

# Electronic structure methods: Augmented Waves, Pseudopotentials and the Projector Augmented Wave Method

Peter E. Blöchl<sup>1</sup>, Johannes Kästner<sup>1</sup>, and Clemens J. Först<sup>1,2</sup>

<sup>1</sup> *Clausthal University of Technology, Institute for Theoretical Physics,  
Leibnizstr.10, D-38678 Clausthal-Zellerfeld, Germany and*

<sup>2</sup> *Vienna University of Technology, Institute for Materials Chemistry,  
Getreidemarkt 9/165-TC, A-1060 Vienna, Austria*

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The main goal of electronic structure methods is to solve the Schrödinger equation for the electrons in a molecule or solid, to evaluate the resulting total energies, forces, response functions and other quantities of interest. In this paper we describe the basic ideas behind the main electronic structure methods such as the pseudopotential and the augmented wave methods and provide selected pointers to contributions that are relevant for a beginner. We give particular emphasis to the Projector Augmented Wave (PAW) method developed by one of us, an electronic structure method for ab-initio molecular dynamics with full wavefunctions. We feel that it allows best to show the common conceptual basis of the most widespread electronic structure methods in materials science.

## I. INTRODUCTION

The methods described below require as input only the charge and mass of the nuclei, the number of electrons and an initial atomic geometry. They predict binding energies accurate within a few tenths of an electron volt and bond-lengths in the 1-2 percent range. Currently, systems with few hundred atoms per unit cell can be handled. The dynamics of atoms can be studied up to tens of pico-seconds. Quantities related to energetics, the atomic structure and to the ground-state electronic structure can be extracted.

In order to lay a common ground and to define some of the symbols, let us briefly touch upon the density functional theory<sup>22,30</sup>. It maps a description for interacting electrons, a nearly intractable problem, onto one of non-interacting electrons in an effective potential.

Within density functional theory, the total energy is written as

$$E[\Psi_n(\mathbf{r}), \mathbf{R}_R] = \sum_n f_n \langle \Psi_n | \frac{-\hbar^2}{2m_e} \nabla^2 | \Psi_n \rangle + \frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{(n(\mathbf{r}) + Z(\mathbf{r}))(n(\mathbf{r}') + Z(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n(\mathbf{r})] \quad (1)$$

Here,  $|\Psi_n\rangle$  are one-particle electron states,  $f_n$  are the state occupations,  $n(\mathbf{r}) = \sum_n f_n \Psi_n^*(\mathbf{r})\Psi_n(\mathbf{r})$  is the electron density and  $Z(\mathbf{r}) = -\sum_R \mathcal{Z}_R \delta(\mathbf{r} - \mathbf{R}_R)$  is the nuclear charge density expressed in electron charges.  $\mathcal{Z}_R$  is the atomic number of a nucleus at position  $\mathbf{R}_R$ . It is implicitly assumed that the infinite self-interaction of the nuclei is removed. The exchange and correlation functional contains all the difficulties of the many-electron problem. The main conclusion of the density functional theory is that  $E_{xc}$  is a functional of the density.

We use Dirac's bra and ket notation. A wavefunction  $\Psi_n$  corresponds to a ket  $|\Psi_n\rangle$ , the complex conjugate wave function  $\Psi_n^*$  corresponds to a bra  $\langle\Psi_n|$ , and a scalar product  $\int d^3r \Psi_n^*(\mathbf{r})\Psi_m(\mathbf{r})$  is written as  $\langle\Psi_n|\Psi_m\rangle$ . Vectors in the 3-d coordinate space are indicated by boldfaced symbols. Note that we use  $\mathbf{R}$  as position vector and  $R$  as atom index.

In current implementations, the exchange and correlation functional  $E_{xc}[n(\mathbf{r})]$  has the form

$$E_{xc}[n(\mathbf{r})] = \int d^3r F_{xc}(n(\mathbf{r}), |\nabla n(\mathbf{r})|)$$

where  $F_{xc}$  is a parameterized function of the density and its gradients. Such functionals are called gradient corrected. In local spin density functional theory,  $F_{xc}$  furthermore depends on the spin density and its derivatives. A review of the earlier developments has been given by Parr<sup>40</sup>.

