Projector augmented-wave method

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What is PAW?

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

Electronic structure calculations

- 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

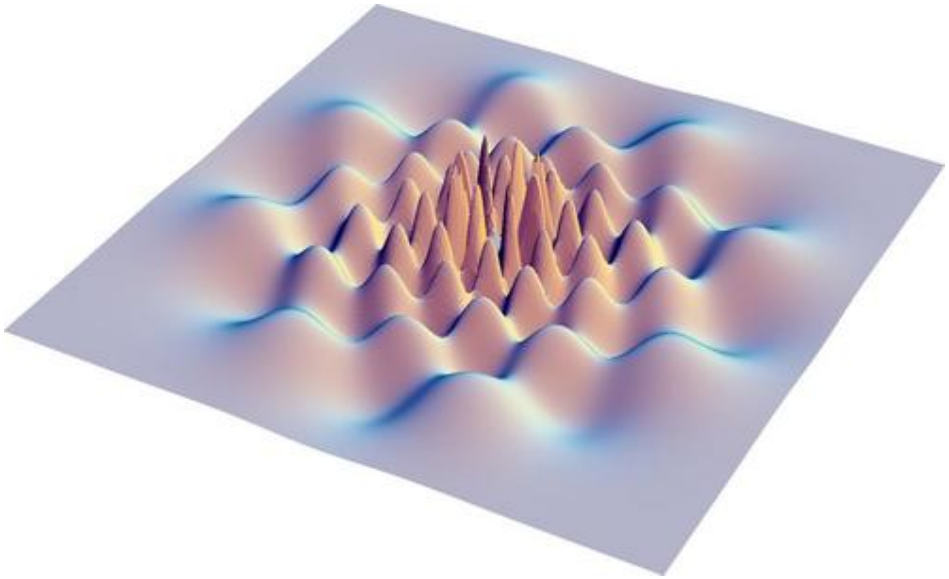
- Combines the versatility of the LAPW method and the formal simplicity of the pseudopotential approach
- Provides full access to the wave function
- Accuracy compares very well with other very accurate methods based on LDA

$\rightarrow$ LAPW is a special case of the PAW method

$\rightarrow$ 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

Motivation for augmented-wave methods

- 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 τ

The PAW method

- Thus the transformation τ gets us from the PS wave function to the true wave function

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

- If we know the transformation τ, 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 τ

- 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 τ_R only acts within a specific augmentation region Ω_R
- The augmentation is the equivalent to the muffin-tin sphere or the so called core-region in the pseudopotential method

The transformation τ

- So we have the transformation of the partial waves

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

within Ω_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 Ω_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 τ

$$\tau = 1 + \sum_i \left(|\Phi_i\rangle - |\tilde{\Phi}_i\rangle \right) \langle \tilde{p}_i |$$

- 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 conincides with $|\Phi_i\rangle$ outside Ω_R
3. The projector functions $|\tilde{p}_i\rangle$

The projector functions

- The PS partial waves $|\tilde{\Phi}_i\rangle$ are plane waves but other choices are possible
- Within Ω_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

PS Operators

- As seen before, we can introduce new, so-called PS operators

$$\begin{aligned}\tilde{A} =& \tau^\dagger A \tau \\ =& A + \sum_{i,j} |\tilde{p}_i\rangle \left(\langle \Phi_i | A | \Phi_j \rangle - \langle \tilde{\Phi}_i | A | \tilde{\Phi}_j \rangle \right) \langle \tilde{p}_j |\end{aligned}$$

- With the expectation value $\langle \tilde{\psi} | \tilde{A} | \tilde{\psi} \rangle$

PS Operators

- 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

Real partial waves

- The partial waves for the expansion of the real wave function are obtained by radially integrating the Schrödinger equation

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

  with the self-consistent atomic potential v_{at} and energies ϵ_i^1
- 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

