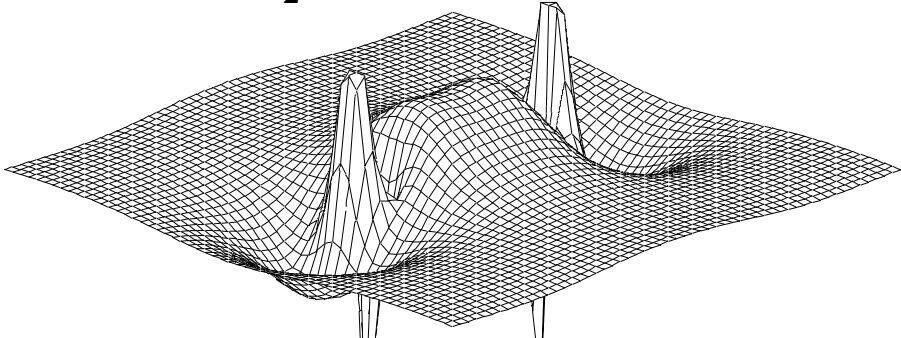
the all-electron wave function obtains the form:

$$|\Psi_n\rangle = |\tilde{\Psi}_n\rangle + \sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle \right) \langle \tilde{p}_j | \tilde{\Psi}_n \rangle$$

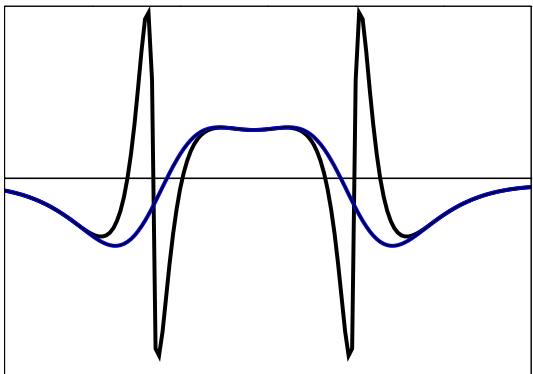
- the projector functions probe the character
of the auxiliary wave function,
- this “wrong” character is replaced
by the “correct” character

PAW Augmentation

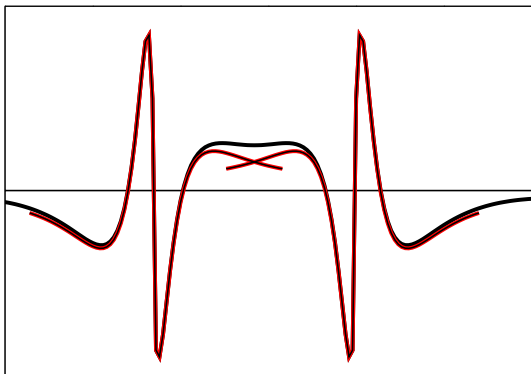
Example: p- σ orbital of Cl₂



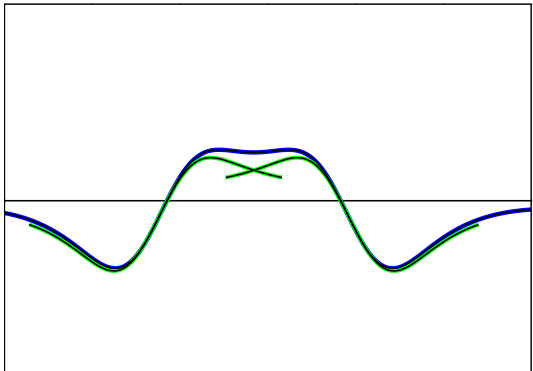
$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle = |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi} \rangle$$



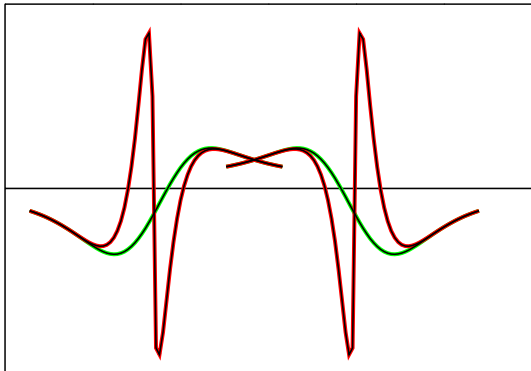
$|\Psi\rangle, |\tilde{\Psi}\rangle$



$|\Psi\rangle, |\Psi^1\rangle$



$|\tilde{\Psi}\rangle, |\tilde{\Psi}^1\rangle$



$|\Psi^1\rangle, |\tilde{\Psi}^1\rangle$

Numerical representation

- auxiliary wave function $\tilde{\Psi}_n$ is represented as plane wave expansion

- partial waves $\phi(r), \tilde{\phi}(r)$ are represented as

- radial functions on a logarithmic radial grid

$$r_i = r_1 \alpha^{i-1} \Rightarrow r_{i+1} = \alpha r_i$$

- multiplied with real spherical harmonics.

