

Projector-Augmented Wave Method:

ab-initio MD with full wave functions

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Reminder: Car-Parrinello Method

Generalization of first principles electronic structure methods invented 1985 by R. Car and M. Parrinello

Goals

- study molecular dynamics on the basis of first principles electronic structure methods
- make structural optimization efficient
- handle large basissets efficiently

Principle

- solve classical equations of motion for nuclei

$$M_i \ddot{R}_i = F = - \frac{\partial E(R_i, [\Psi_n])}{\partial R_i}$$

Density Functional Theory instead of empirical force field

- avoid selfconsistency iterations in each step by introducing a fictitious dynamics for the wave functions.

$$m_\Psi \ddot{\Psi}_n(r) = - \frac{\partial E(R_i, [\Psi_n])}{\partial \Psi_n^*(r)}$$

Classical molecular dynamics

1. Start from a “force field”: Total energy is given as function of all atomic positions

$$E(\vec{R}_1, \dots, \vec{R}_N)$$

2. Newton’s equation of motion

$$M_i \ddot{\vec{R}}_i = \vec{F}_i = -\nabla_{R_i} E(\vec{R}_1, \dots, \vec{R}_N)$$

3. Discretization: Verlet algorithm:

- Replace derivative by differential quotient

$$M_i \frac{\vec{R}_i(t + \Delta) - 2\vec{R}_i(t) + \vec{R}_i(t - \Delta)}{\Delta^2} = \vec{F}_i$$

- Resolve for $\vec{R}_i(t + \Delta)$

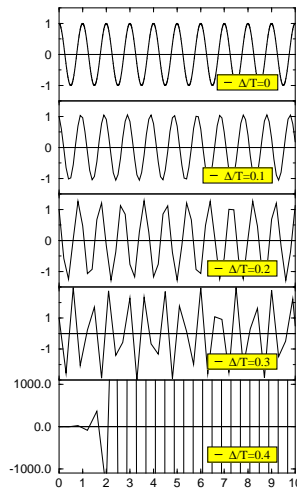
$$\vec{R}_i(t + \Delta) = 2\vec{R}_i(t) - \vec{R}_i(t - \Delta) + \vec{F}_i \frac{\Delta^2}{M_i}$$

- Short-hand notation

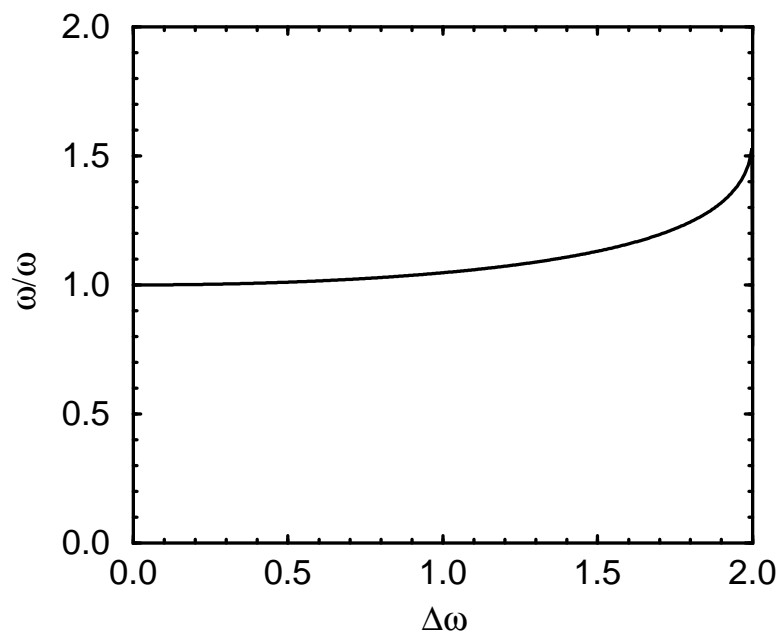
$$R(+)= = 2R(0) - R(-) + F(0) \frac{\Delta^2}{M}$$

Stability of the Verlet Algorithm

- **Stability limit:** Timestep must be smaller than a third of the smallest oscillation period.



- **Accuracy:** frequencies are overestimated by 1% of the time step is a tenths of an oscillation period.