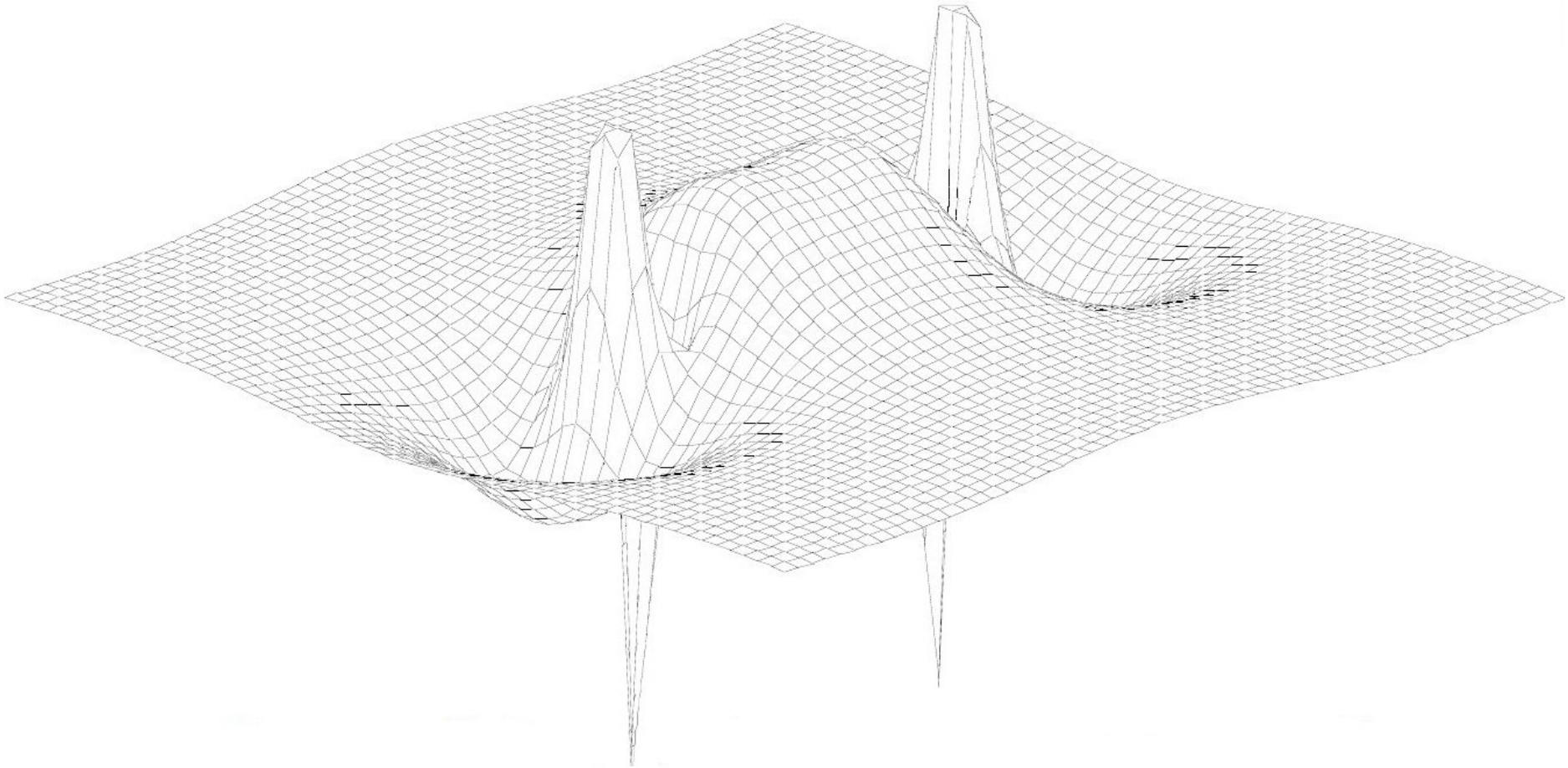
- The number of partial waves is simply increased until the scattering properties of the valence band region are described satisfactorily
- Often one partial wave per site and angular momentum is sufficient
- Even for difficult cases such as transition metals two partial waves yield satisfactory description

Pseudo partial waves

- 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 $\omega_i(r)$

$$\left(-\frac{1}{2}\nabla^2 + \omega_i(r) - \epsilon_i^1\right)|\tilde{\phi}_i\rangle = 0$$