- projector functions are Bessel-transformed from a radial grid into Fourier space

- projector functions are smooth and local

- scalar product $\langle \tilde{p} | \tilde{\Psi}_n \rangle$ evaluated in Fourier space

PAW Expectation values

Expectation value for a “sufficiently local” one-particle operator

$$\begin{aligned}
 \langle A \rangle &= \sum_n f_n \langle \Psi_n | A | \Psi_n \rangle \\
 &= \sum_n f_n \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle && \text{plane wave part} \\
 &+ \sum_{i,j} D_{i,j} \langle \phi_i | A | \phi_j \rangle && \text{one-center exps. of true WF} \\
 &- \sum_{i,j} D_{i,j} \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle && \text{one-center exps. of aux. WF} \\
 &+ \sum_n \langle \Psi_n^c | A | \Psi_n^c \rangle && \text{core contribution}
 \end{aligned}$$

with a one-center density matrix

$$D_{i,j} = \sum_n \langle \tilde{p}_j | \tilde{\Psi}_n \rangle f_n \langle \tilde{\Psi}_n | \tilde{p}_i \rangle$$

and the core states $|\Psi_n^c\rangle$!

Similarity to pseudopotentials:

$$\begin{aligned}
 \langle A \rangle &= \sum_n \langle \tilde{\Psi}_n | \tilde{A} | \tilde{\Psi}_n \rangle \\
 \tilde{A} &= A + \sum_{i,j} |\tilde{p}_i\rangle \left(\langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle \right) \langle \tilde{p}_j|
 \end{aligned}$$

Pseudo-operator has the form of a separable pseudopotential.

⇒ PAW provides a rule to obtain expectation values in a pseudopotential calculation.

PAW Electron Density

Electron density $n(\mathbf{r})$ turns into a plane wave part $\tilde{n}(\mathbf{r})$ and two one-center components $n^1(\mathbf{r})$ and $\tilde{n}^1(\mathbf{r})$

$$\begin{aligned}n(\mathbf{r}) &= \tilde{n}(\mathbf{r}) + n^1(\mathbf{r}) - \tilde{n}^1(\mathbf{r}) \\ &= \sum_n f_n \tilde{\Psi}_n^*(\mathbf{r}) \tilde{\Psi}_n(\mathbf{r}) + \tilde{n}^c \\ &\quad + \sum_{i,j} \phi_i^*(\mathbf{r}) D_{i,j} \phi_j(\mathbf{r}) + n^c \\ &\quad - \sum_{i,j} \tilde{\phi}_i^*(\mathbf{r}) D_{i,j} \tilde{\phi}_j(\mathbf{r}) - \tilde{n}^c \\ D_{i,j} &= \sum_n \langle \tilde{p}_i | \tilde{\Psi}_n \rangle f_n \langle \tilde{\Psi}_n | \tilde{p}_j \rangle\end{aligned}$$

Electron density divided (like the wave function) into

- plane wave part
- two expansions per atom in radial functions times spherical harmonics

PAW Total energy

Total energy divided into plane wave integral
and two one-center expansions per atom

$$E([\tilde{\Psi}_n], R_i) = \tilde{E} + E^1 - \tilde{E}^1$$

Plane wave part:

$$\begin{aligned} \tilde{E} = & \sum_n f_n \langle \tilde{\Psi}_n | -\frac{1}{2} \nabla^2 | \tilde{\Psi}_n \rangle \\ & + E_H[\tilde{n}(r) + \hat{n}(r)] + E_{xc}[\tilde{n}(r)] + \int d^3r \bar{v}(r) \tilde{n}(r) \end{aligned}$$

One-center expansion of plane wave part

$$\begin{aligned} \tilde{E}^1 = & \sum_n D_{i,j} \langle \tilde{\phi}_i | -\frac{1}{2} \nabla^2 | \tilde{\phi}_j \rangle \\ & + E_H[\tilde{n}^1(r) + \hat{n}(r)] + E_{xc}[\tilde{n}^1(r)] + \int d^3r \bar{v}(r) \tilde{n}^1(r) \end{aligned}$$

One-center expansion of true density

$$\begin{aligned} E^1 = & \sum_n D_{i,j} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_j \rangle \\ & + E_H[n^1(r) + Z(r)] + E_{xc}[n^1(r)] \end{aligned}$$

**Everything else (Hamiltonian, Forces) follows
from this total energy functional**

PAW Approximations

The following approximations have been made

- frozen core approximation (can be overcome)
- truncate plane wave expansion (basis set)
- truncate partial wave expansion (augmentation)