Born Oppenheimer approximation

- DFT requires the wave function to be in the instantaneous electronic ground state.
 - no wave function dynamics!
 - wave functions adapt to the changing atomic positions adiabatically
- Born-Oppenheimer surface
 - consider $E(\vec{R}_1, \dots, \vec{R}_n)$ obtained from an independent self consistent electronic structure calculation at each set of atomic positions
- Simple-minded approach (expensive):
 1. perform fully self-consistent calculation for an atomic structure $\{\vec{R}_1, \dots, \vec{R}_n\}$
 2. calculate forces
$$F = -\nabla E(\vec{R}_1, \dots, \vec{R}_n)$$
 3. propagate atomic positions
$$R(+)=2R(0)-R(-)+F\frac{\Delta^2}{M}$$
 4. continue with step 1

The Car-Parrinello way

- Replace the time dependent Schrödinger equation by a classical equation of motion

$$i\hbar \frac{d}{dt} |\Psi_n(t)\rangle = \hat{H} |\Psi_n(t)\rangle$$

$$\rightarrow m_\Psi \frac{d^2}{dt^2} |\Psi_n(t)\rangle = -H |\Psi_n(t)\rangle$$

Dynamics does not matter as long as the Born-Oppenheimer principle holds

- Atoms and wave functions are treated on equal footing

$$M_i \ddot{R}_i = - \frac{dE(R, |\Psi\rangle)}{dR_i}$$

$$m_\Psi |\ddot{\Psi}_n\rangle f_n = - \frac{dE(R, |\Psi\rangle)}{d\langle \Psi_n |} + \sum_m |\Psi_m\rangle \Lambda_{m,n}$$

- Fictitious Lagrangian

$$\mathcal{L} = \frac{1}{2} \sum_i M \dot{R}_i^2 + \sum_n f_n \langle \dot{\Psi}_n | m_\Psi | \dot{\Psi} \rangle - E(R, \Psi)$$

$$+ \sum_{n,m} (\langle \Psi_n | \Psi_m \rangle - \delta_{n,m}) \Lambda_{n,m}$$

$$E(R, \Psi) = \sum_n f_n \langle \Psi_n | - \frac{1}{2} \nabla^2 | \Psi_n \rangle$$

$$+ \frac{1}{2} \int d^3 r \int d^3 r' \frac{n(r)n(r')}{|r - r'|} + E_{xc}[n(r)]$$

$$n(r) = \sum_n f_n \Psi_n^*(r) \Psi_n(r)$$

Motivation for the fictitious Lagrangian

- **dynamics and optimization is treated on equal footing**
- **the electronic ground state is obtained, when a small friction is added.**
- **all tricks of the trade from classical molecular dynamics can be used. (e.g. thermostats)**
- **no self-consistency iterations during dynamics; fast!**

Requirements:

- **the total energy must be a unique functional of wave function coefficients and atomic positions**
- **excludes potential dependent basis sets as in LMTO and LAPW**
- **time scales of the dynamics must be under control**

Historical context

Historical context of electronic structure methods

scattered Waves (KKR, APW)	empirical pseudopotentials
energy independent basisfunctions (LMTO,LAPW)	ab-initio pseudopotentials
energy- and potential independent augmented waves (PAW)	

PAW joins all-electron and pseudopotential methods

PAW built around a consistent transformation theory

$$\begin{aligned} |\Psi\rangle &= \hat{T}|\tilde{\Psi}\rangle \\ \langle\hat{A}\rangle &= \langle\tilde{\Psi}|\hat{T}^\dagger\hat{A}\hat{T}|\tilde{\Psi}\rangle = \langle\tilde{\Psi}|\tilde{A}|\tilde{\Psi}\rangle \\ T(R_1, \dots, R_n) &= 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle\tilde{p}_i| \end{aligned}$$

Properties of PAW

- ab-initio molecular dynamics
- full all-electron wave functions
(accurate hyperfine parameters)
- simple force calculations
- “fast as pseudopotentials and accurate as LAPW”
- pseudopotentials as approximation of PAW
- rigorous mathematical basis (exact when converged)

Philosophy

- **Focus on a total energy functional and not on potentials**
- **All approximations are included in the total energy functional**
- **Forces are analytic derivatives of the total energy**

- **Provide a well-defined language for quantum mechanical calculations**
- **Transformation theory provides link between numerically convenient and physical wave functions**