The electronic ground state is determined by minimizing the total energy functional  $E[\Psi_n]$  of Eq. 1 at a fixed ionic geometry. The one-particle wavefunctions have to be orthogonal. This constraint is implemented with the method of Lagrange multipliers. We obtain the ground state wavefunctions from the extremum condition for

$$F[\Psi_n(\mathbf{r}), \Lambda_{m,n}] = E[\Psi_n] - \sum_{n,m} [\langle\Psi_n|\Psi_m\rangle - \delta_{n,m}] \Lambda_{m,n} \quad (2)$$

with respect to the wavefunctions and the Lagrange multipliers  $\Lambda_{m,n}$ . The extremum condition for the wavefunctions has the form

$$H|\Psi_n\rangle f_n = \sum_m |\Psi_m\rangle \Lambda_{m,n} \quad (3)$$

where  $H = -\frac{\hbar^2}{2m_e}\nabla^2 + v_{\text{eff}}(\mathbf{r})$  is the effective one-particle Hamilton operator. The effective potential depends itself on the electron density via

$$v_{\text{eff}}(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{n(\mathbf{r}') + Z(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{xc}(\mathbf{r})$$

where  $\mu_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$  is the functional derivative of the exchange and correlation functional.

After a unitary transformation that diagonalizes the matrix of Lagrange multipliers  $\Lambda_{m,n}$ , we obtain the Kohn-Sham equations.

$$H|\Psi_n\rangle = |\Psi_n\rangle\epsilon_n \quad (4)$$

The one-particle energies  $\epsilon_n$  are the eigenvalues of  $\Lambda_{n,m} \frac{f_n + f_m}{2f_n f_m}$ <sup>9</sup>.

The remaining one-electron Schrödinger equations, namely the Kohn-Sham equations given above, still pose substantial numerical difficulties: (1) in the atomic region near the nucleus, the kinetic energy of the electrons is large, resulting in rapid oscillations of the wavefunction that require fine grids for an accurate numerical representation. On the other hand, the large kinetic energy makes the Schrödinger equation stiff, so that a change of the chemical environment has little effect on the shape of the wavefunction. Therefore, the wavefunction in the atomic region can be represented well already by a small basis set. (2) In the bonding region between the atoms the situation is opposite. The kinetic energy is small and the wavefunction is smooth. However, the wavefunction is flexible and responds strongly to the environment. This requires large and nearly complete basis sets.

Combining these different requirements is non-trivial and various strategies have been developed.

- The atomic point of view has been most appealing to quantum chemists. Basis functions that resemble atomic orbitals are chosen. They exploit that the wavefunction in the atomic region can be described by a few basis functions, while the chemical bond is described by the overlapping tails of these atomic orbitals. Most techniques in this class are a compromise of, on the one hand, a well adapted basis set, where the basis functions are difficult to handle, and on the other hand numerically convenient basis functions such as Gaussians, where the inadequacies are compensated by larger basis sets.

- Pseudopotentials regard an atom as a perturbation of the free electron gas. The most natural basis functions are plane-waves. Plane waves basis sets are in principle complete and suitable for sufficiently smooth wavefunctions. The disadvantage of the comparably large basis sets required is offset by their extreme numerical simplicity. Finite plane-wave expansions are, however, absolutely inadequate to describe the strong oscillations of the wavefunctions near the nucleus. In the pseudopotential approach the Pauli repulsion of the core electrons is therefore described by an effective potential that expels the valence electrons from the core region. The resulting wavefunctions are smooth and can be represented well by plane-waves. The price to pay is that all information on the charge density and wavefunctions near the nucleus is lost.
- Augmented wave methods compose their basis functions from atom-like wavefunctions in the atomic regions and a set of functions, called envelope functions, appropriate for the bonding in between. Space is divided accordingly into atom-centered spheres, defining the atomic regions, and an interstitial region in between. The partial solutions of the different regions, are matched at the interface between atomic and interstitial regions.

The projector augmented wave method is an extension of augmented wave methods and the pseudopotential approach, which combines their traditions into a unified electronic structure method.

After describing the underlying ideas of the various approaches let us briefly review the history of augmented wave methods and the pseudopotential approach. We do not discuss the atomic-orbital based methods, because our focus is the PAW method and its ancestors.

## II. AUGMENTED WAVE METHODS

The augmented wave methods have been introduced in 1937 by Slater<sup>49</sup> and were later modified by Korringa<sup>31</sup>, Kohn and Rostokker<sup>29</sup>. They approached the electronic structure as a scattered-electron problem. Consider an electron beam, represented by a plane-wave, traveling through a solid. It undergoes multiple scattering at the atoms. If for some energy, the outgoing scattered waves interfere destructively, a bound state has been determined. This approach can be translated into a basis set method with energy and potential dependent

basis functions. In order to make the scattered wave problem tractable, a model potential had to be chosen: The so-called muffin-tin potential approximates the true potential by a constant in the interstitial region and by a spherically symmetric potential in the atomic region.

