Projector augmented-wave method

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What is PAW?

- An approach for electronic structure calculations
- Is used to treat first-row and transition-metal elements with reasonable effort
- Provides access to the full wave function
- Generalizes the most common electronic structure methods like the LAPW and pseudopotential method
1 Introduction
   The projector augmented-wave method
   Overview
   Introduction to augmented-wave methods

2 Formalism
   Projector augmented-wave functions
   Operators

3 Construction of partial waves and projectors
   Partial waves
   Projector functions

4 Numerical tests
   Scattering properties
   Real wave function

5 Comparison to other methods
   Pseudopotentials
   General APW
   LAPW

6 Conclusion
The majority of electronic structure calculations are based on LDA.

To solve the resulting Schrödinger equation of the LDA there are two main approaches:

**The linear methods (APW)**
- very accurate linear augmented-plane-wave method (LAPW)
- linear muffin-tin orbital method (LMTO)

**The pseudopotential method**
- formal simplicity
- full wave function not accessible
The PAW method

- Combines the versatility of the LAPW method and the formal simplicity of the pseudopotential approach
- Provides full access to the wave function
- Accuracy compares very well with other very accurate methods based on LDA

→ LAPW is a special case of the PAW method
→ Pseudopotential approach is obtained by an approximation of the PAW
Motivation for augmented-wave methods

- Real electron wave functions have very different behaviour in space
  - Rapid oscillations close to the nucleus
  - Smooth behaviour in the interstitial region
- Difficult for approximations and numerical treatment

An electron in a hydrogen atom
The idea of augmented-wave methods is to divide the wave function \( |\psi\rangle \) into parts:
- Partial wave expansion in a sphere around the atom (augmentation region)
- Envelope functions outside the spheres (interstitial region)
- Envelope functions and partial-wave expansions are then matched at the sphere radius
The PAW method

The PAW method is now a very general augmentation scheme:

- Consider a partial wave expansion for the full one-electron Kohn-Sham wave function $|\psi\rangle$ within the augmentation region

$$|\psi\rangle = \sum_i |\Phi_i\rangle c_i$$

with the computationally difficult partial waves $|\Phi_i\rangle$ (solutions of the radial Schrödinger equation)

- Therefore we transform the $|\Phi_i\rangle$ into pseudo (PS) wave functions $|\tilde{\Phi}_i\rangle$ which are computationally convenient

- These PS wave functions will be identified with the envelope functions and are obtained by a linear transformation $\tau$
Thus the transformation $\tau$ gets us from the PS wave function to the true wave function

$$|\psi\rangle = \tau |\tilde{\psi}\rangle$$

If we know the transformation $\tau$, we can calculate physical quantities, i.e. expectation values

$$\langle A \rangle = \langle \psi | A | \psi \rangle = \langle \tilde{\psi} | \tau^\dagger A \tau | \tilde{\psi} \rangle$$

either directly as $\langle \psi | A | \psi \rangle$ or as an expectation value $\langle \tilde{\psi} | \tilde{A} | \tilde{\psi} \rangle$ of the PS operator $\tilde{A} = \tau^\dagger A \tau$
The transformation $\tau$

- For the transformation we consider one that only differ from the identity by a sum of local, atom-centered contributions

$$\tau = 1 + \sum_R \tau_R$$

so that the real and the PS wave function coincide outside the augmentation region.

- Hence each contribution $\tau_R$ only acts within a specific augmentation region $\Omega_R$.