- **Use plane wave expansions and one-center expansions**
- **Only smooth functions in plane wave expressions**
- **Only one-center integrals from the one-center expansions**

PAW Transformation theory

- start with **auxiliary wave functions** $\tilde{\Psi}_n(r)$
- define a **transformation operator** $\hat{\mathcal{T}}$,

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

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

$$(\mathcal{T}^\dagger H \mathcal{T} - \mathcal{T}^\dagger \mathcal{T} \epsilon_n) \tilde{\Psi}_n(r) = 0$$

- **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**

PAW Transformation operator

Define a transformation from auxiliary (pseudo) wave functions $|\tilde{\Psi}\rangle$ to the true all-electron wave functions $|\Psi\rangle$.

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

- index $i = \vec{R}, \ell, m, \alpha$
- all-electron partial waves $|\phi_i\rangle$ are constructed from true atomic potential
- pseudo partial waves $|\tilde{\phi}_i\rangle$ from a pseudopotential with

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

- projector functions $|\tilde{p}_i\rangle$ are chosen such that

$$|\tilde{\Psi}\rangle = \sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi}\rangle \text{ for } |\vec{r} - \vec{R}| < r_c$$

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

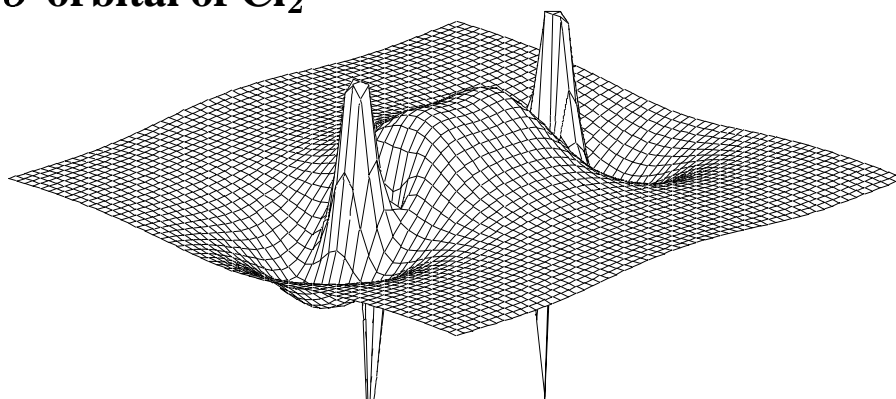
Transformation operator \mathcal{T}

$$\Leftrightarrow |\Psi_n\rangle = \mathcal{T} |\tilde{\Psi}_n\rangle$$

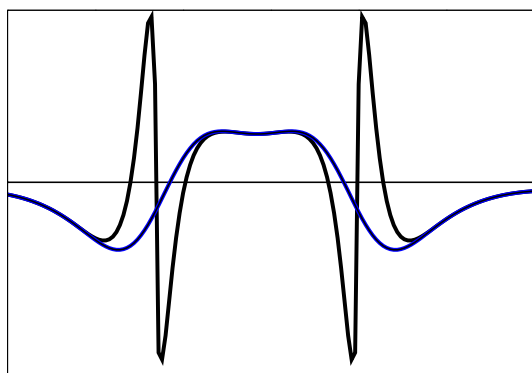
$$\mathcal{T} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i |$$

PAW Augmentation

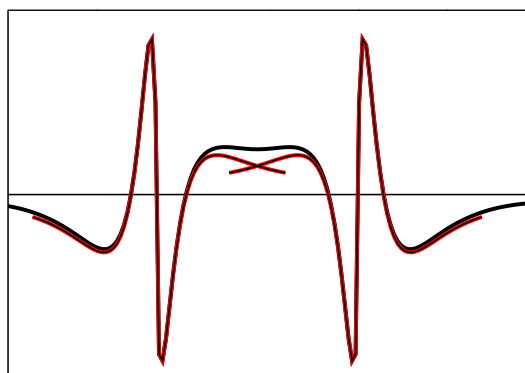
Example: p- σ orbital of Cl₂



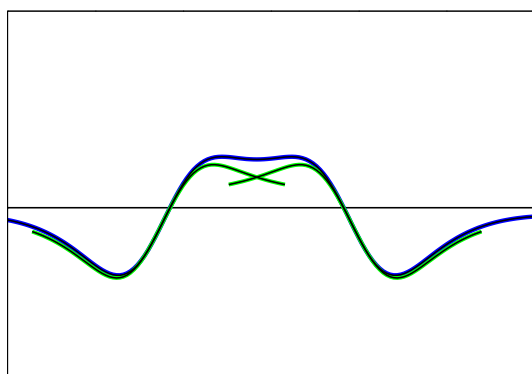
$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle = |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi} \rangle$$



