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.

\[ m \Psi_n (r) = - \frac{\partial E(R_i, [\Psi_n])}{\partial \Psi^*_n (r)} \]
Classical molecular dynamics

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

\[ E(\vec{R}_1, \ldots, \vec{R}_N) \]

2. Newton’s equation of motion

\[ M_i \ddot{\vec{R}}_i = \vec{F}_i = -\nabla_{\vec{R}_i} E(\vec{R}_1, \ldots, \vec{R}_N) \]

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 $E(\vec{R}_1, \ldots, \vec{R}_n)$ 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 $\{\vec{R}_1, \ldots, \vec{R}_n\}$
  2. calculate forces
     $$F = -\nabla E(\vec{R}_1, \ldots, \vec{R}_n)$$
  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

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

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

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

- Atoms and wave functions are treated on equal footing

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

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

- Fictitious Lagrangian

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

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

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

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

\[ n(r) = \sum_n f_n \Psi_n^*(r) \Psi_n(r) \]
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**

<table>
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PAW joins all-electron and pseudopotential methods

PAW built around a consistent transformation theory

\[ |\Psi\rangle = \hat{T}|\tilde{\Psi}\rangle \]
\[ \langle \hat{A} \rangle = \langle \tilde{\Psi}|\hat{T}^{\dagger}\hat{A}\hat{T}|\tilde{\Psi}\rangle = \langle \tilde{\Psi}|\tilde{A}|\tilde{\Psi}\rangle \]
\[ T(R_1, \cdots, R_n) = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle)\langle \tilde{\phi}_i| \]

**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 \( \hat{T} \),
  \[
  \Psi_n(r) = \hat{T} \tilde{\Psi}_n(r),
  \]
  that maps the auxiliary wave functions \( \tilde{\Psi}_n(r) \)
  onto true wave functions \( \Psi_n(r) \)
- express total energy by auxiliary wave functions
  \[
  E = E[\Psi_n(r)] = E[\hat{T} \tilde{\Psi}_n(r)]
  \]
- 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 \( \hat{T} \) 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 $i = \bar{R}, \ell, m, \alpha$
- all-electron partial waves $|\phi_i\rangle$ are constructed from true atomic potential
- pseudo partial waves $|\tilde{\phi}_i\rangle$ from a pseudopotential with
  $$
  \tilde{\phi}_i(\vec{r}) = \phi_i(\vec{r}) \text{ for } |\vec{r} - \bar{R}| > r_c
  $$
- projector functions $|\tilde{p}_i\rangle$ are chosen such that
  $$
  |\tilde{\Psi}\rangle = \sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi} \rangle \text{ for } |\vec{r} - \bar{R}| < r_c
  $$

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

**Transformation operator $\mathcal{T}$**

$$
\Leftrightarrow |\Psi_n\rangle = \mathcal{T} |\tilde{\Psi}_n\rangle
\quad \mathcal{T} = 1 + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i |
$$
PAW Augmentation

Example: p-σ orbital of Cl₂

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

s-type projector functions

p-type projector functions

d-type projector function

Projector functions probe the character of the wave function
Rationale (I)

- choose $\hat{T} = 1 + \sum_R \hat{S}_R$ as one plus atomic terms
- define the operator $1 + S_R$ by the mapping for a complete set of basis functions
- choose a basisset 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
  
  \[ |\phi_{R,\ell,m,\alpha}\rangle = (1 + S_R) |\tilde{\phi}_{R,\ell,m,\alpha}\rangle \]
  
  \[ \Rightarrow S_R |\tilde{\phi}_{R,\ell,m,\alpha}\rangle = |\phi_{R,\ell,m,\alpha}\rangle - |\tilde{\phi}_{R,\ell,m,\alpha}\rangle \]

- 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)