Convergence:

- plane wave convergence comparable to ultrasoft pseudopotentials ($E_{PW}=30$ Ry)
- 1-2 partial waves per site and angular momentum sufficient

Charge and energy transferability problems of the pseudopotential approach are under control

The auxiliary Hamiltonian

effective Schrödinger-like equation for auxiliary wave functions

$$\left(\tilde{H} - \epsilon_n \tilde{O}\right) |\tilde{\Psi}_n\rangle = 0$$

where

$$\tilde{H} = \mathcal{T}^\dagger H \mathcal{T} = -\frac{1}{2} \nabla^2 + \tilde{v} + \sum_{i,j} |\tilde{p}_i\rangle h_{i,j} \langle \tilde{p}_j|$$

$$\tilde{O} = \mathcal{T}^\dagger \mathcal{T} = 1 + \sum_{i,j} |\tilde{p}_i\rangle o_{i,j} \langle \tilde{p}_j|$$

have the form of a separable pseudopotential

$h_{i,j}$ and $o_{i,j}$ have closed expressions

$$h_{i,j} = \langle \phi_i | -\frac{1}{2} \nabla^2 + v | \phi_j \rangle - \langle \tilde{\phi}_i | -\frac{1}{2} \nabla^2 + \tilde{v} | \tilde{\phi}_j \rangle$$

$$o_{i,j} = \langle \phi_i | \phi_j \rangle - \langle \tilde{\phi}_i | \tilde{\phi}_j \rangle$$

- are evaluated atom-by-atom on radial grids with spherical harmonics
- depend on the actual, non-spherical potential

Closure relation for projector functions

- **Closure: Auxiliary partial waves obey the effective PAW Schrödinger Eq. for the atom**

$$\left[-\frac{1}{2}\nabla^2 + \tilde{v} - \epsilon_k + \sum_{i,j} |\tilde{p}_i\rangle (h_{i,j} - \epsilon_k o_{i,j}) \langle \tilde{p}_j| \right] |\tilde{\phi}_k\rangle = 0$$

This restricts the Hilbert space for the projector functions

$$|\tilde{p}_i\rangle = \sum_j \left[-\frac{1}{2}\nabla^2 + \tilde{v} - \epsilon_j \right] |\tilde{\phi}_j\rangle c_{j,i}$$

Coefficients $c_{i,j}$ are determined from the biorthogonality condition.

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{i,j}$$

- **Converging set: Additional degree of freedom**

$$\sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i| = \sum_{i,j,k} \underbrace{(|\phi_i\rangle - |\tilde{\phi}_i\rangle) A_{i,k}}_{|\phi'_k\rangle - |\tilde{\phi}'_k\rangle} \underbrace{A_{k,j}^{-1} \langle \tilde{p}_j|}_{\langle \tilde{p}'_k|}$$

is used to provide a set that can be truncated for any number of partial waves.

Projector functions are uniquely defined with the definition of partial waves

Comparison with pseudopotentials

PAW Total energy:

$$E = \tilde{E} + \sum_R (E_R^1 - \tilde{E}_R) = \tilde{E} + \Delta E$$

with

$$\Delta E = \Delta E(D_{i,j})$$

therefore

$$\begin{aligned} \Delta E(D_{i,j}) &= \Delta E(D_{i,j}^{at}) + \sum_{i,j} \frac{\partial \Delta E}{\partial D_{i,j}} (D_{i,j} - D_{i,j}^{at}) + \dots \\ &= E_{self} + \sum_n f_n \langle \tilde{\Psi} | v_{ps} | \tilde{\Psi} \rangle + \dots \end{aligned}$$

- PAW calculates this expression exactly
- the PP method truncates the Taylor expansion after the linear term
→ charge transferability problem!

PAW creates pseudopotentials that adjust to the instantaneous electronic structure

Comparison with Ultrasoft Pseudopotentials

For an identical implementation both methods should require

- same computational effort
- same plane wave cutoff for the wave functions

Implementations differ:

- **USPP: Plane wave cutoff for the density equivalent to that of norm-conserving pseudopotentials**
→ support grids required
- **PAW uses one-center expansions with radial grids and a smooth compensation density**
→ lower cutoff for the density than USPP

Where do we need PAW?