Augmented wave methods reached adulthood in the 1970s: O.K. Andersen<sup>1</sup> showed that the energy dependent basis set of Slater's APW method can be mapped onto one with energy independent basis functions, by linearizing the partial waves for the atomic regions in energy. In the original APW approach, one had to determine the zeros of the determinant of an energy dependent matrix, a nearly intractable numerical problem for complex systems. With the new energy independent basis functions, however, the problem is reduced to the much simpler generalized eigenvalue problem, which can be solved using efficient numerical techniques. Furthermore, the introduction of well defined basis sets paved the way for full-potential calculations<sup>32</sup>. In that case the muffin-tin approximation is used solely to define the basis set  $|\chi_i\rangle$ , while the matrix elements  $\langle\chi_i|H|\chi_j\rangle$  of the Hamiltonian are evaluated with the full potential.

In the augmented wave methods one constructs the basis set for the atomic region by solving the radial Schrödinger equation for the spheridized effective potential

$$\left[ \frac{-\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) - \epsilon \right] \phi_{\ell,m}(\epsilon, \mathbf{r}) = 0$$

as function of energy. Note that a partial wave  $\phi_{\ell,m}(\epsilon, \mathbf{r})$  is an angular momentum eigenstate and can be expressed as a product of a radial function and a spherical harmonic. The energy dependent partial wave is expanded in a Taylor expansion about some reference energy  $\epsilon_{\nu,\ell}$

$$\phi_{\ell,m}(\epsilon, \mathbf{r}) = \phi_{\nu,\ell,m}(\mathbf{r}) + (\epsilon - \epsilon_{\nu,\ell}) \dot{\phi}_{\nu,\ell,m}(\mathbf{r}) + O((\epsilon - \epsilon_{\nu,\ell})^2)$$

where  $\phi_{\nu,\ell,m}(\mathbf{r}) = \phi_{\ell,m}(\epsilon_{\nu,\ell}, \mathbf{r})$ . The energy derivative of the partial wave  $\dot{\phi}_{\nu}(\mathbf{r}) = \left. \frac{\partial \phi(\epsilon, \mathbf{r})}{\partial \epsilon} \right|_{\epsilon_{\nu,\ell}}$  solves the equation

$$\left[ \frac{-\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) - \epsilon_{\nu,\ell} \right] \dot{\phi}_{\nu,\ell,m}(\mathbf{r}) = \phi_{\nu,\ell,m}(\mathbf{r})$$

Next one starts from a regular basis set, such as plane-waves, Gaussians or Hankel functions. These basis functions are called envelope functions  $|\tilde{\chi}_i\rangle$ . Within the atomic region they are replaced by the partial waves and their energy derivatives, such that the resulting

wavefunction is continuous and differentiable.

$$\chi_i(\mathbf{r}) = \tilde{\chi}_i(\mathbf{r}) - \sum_R \theta_R(\mathbf{r}) \tilde{\chi}_i(\mathbf{r}) + \sum_{R,\ell,m} \theta_R(\mathbf{r}) \left[ \phi_{\nu,R,\ell,m}(\mathbf{r}) a_{R,\ell,m,i} + \dot{\phi}_{\nu,R,\ell,m}(\mathbf{r}) b_{R,\ell,m,i} \right] \quad (5)$$

$\theta_R(\mathbf{r})$  is a step function that is unity within the augmentation sphere centered at  $\mathbf{R}_R$  and zero elsewhere. The augmentation sphere is atom-centered and has a radius about equal to the covalent radius. This radius is called the muffin-tin radius, if the spheres of neighboring atoms touch. These basis functions describe only the valence states; the core states are localized within the augmentation sphere and are obtained directly by radial integration of the Schrödinger equation within the augmentation sphere.

The coefficients  $a_{R,\ell,m,i}$  and  $b_{R,\ell,m,i}$  are obtained for each  $|\tilde{\chi}_i\rangle$  as follows: The envelope function is decomposed around each atomic site into spherical harmonics multiplied by radial functions.

$$\tilde{\chi}_i(\mathbf{r}) = \sum_{\ell,m} u_{R,\ell,m,i}(|\mathbf{r} - \mathbf{R}_R|) Y_{\ell,m}(\mathbf{r} - \mathbf{R}_R) \quad (6)$$

Analytical expansions for plane-waves, Hankel functions or Gaussians exist. The radial parts of the partial waves  $\phi_{\nu,R,\ell,m}$  and  $\dot{\phi}_{\nu,R,\ell,m}$  are matched with value and derivative to  $u_{R,\ell,m,i}(|\mathbf{r}|)$ , which yields the expansion coefficients  $a_{R,\ell,m,i}$  and  $b_{R,\ell,m,i}$ .