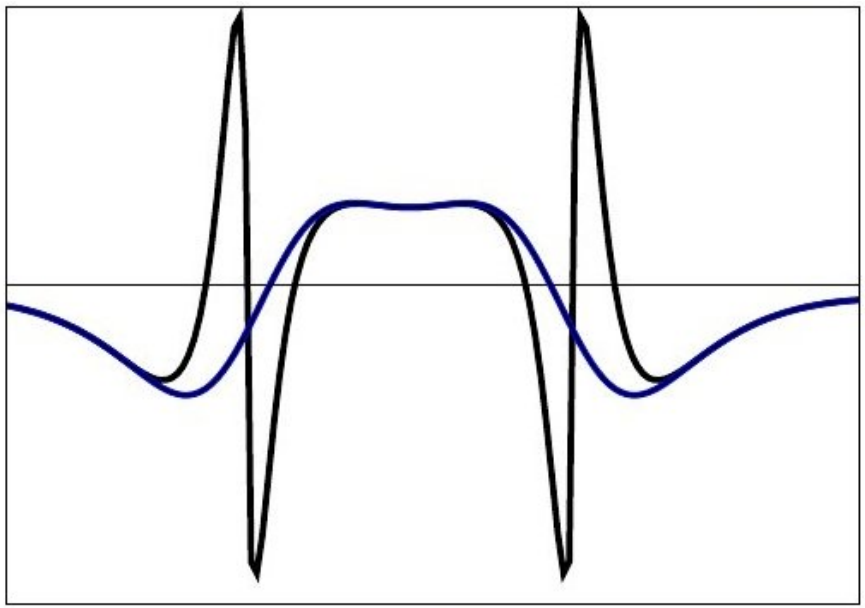
Bonding p-σ-orbital of the Cl_2 molecule