- The augmentation is the equivalent to the muffin-tin sphere or the so called core-region in the pseudopotential method.
The transformation $\tau$

- So we have the transformation of the partial waves

$$|\Phi_i\rangle = (1 + \tau_R)|\tilde{\Phi}_i\rangle$$

within $\Omega_R$

- For the real wave function we have

$$|\psi\rangle = \sum_i |\Phi_i\rangle c_i = \tau \sum_i |\tilde{\Phi}_i\rangle c_i = \tau |\tilde{\psi}\rangle$$

and we can express $|\psi\rangle$ as

$$|\psi\rangle = |\tilde{\psi}\rangle - \sum_i |\tilde{\Phi}_i\rangle c_i + \sum_i |\Phi_i\rangle c_i$$

where for a particular choice of $|\psi\rangle$ and $|\tilde{\psi}\rangle$ the coefficients $c_i$ are left to be determined
The projector functions

- The coefficients are functionals of the PS wave functions and are determined by the scalar product with a special projector function
  \[ c_i = \langle \tilde{p}_i | \tilde{\psi} \rangle \]
- Within the augmentation region \( \Omega_R \) they must fulfill
  \[
  |\tilde{\psi}\rangle = \sum_i |\tilde{\Phi}_i\rangle \langle \tilde{p}_i | \tilde{\psi} \rangle \]

  \[ \Rightarrow \langle \tilde{p}_i | \tilde{\Phi}_j \rangle = \delta_{ij} \]
The projector functions

- In summary we have for the transformation $\tau$
  \[
  \tau = 1 + \sum_i \left( |\Phi_i\rangle - |\tilde{\Phi}_i\rangle \right) \langle \tilde{p}_i |\tilde{p}_i\rangle
  \]

- Thus the real wave function is obtained from
  \[
  |\psi\rangle = |\tilde{\psi}\rangle + \sum_i \left( |\Phi_i\rangle - |\tilde{\Phi}_i\rangle \right) \langle \tilde{p}_i |\tilde{\psi}\rangle
  \]

We have three components for this transformation:

1. The real partial waves $|\Phi_i\rangle$ (e.g. solutions of the radial Schrödinger equation for an isolated atom)
2. The PS partial waves $|\tilde{\Phi}_i\rangle$ that coincides with $|\Phi_i\rangle$ outside $\Omega_R$
3. The projector functions $|\tilde{p}_i\rangle$
The projector functions

- The PS partial waves $|\Phi_i\rangle$ are plane waves but other choices are possible.
- Within $\Omega_R$ the partial waves form complete sets of functions.
- But for practical calculations the number of partial waves and projector functions has to be truncated.

Typically good convergence is achieved for a plane-wave cutoff of 30 Ry and one or two partial waves per site.
As seen before, we can introduce new, so-called PS operators

\[ \tilde{A} = \tau \dagger A \tau \]

\[ = A + \sum_{i,j} \langle \tilde{p}_i \rangle \left( \langle \Phi_i | A | \Phi_j \rangle - \langle \tilde{\Phi}_i | A | \tilde{\Phi}_j \rangle \right) \langle \tilde{p}_j \rangle \]

With the expectation value \( \langle \tilde{\psi} | \tilde{A} | \tilde{\psi} \rangle \)
An important feature of the expectation value is its invariance under the addition of a term

\[ B - \sum_{i,j} |\tilde{p}_i\rangle \langle \tilde{\Phi}_i | B |\tilde{\Phi}_j \rangle \langle \tilde{p}_j| \]

This freedom is used for operators that can't be easily evaluated in a plane-wave expansion.

Example: Coulomb-potential

- Problematic due to the singularity at the nucleus
- By adding such term it is possible to replace the singularity by a smooth continuation without influencing the expectation value
- The resulting expression is less sensitive to a truncation of the number of plane waves
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The partial waves for the expansion of the real wave function are obtained by radially integrating the Schrödinger equation

$$\left( -\frac{1}{2} \nabla^2 + v_{at} - \epsilon^1_i \right) |\phi_i\rangle = 0$$

with the self-consistent atomic potential $v_{at}$ and energies $\epsilon^1_i$.

The partial waves are chosen to describe the physical states reasonably well:

- The energy for the first partial wave is usually the energy of the lowest bound valence state.
- The energy for the second partial wave is chosen with respect to a reasonably behaviour of the scattering properties.
Real partial waves

- The number of partial waves is simply increased until the scattering properties of the valence band region are described satisfactorily.
- Often one partial wave per site and angular momentum is sufficient.
- Even for difficult cases such as transition metals two partial waves yield satisfactory description.
To obtain the PS partial waves we use a similar approach.