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

- if \( T \) 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
  \[ |\Psi\rangle = 1 + \sum_{R,\ell,m,\alpha} \left( |\phi_{R,\ell,m,\alpha}\rangle - |\tilde{\phi}_{R,\ell,m,\alpha}\rangle \right) \langle \tilde{p}_{R,\ell,m,\alpha} | \tilde{\Psi} \rangle \]

- projector functions \( \langle \tilde{p}_{R,\ell,m,\alpha} | \) must obey
  \[ |\tilde{\Psi}\rangle = \sum_{R,\ell,m,\alpha} |\tilde{\phi}_{R,\ell,m,\alpha}\rangle \langle \tilde{p}_{R,\ell,m,\alpha} | \tilde{\Psi}\rangle \]
  \[ \Rightarrow \forall i : \quad |\tilde{\phi}_i\rangle = \sum_j |\tilde{\phi}_j\rangle \langle \tilde{p}_j | \tilde{\phi}_i\rangle \]
  \[ \Rightarrow \langle \tilde{p}_j | \tilde{\phi}_i\rangle = \delta_{i,j} \]
PAW Expectation values

Expectation value for a “sufficiently local” one-particle operator
\[
\langle A \rangle = \sum_n \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle + \sum_{i,j} D_{i,j} \langle \phi_i | A | \phi_j \rangle - \sum_{i,j} D_{i,j} \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle
\]
\[+ \sum_n \langle \Psi^c_n | A | \Psi^c_n \rangle \]

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 \( |\Psi^c_n \rangle \)!

Similarity to pseudopotentials:
\[
\langle A \rangle = \sum_n \langle \tilde{\Psi}_n | \tilde{A} | \tilde{\Psi}_n \rangle
\]
\[\tilde{A} = A + \sum_{i,j} |\tilde{p}_i \rangle \langle \phi_i | A | \phi_j \rangle - \langle \tilde{\phi}_i | A | \tilde{\phi}_j \rangle \rangle \langle \tilde{p}_j | \]

Pseudo-operator has the form of a separable pseudopotential.

\[\Rightarrow \text{PAW provides a rule to obtain expectation values in a pseudopotential calculation.}\]
PAW Expectation values in detail

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

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

\[
\begin{array}{ccc}
| \Psi \rangle & A & | \Psi \rangle \\
\hline
\langle \tilde{\Psi} | A | \tilde{\Psi} \rangle & + \langle \tilde{\Psi} | A | \Psi^1 \rangle & - \langle \tilde{\Psi} | A | \tilde{\Psi}^1 \rangle \\
\langle \Psi^1 | A | \tilde{\Psi} \rangle & + \langle \Psi^1 | A | \Psi^1 \rangle & - \langle \Psi^1 | A | \tilde{\Psi}^1 \rangle \\
- \langle \tilde{\Psi}^1 | A | \tilde{\Psi} \rangle & - \langle \tilde{\Psi}^1 | A | \Psi^1 \rangle & + \langle \tilde{\Psi}^1 | A | \tilde{\Psi}^1 \rangle
\end{array}
\]

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

and a remainder, which is ignored

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

Remainder vanishes if $\tilde{\Psi} = \tilde{\Psi}^1$ inside the augmentation region
Electron density $n(r)$ turns into a plane wave part $\tilde{n}(r)$ and two one-center components $n^1(r)$ and $\tilde{n}^1(r)$

$$n(r) = \tilde{n}(r) + n^1(r) - \tilde{n}^1(r)$$

$$= \sum_n f_n \tilde{\Psi}_n^*(r)\tilde{\Psi}_n(r) + \tilde{n}^c$$

$$+ \sum_{i,j} \phi_i^*(r)D_{i,j}\phi_j(r) + n^c$$

$$- \sum_{i,j} \tilde{\phi}_i^*(r)D_{i,j}\tilde{\phi}_j(r) - \tilde{n}^c$$

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

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:**

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

**One-center expansion of plane wave part**

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

**One-center expansion of true density**

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

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 (basisset)
- 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

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

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