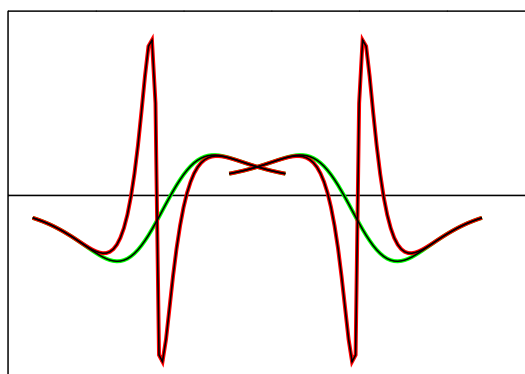
$|\Psi\rangle, |\tilde{\Psi}\rangle$



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



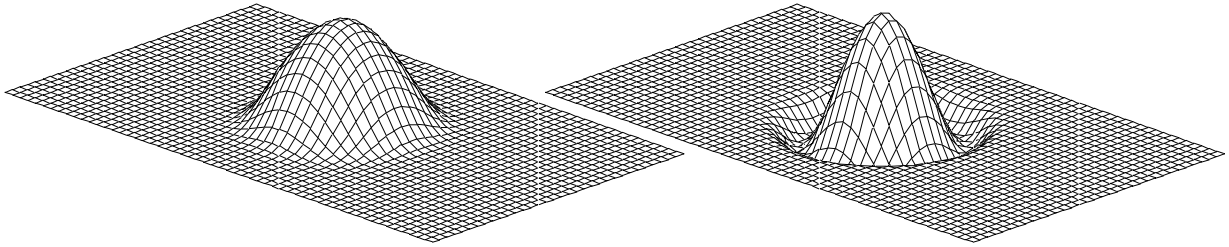
$|\tilde{\Psi}\rangle, |\tilde{\Psi}^1\rangle$



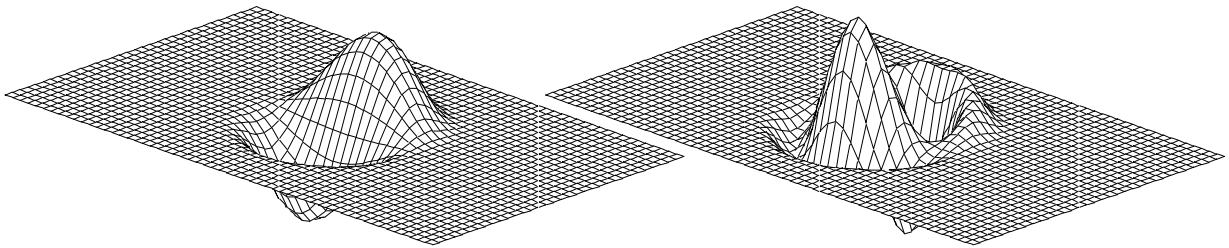
$|\Psi^1\rangle, |\tilde{\Psi}^1\rangle$

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

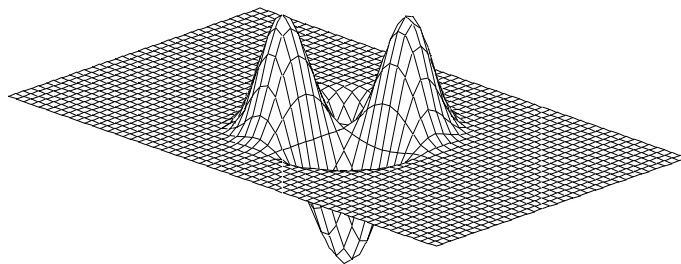
s-type projector functions



p-type projector functions



d-type projector function



Projector functions probe the character of the wave function

Rationale (I)