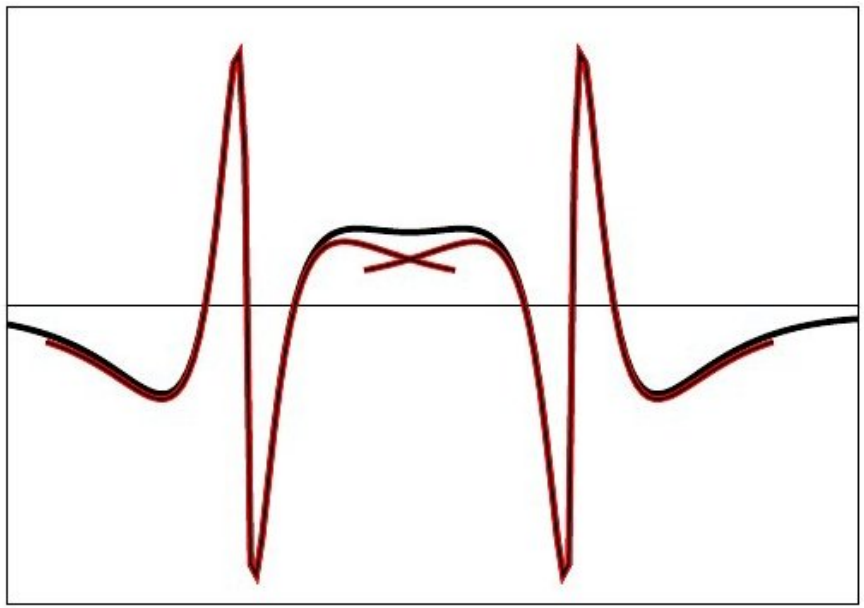


Decomposition of the wave function

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

$$= |\tilde{\psi}\rangle + |\psi_{pw}\rangle - |\tilde{\psi}_{pw}\rangle$$





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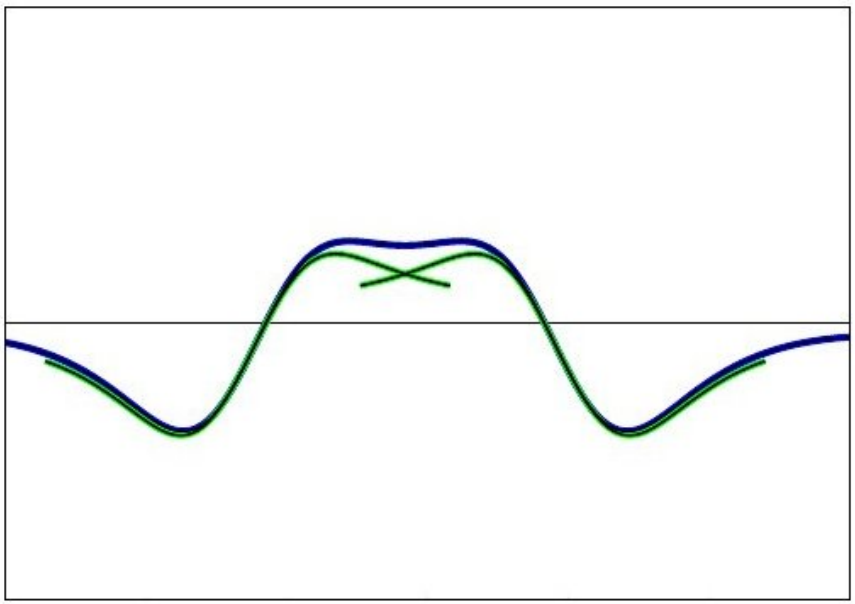
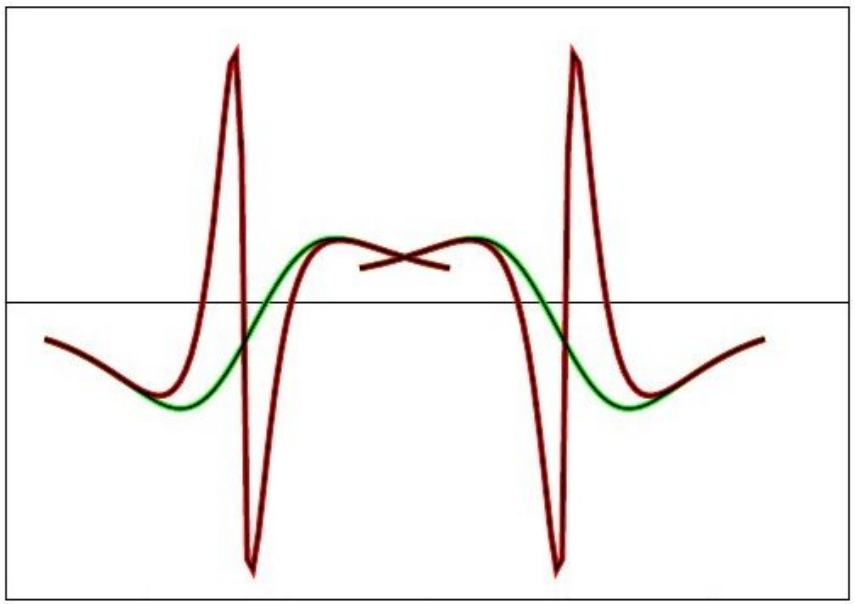