As we have seen we are allowed to change the PS potential (e.g. to a smooth one).

This is done by either approximating the real potential by a polynomial or introducing cutoff functions.

Then the PS partial waves are obtained as solutions of the Schrödinger equation with a reasonable smooth potential $\omega_i(r)$

$$\left(-\frac{1}{2}\nabla^2 + \omega_i(r) - \epsilon^i\right)\tilde{\phi}_i = 0$$
Bonding $p-\sigma$-orbital of the Cl$_2$ molecule
Decomposition of the wave function

\[ |\psi\rangle = |\tilde{\psi}\rangle + \sum_i \left( |\Phi_i\rangle - |\tilde{\Phi}_i\rangle \right) \langle \tilde{p}_i | \tilde{\psi} \rangle \]

\[ = |\tilde{\psi}\rangle + |\psi_{pw}\rangle - |\tilde{\psi}_{pw}\rangle \]
Decomposition of the wave function

\[ |\psi\rangle = |\tilde{\psi}\rangle + \sum_i \left( |\Phi_i\rangle - |\tilde{\Phi}_i\rangle \right) \langle \tilde{p}_i | \tilde{\psi} \rangle \]

\[ = |\tilde{\psi}\rangle + |\psi_{pw}\rangle - |\tilde{\psi}_{pw}\rangle \]
The projector functions are calculated as

$$|\tilde{p}_i\rangle = \left(-\frac{1}{2} \nabla^2 + \tilde{v}_{at} - \epsilon^1_i \right) |\tilde{\phi}_i\rangle$$

To fulfill the condition $\langle \tilde{p}_i | \tilde{\Phi}_j \rangle = \delta_{ij}$ they need to be orthogonalized (e.g. Gram-Schmidt process)

The projector functions and partial waves are finally rescaled to avoid very small or very large numbers

$$c |\tilde{p}_i\rangle, \frac{1}{c} |\tilde{\phi}_i\rangle$$
Projector functions of the Cl atom

s-type projector functions

p-type projector functions
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In principle the scattering properties of an atom can be arbitrarily improved by increasing the number of partial waves.

First row elements are well described with one partial wave per angular momentum.

Two partial waves are sufficient for the narrow d states.
Scattering properties of the Mn atom:

Triangles (s), circles (p) and squares (d) are exact results.
Dashed lines with one partial wave
Solid lines with two partial waves
• Deviations are mainly caused by partial-wave truncation
• PAW also works for difficult situations (high-oxidation states)
• The PAW method matches accuracy of the best LDA schemes
Comparison to other methods

Pseudopotentials
General APW
LAPW
Pseudopotential method

- The real potential is replaced by an effective potential
- The core and core electrons are considered as 'frozen'
- The valence electrons are subjected to the effective potential
- For the right approximations in the potential the PAW method can be reduced to the pseudopotential method
Augmented-plane-wave method

- The APW methods try to generate solutions for the LDA electronic problem
- Divide space into two parts: atom centered sphere and the intermediate region
- Partial-wave expansion of the true wave function in each region
- Then the partial waves are matched at the sphere radius with value and derivative (computationally demanding)
In the linear augmented-plane-wave method the real wave function $|\psi\rangle$ is expressed as

$$|\psi\rangle = (1 - \Theta_R) |\tilde{\psi}\rangle + \Theta_R \sum (a_\nu |\phi_\nu\rangle + b_\nu |\dot{\phi}_\nu\rangle)$$

The coefficients $a_\nu$, $b_\nu$ are determined by requiring that the wave function is smooth and continuous at the sphere radius.

The PAW method can be reduced to the LAPW method for a suitable choice of partial waves and projector functions.
• The PAW method uses the more general projector augmentation principle to match the partial waves
• The scalar product $c_i = \langle \tilde{p}_i | \tilde{\psi} \rangle$ is the most general scheme for determining the right coefficients
• Allows highly accurate calculations with acceptable computational effort
• Can be incorporated into existing pseudopotential codes with minor effort
• Presentations from