[Kresse, Joubert PRB59,1759(1999)]

- **Magnetization energies**

Pseudopotentials introduce errors of order $0.06 \text{ eV}/\mu_B$

- **Energy difference between magnetic and non-magnetic iron**

	LAPW	PAW	US-PP
Fe(bcc)	-0.073 eV	-0.073 eV	-0.191 eV
Fe(fcc)	0.078 eV	0.061 eV	0.070 eV
Fe(hcp)	0	0	0

- **Surface magnetism of V(001):**

	LAPW	PAW	US-PP
magnetic moment V(001)	$\approx 0\mu_B$	$0\mu_B$	$0.75\mu_B$

- **alkali, alkaline earth, and early transition metals**

- **Lattice constant of CaF_2 too small by 2% in PSP calculations**

Summary:

- **Pseudopotentials are accurate in most cases**
- **Pseudopotentials can be made accurate, but at a tremendous computational cost (hard pseudopotentials)**
- **PAW is comparable to other all-electron schemes (LAPW)**

Electric field gradients

Comparison with LAPW

H. Petrilli, P.E. Blöchl, P. Blaha, K. Schwarz, PRB 57,14690 (1998)

	$V_{zz}[\text{V}/\text{m}^2]$	PAW-LAPW	expt-LAPW
Cl_2	54.23	1.0 %	2.8 %
Br_2	94.44	-2.2 %	-0.9 %
I_2	119.01	0.2 %	-4.9 %
$\text{Li}_3\text{N}:\text{Li}(1)$	-0.71	2.9 %	-13.0 %
$\text{Li}_3\text{N}:\text{Li}(2)$	+0.33	-2.9 %	-11.8 %
$\text{Li}_3\text{N}:\text{N}$	1.02	-9.7 %	-8.0 %
$\text{Fe}(\text{C}_5\text{H}_5)_2$	10.67	-7.2 %	23.5 %
FeS_2 (pyrite)	-3.40	-2.0 %	5.5 %
FeS (marcasite)	-3.21	-4.5 %	-10.7 %
FeSi	4.92	0.0 %	-9.6 %
Fe_2O_3	1.84	-7.5 %	8.5 %
$\text{TiO}_2:\text{Ti}$	-2.06	-1.4 %	9.1 %
$\text{TiO}_2:\text{O}$	+2.14	0.5 %	11.7 %
Cu_2O	-8.60	3.6 %	22.9 %
average		4.4 %	12.0 %

PAW is three times better than experiment!

Hyperfine parameters

E'_1 center in SiO_2

	PAW	expt	PP
Si1	-45.4	-45.4	-51.3
	-39.6	-39.1	-44.6
	-39.6	-39.1	-44.5
Si(1a)	-1.4	-1.0	-2.4
	-1.2	-0.8	-1.8
	-1.2	-0.8	-1.8
Si(1b)	-1.5	-0.9	2.2
	-1.3	-0.8	1.6
	-1.3	-0.8	1.6

H^0 in SiO_2

	PAW	expt
H	50.29	51.91

H^0 in vacuum

	PAW	exact
H	50.93	50.73

PAW options (CP-PAW Code)

- ab-initio molecular dynamics (Car-Parrinello)
- all-electron wave functions and densities
- **electric field gradients(EFG), hyperfine parameters**
- gradient corrected density functionals (various forms)
- spin unrestricted, **non-collinear spin**
- **isolated molecules** and extended crystals
- **QM-MM coupling**
- activation energies
- crystal orbital populations (local chemical bond analysis)
- general k-points
- variable occupations and finite electron-temperature
- variable cell shape (Parrinello-Rahman)
- LDA+U*
- **GW approximation***
- **object oriented** program architecture (Fortran 90)
- efficiently parallelized (MPI)
- portable (Intel-Linux, IBM-AIX, Dec-Alpha-Linux)

*) Strasbourg version

Implementations of PAW

- **CP-PAW; P. Blöchl, Clausthal University of Technology**
- **PWPAW; A. Tackett, N. Holzwarth, Wake Forest U., USA**
- **NWChem; M. Valiev, J.H. Weare. UC San Diego**
- **VASP Code; G. Kresse et al., Vienna University**
- **F. Mauri, Princeton University**
- ***EStCoMPP; S. Blügel, Osnabrück University**
- **AbInit, X. Gonze, PCPM Louvain-la-Neuve, Belgium**
- ***DFT++; S. Ismail-Beigi, T. Arias, UC Berkeley, Cornell U.**
- ***SFHIngX (Planned), S. Boeck+Neugebauer+Co., Berlin**

Conclusion

- **all-electron method for ab-initio molecular dynamics**
- **rigorous theoretical basis**
- **accurate and efficient**
- **extends and joins all-electron methods with the pseudopotential approach**
 - **pseudopotentials as approximation of PAW**
 - **extends the tradition of Linear Methods (LMTO,LAPW)**

**Projector Augmented Wave Method
P.E. Blöchl, Phys. Rev. B 50, 17953 (1994)**

**The Projector Augmented Wave Method: Ab-initio Molecular
Dynamics Simulations with Full Wave Functions**

**P.E. Blöchl, C. Först and J. Schimpl,
Bull. Mater. Sci. 26, 33 (2003).**

<http://www.arxiv.org/abs/cond-mat/0201015>