Projector functions

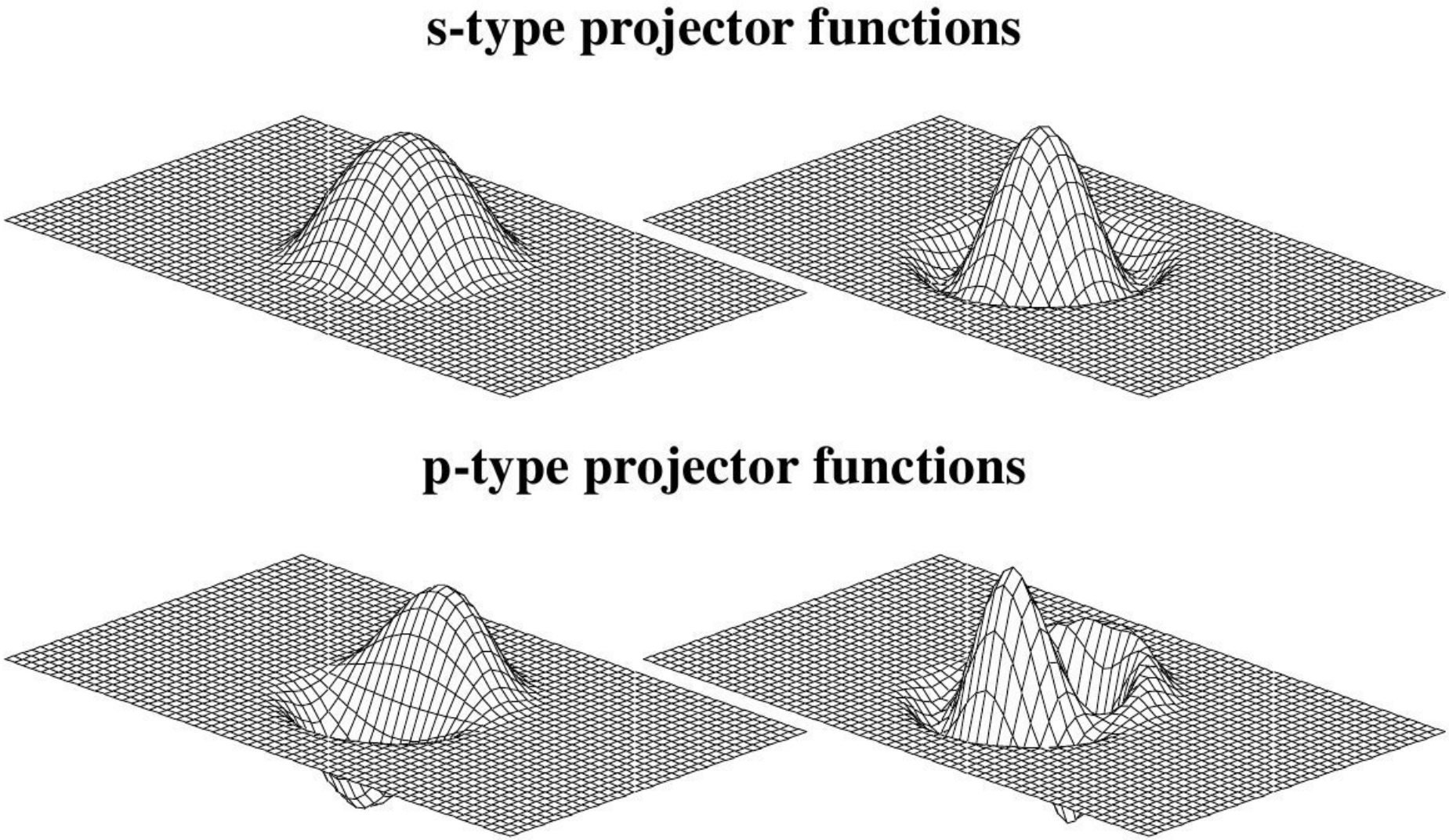
- The projector functions are calculated as