If the envelope functions are plane-waves, the resulting method is called the linear augmented plane-wave (LAPW) method. If the envelope functions are Hankel functions, the method is called linear muffin-tin orbital (LMTO) method .

A good review of the LAPW method<sup>1</sup> has been given by Singh<sup>46</sup>. Let us now briefly mention the major developments of the LAPW method: Soler<sup>50</sup> introduced the idea of additive augmentation: While augmented plane-waves are discontinuous at the surface of the augmentation sphere if the expansion in spherical harmonics in Eq. 5 is truncated, Soler replaced the second term in Eq. 5 by an expansion of the plane-wave with the same angular momentum truncation as in the third term. This dramatically improved the convergence of the angular momentum expansion. Singh<sup>45</sup> introduced so-called local orbitals, which are non-zero only within a muffin-tin sphere, where they are superpositions of  $\phi$  and  $\dot{\phi}$  functions from different expansion energies. Local orbitals substantially increase the energy transferability. Sjöstedt<sup>47</sup> relaxed the condition that the basis functions are differentiable at the sphere radius. In addition she introduced local orbitals, which are confined inside the sphere, and that also have a kink at the sphere boundary. Due to the large energy-cost of kinks, they

will cancel, once the total energy is minimized. The increased variational degree of freedom in the basis leads to a dramatically improved plane-wave convergence<sup>37</sup>.

The second variant of the linear methods is the LMTO method<sup>1</sup>. A good introduction into the LMTO method is the book by Skriver<sup>48</sup>. The LMTO method uses Hankel functions as envelope functions. The atomic spheres approximation (ASA) provides a particularly simple and efficient approach to the electronic structure of very large systems. In the ASA the augmentation spheres are blown up so that their volume are equal to the total volume and the first two terms in Eq. 5 are ignored. The main deficiency of the LMTO-ASA method is the limitation to structures that can be converted into a closed packed arrangement of atomic and empty spheres. Furthermore energy differences due to structural distortions are often qualitatively incorrect. Full potential versions of the LMTO method, that avoid these deficiencies of the ASA have been developed. The construction of tight binding orbitals as superposition of muffin-tin orbitals<sup>2</sup> showed the underlying principles of the empirical tight-binding method and prepared the ground for electronic structure methods that scale linearly instead of with the third power of the number of atoms. The third generation LMTO<sup>3</sup> allows to construct true minimal basis sets, which require only one orbital per electron-pair for insulators. In addition they can be made arbitrarily accurate in the valence band region, so that a matrix diagonalization becomes unnecessary. The first steps towards a full-potential implementation, that promises a good accuracy, while maintaining the simplicity of the of the LMTO-ASA method are currently under way. Through the minimal basis-set construction the LMTO method offers unrivaled tools for the analysis of the electronic structure and has been extensively used in hybrid methods combining density functional theory with model Hamiltonians for materials with strong electron correlations<sup>19</sup>

### III. PSEUDOPOTENTIALS

Pseudopotentials have been introduced to (1) avoid describing the core electrons explicitly and (2) to avoid the rapid oscillations of the wavefunction near the nucleus, which normally require either complicated or large basis sets.

The pseudopotential approach traces back to 1940 when C. Herring invented the orthogonalized plane-wave method<sup>20</sup>. Later, Phillips<sup>43</sup> and Antoncik<sup>4</sup> replaced the orthogonality condition by an effective potential, which mimics the Pauli-repulsion by the core electrons

and thus compensates the electrostatic attraction by the nucleus. In practice, the potential was modified, for example, by cutting off the singular potential of the nucleus at a certain value. This was done with a few parameters that have been adjusted to reproduce the measured electronic band structure of the corresponding solid.

Hamann, Schlüter and Chiang<sup>18</sup> showed in 1979 how pseudopotentials can be constructed in such a way, that their scattering properties are identical to that of an atom to first order in energy. These first-principles pseudopotentials relieved the calculations from the restrictions of empirical parameters. Highly accurate calculations have become possible especially for semiconductors and simple metals. An alternative approach towards first-principles pseudopotentials<sup>58</sup> preceded the one mentioned above.

### A. The idea behind Pseudopotential construction

In order to construct a first-principles pseudopotential, one starts out with an all-electron density-functional calculation for a spherical atom. Such calculations can be performed efficiently on radial grids. They yield the atomic potential and wavefunctions  $\phi_{\ell,m}(\mathbf{r})$ . Due to the spherical symmetry, the radial parts of the wavefunctions for different magnetic quantum numbers  $m$  are identical.