- choose $\hat{\mathcal{T}} = 1 + \sum_R \hat{S}_R$ as one plus atomic terms
- define the operator $1 + S_R$ by the mapping for a complete set of basis functions
- choose a basis set of atomic orbitals $|\phi_{R,\ell,m,\alpha}\rangle$.
Solve the radial Schrödinger equation for the isolated, self-consistent atom for a set of energies.
- for each $|\phi_{R,\ell,m,\alpha}\rangle$ choose an auxiliary basis function $|\tilde{\phi}_{R,\ell,m,\alpha}\rangle$, so that they are identical outside some augmentation region
- define the operator S_R by

$$\begin{aligned} |\phi_{R,\ell,m,\alpha}\rangle &= (1 + S_R)|\tilde{\phi}_{R,\ell,m,\alpha}\rangle \\ \Rightarrow S_R|\tilde{\phi}_{R,\ell,m,\alpha}\rangle &= |\phi_{R,\ell,m,\alpha}\rangle - |\tilde{\phi}_{R,\ell,m,\alpha}\rangle \end{aligned}$$

- decompose auxiliary wave function locally into smooth partial waves

$$|\tilde{\Psi}\rangle = \sum_{R,\ell,m,\alpha} |\tilde{\phi}_{R,\ell,m,\alpha}\rangle c_{R,\ell,m,\alpha}$$

and obtain the transformation as

$$|\Psi\rangle = 1 + \sum_{R,\ell,m,\alpha} (|\phi_{R,\ell,m,\alpha}\rangle - |\tilde{\phi}_{R,\ell,m,\alpha}\rangle) c_{R,\ell,m,\alpha}$$

with yet unknown coefficients

Rationale (II)

$$|\Psi\rangle = 1 + \sum_{R,\ell,m,\alpha} (|\phi_{R,\ell,m,\alpha}\rangle - |\tilde{\phi}_{R,\ell,m,\alpha}\rangle) c_{R,\ell,m,\alpha}$$

- if \mathcal{T} is to be a linear operator, the coefficients $c_{R,\ell,m,\alpha}$ have the form of a linear functional of the auxiliary wave function, i.e.

$$c_{R,\ell,m,\alpha} = \langle \tilde{p}_{R,\ell,m,\alpha} | \tilde{\Psi} \rangle$$

thus

$$|\Psi\rangle = 1 + \sum_{R,\ell,m,\alpha} (|\phi_{R,\ell,m,\alpha}\rangle - |\tilde{\phi}_{R,\ell,m,\alpha}\rangle) \langle \tilde{p}_{R,\ell,m,\alpha} | \tilde{\Psi} \rangle$$

- projector functions $\langle \tilde{p}_{R,\ell,m,\alpha} |$ must obey

$$\begin{aligned} |\tilde{\Psi}\rangle &= \sum_{R,\ell,m,\alpha} |\tilde{\phi}_{R,\ell,m,\alpha}\rangle \langle \tilde{p}_{R,\ell,m,\alpha} | \tilde{\Psi} \rangle \\ \Rightarrow \forall_i : \quad |\tilde{\phi}_i\rangle &= \sum_j |\tilde{\phi}_j\rangle \langle \tilde{p}_j | \tilde{\phi}_i \rangle \\ &\Rightarrow \langle \tilde{p}_j | \tilde{\phi}_i \rangle = \delta_{i,j} \end{aligned}$$

PAW Expectation values

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

$$\langle A \rangle = \sum_n \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle + \sum_{i,j} D_{i,j} \langle \phi_i | A | \phi_j \rangle - \sum_{i,j} D_{i,j} \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle + \sum_n \langle \Psi_n^c | A | \Psi_n^c \rangle$$

with a one-center density matrix

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

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

Similarity to pseudopotentials:

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

Pseudo-operator has the form of a separable pseudopotential.