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

- 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

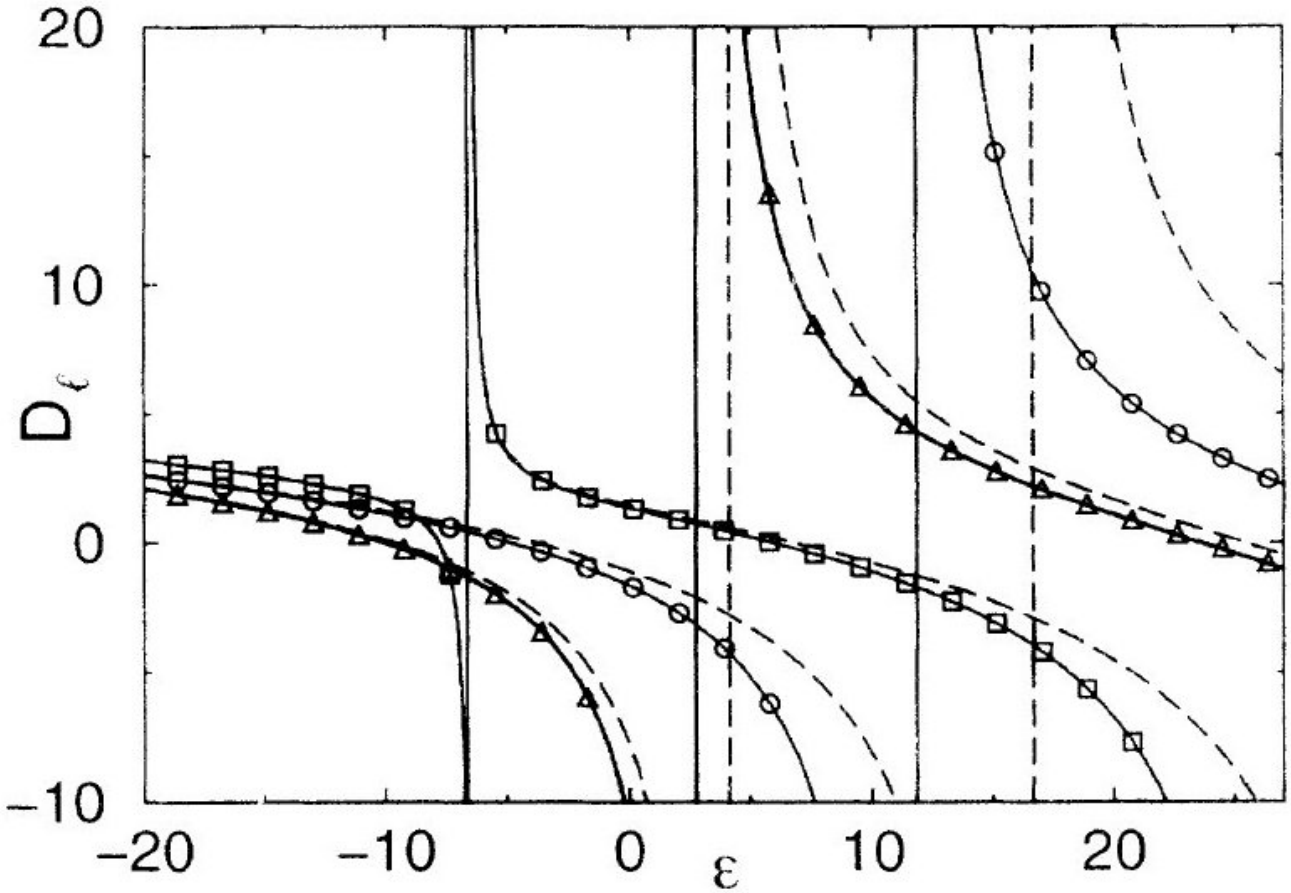


Scattering properties

- 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

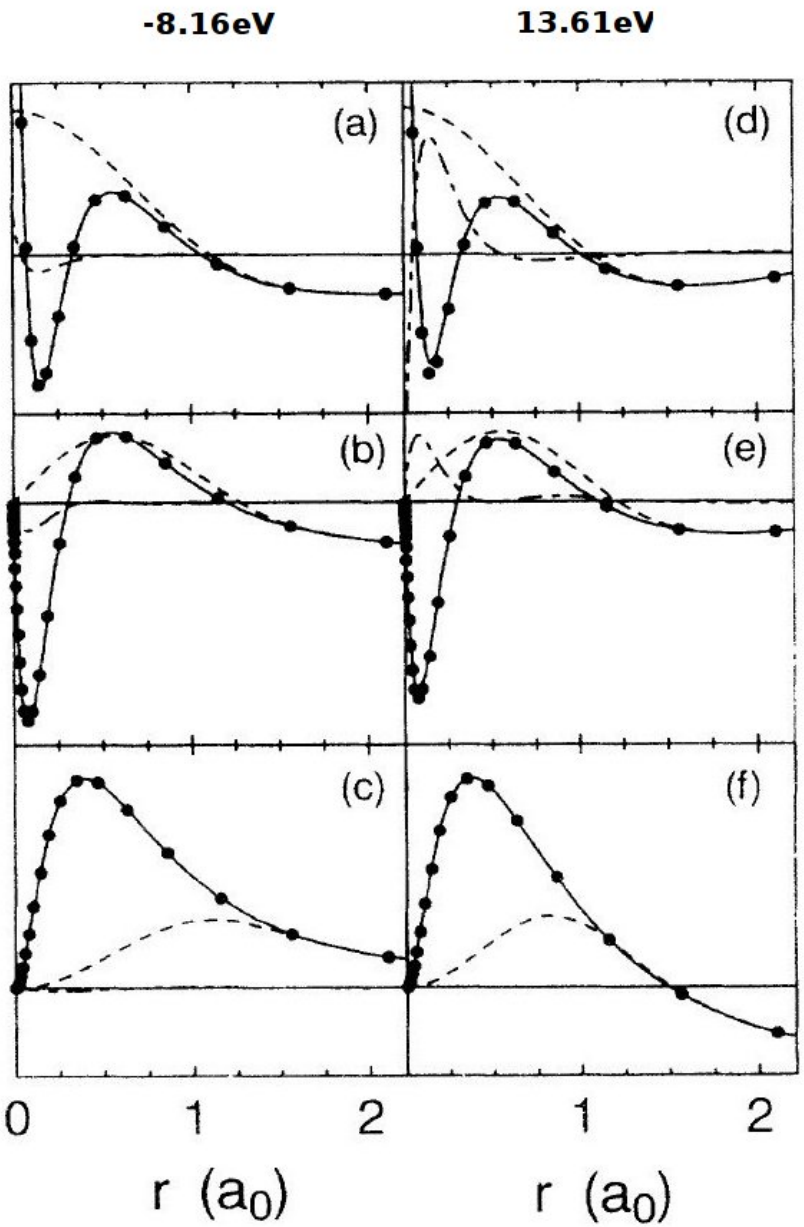
Scattering properties

Scattering properties of the Mn atom:



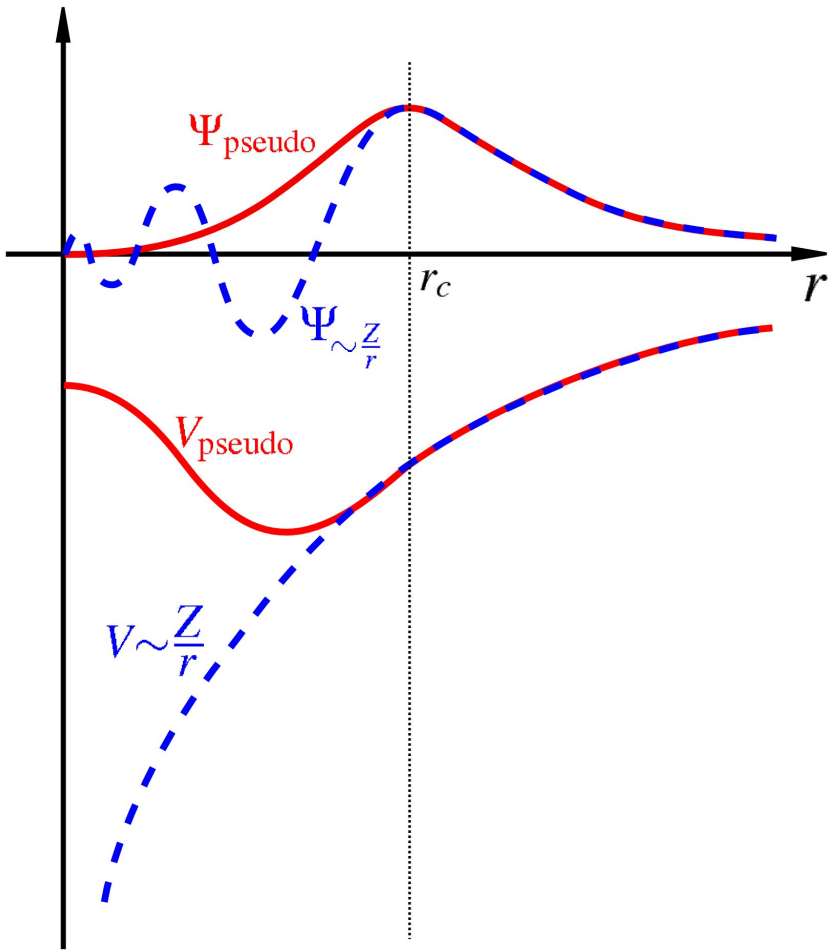
Triangles(s), circles(p) and squares(d) are exact results
Dashed lines with one partial wave
Solid lines with two partial waves

Real wave function



- 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

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

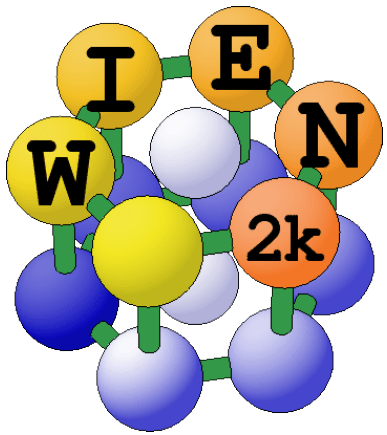
- The APW methods try to generate solutions for the LDA electronic problem
- Divide space into two parts: atom centered sphere and the indermediate region
- Partial-wave expansion of the true wave function in each region
- Then the partial waves are matched at the sphere radius with value and derivative (computationally demanding)

LAPW

- In the linear augmented-plane-wave method the real wave funktion $|\psi\rangle$ is expressed as

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

- The coefficients a_ν, b_ν 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



PAW

- 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

Literature

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- Presentations from http://orion.pt.tu-clausthal.de/atp/projects/paw.html