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

PAW Expectation values in detail

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

$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle$$

$$\langle \Psi | A | \Psi \rangle = \begin{array}{|c|c|c|} \hline \langle \tilde{\Psi} | A | \tilde{\Psi} \rangle & + \langle \tilde{\Psi} | A | \Psi^1 \rangle & - \langle \tilde{\Psi} | A | \tilde{\Psi}^1 \rangle \\ \hline \langle \Psi^1 | A | \tilde{\Psi} \rangle & + \langle \Psi^1 | A | \Psi^1 \rangle & - \langle \Psi^1 | A | \tilde{\Psi}^1 \rangle \\ \hline - \langle \tilde{\Psi}^1 | A | \tilde{\Psi} \rangle & - \langle \tilde{\Psi}^1 | A | \Psi^1 \rangle & + \langle \tilde{\Psi}^1 | A | \tilde{\Psi}^1 \rangle \\ \hline \end{array}$$

$$\langle \Psi | A | \Psi \rangle = \langle \tilde{\Psi} | A | \tilde{\Psi} \rangle + \langle \Psi^1 | A | \Psi^1 \rangle - \langle \tilde{\Psi}^1 | A | \tilde{\Psi}^1 \rangle$$

and a remainder, which is ignored

$$+ \langle \tilde{\Psi} - \tilde{\Psi}^1 | A | \Psi^1 - \tilde{\Psi}^1 \rangle + \langle \Psi^1 - \tilde{\Psi}^1 | A | \tilde{\Psi} - \tilde{\Psi}^1 \rangle$$

Remainder vanishes if $\tilde{\Psi} = \tilde{\Psi}_1$ inside the augmentation region

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:

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

One-center expansion of plane wave part

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

One-center expansion of true density

$$\begin{aligned}E^1 &= \sum_n D_{i,j} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_j \rangle \\ &+ \frac{1}{2} \int d^3 r \int d^3 r' \frac{(n^1(r) + Z(r))(n^1(r') + Z(r'))}{|\mathbf{r} - \mathbf{r}'|} \\ &+ \int d^3 r n^1(r) \epsilon_{xc}(r, [n^1])\end{aligned}$$

**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 (High-spin atoms)

Implement LDA+U

$$|\tilde{\Psi}\rangle \approx \sum_i |\tilde{\chi}_i\rangle c_i$$

Let us define a functional \mathcal{F}

$$\mathcal{F} = (\langle \tilde{\Psi} | - \sum_i c_i^* \langle \tilde{\chi}_i |) \sum_{k,l} |\tilde{p}_k\rangle w_{k,l} \langle \tilde{p}_l | (|\tilde{\Psi}\rangle - \sum_j |\tilde{\chi}_j\rangle c_j)$$

Minimize functional with respect to c_i

$$|\tilde{\Psi}\rangle = \sum_{i,j} |\tilde{\chi}_i\rangle (\sum_{k,l} \langle \tilde{\chi}_i | \tilde{p}_k\rangle w_{k,l} \langle \tilde{p}_l | \tilde{\chi}_j\rangle)^{-1}_{i,j} (\sum_{k,l} \langle \tilde{\chi}_j | \tilde{p}_k\rangle w_{k,l} \langle \tilde{p}_l | \tilde{\Psi}\rangle)$$

Transform from auxiliary to the true wave functions

$$|\Psi\rangle = |\chi_i\rangle \langle \mathcal{P}_i | \tilde{\Psi}\rangle$$

$$\mathcal{P}_i = \sum_l q_l \langle \tilde{p}_l |$$

$$q_l = \sum_j (\sum_{k,l} \langle \tilde{\chi}_i | \tilde{p}_k\rangle w_{k,l} \langle \tilde{p}_l | \tilde{\chi}_j\rangle)^{-1}_{i,j} \sum_k \langle \tilde{\chi}_j | \tilde{p}_k\rangle w_{k,l}$$

Implement LDA+U by adding a total energy contribution

$$\Delta E = Q[\sum_i |\chi_i\rangle \langle \mathcal{P}_i | \tilde{\Psi}\rangle]$$

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.**
- **M. Valiev, J.H. Weare. UC San Diego**
- **VASP Code; G. Kresse et al. Vienna University**
- **EStCoMPP; S. Blügel, Osnabrück University**
- **F. Mauri, University Pierre and Marie Curie, Paris**
- **DFT++; S. Ismail-Beigi, T. Arias, UC Berkeley, Cornell U.**

Conclusion

- **all-electron method for ab-initio molecular dynamics**
- **rigorous theoretical basis**
- **accurate, efficient, and simple**
- **extends and joins all-electron methods with the pseudopotential approach**
 - **Linear Methods as very “special case” of PAW**
 - **Pseudopotentials as approximation of PAW**

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