For the valence wavefunctions one constructs pseudo wavefunctions  $|\tilde{\phi}_{\ell,m}\rangle$ : There are numerous ways<sup>6,27,35,52</sup> to construct the pseudo wavefunctions. They must be identical to the true wave functions outside the augmentation region, which is called core-region in the context of the pseudopotential approach. Inside the augmentation region the pseudo wavefunction should be node-less and have the same norm as the true wavefunctions, that is  $\langle \tilde{\phi}_{\ell,m} | \tilde{\phi}_{\ell,m} \rangle = \langle \phi_{\ell,m} | \phi_{\ell,m} \rangle$  (compare Figure 1).

From the pseudo wavefunction, a potential  $u_{\ell}(\mathbf{r})$  can be reconstructed by inverting the respective Schrödinger equation.

$$\left[ -\frac{\hbar^2}{2m_e} \nabla^2 + u_{\ell}(\mathbf{r}) - \epsilon_{\ell,m} \right] \tilde{\phi}_{\ell,m}(\mathbf{r}) = 0 \Rightarrow u_{\ell}(\mathbf{r}) = \epsilon + \frac{1}{\tilde{\phi}_{\ell,m}(\mathbf{r})} \cdot \frac{\hbar^2}{2m_e} \nabla^2 \tilde{\phi}_{\ell,m}(\mathbf{r})$$

This potential  $u_{\ell}(\mathbf{r})$  (compare Figure 1), which is also spherically symmetric, differs from one main angular momentum  $\ell$  to the other.

Next we define an effective pseudo Hamiltonian

$$\tilde{H}_{\ell} = -\frac{\hbar^2}{2m_e} \nabla^2 + v_{\ell}^{ps}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{\tilde{n}(\mathbf{r}') + \tilde{Z}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{xc}([n(\mathbf{r})], \mathbf{r})$$



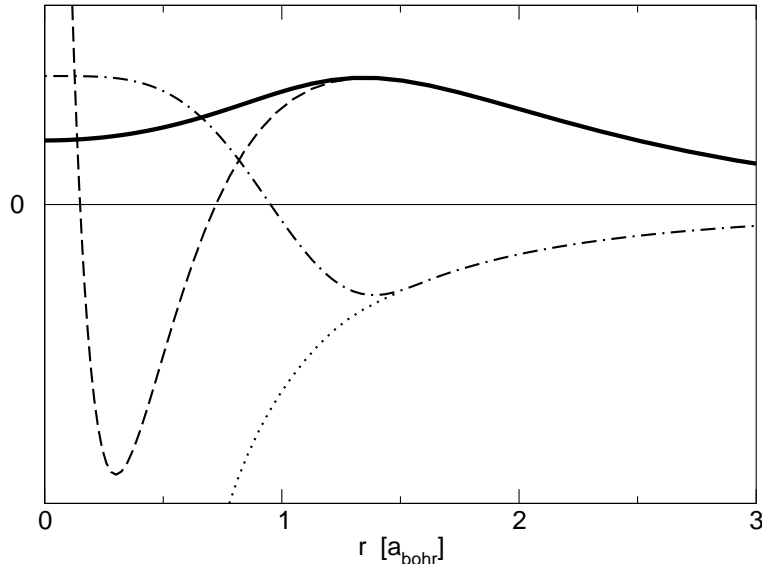


FIG. 1: Illustration of the pseudopotential concept at the example of the 3s wavefunction of Si. The solid line shows the radial part of the pseudo wavefunction  $\tilde{\phi}_{\ell,m}$ . The dashed line corresponds to the all-electron wavefunction  $\phi_{\ell,m}$  which exhibits strong oscillations at small radii. The angular momentum dependent pseudopotential  $u_{\ell}$  (dash-dotted line) deviates from the all-electron one  $v_{eff}$  (dotted line) inside the augmentation region. The data are generated by the fhi98PP code<sup>15</sup>.

and determine the pseudopotentials  $v_{\ell}^{ps}$  such that the pseudo Hamiltonian produces the pseudo wavefunctions, that is

$$v_{\ell}^{ps}(\mathbf{r}) = u_{\ell}(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0} \int d^3r' \frac{\tilde{n}(\mathbf{r}') + \tilde{Z}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \mu_{xc}([\tilde{n}(\mathbf{r})], \mathbf{r}) \quad (7)$$

This process is called “unscreening”.

$\tilde{Z}(\mathbf{r})$  mimics the charge density of the nucleus and the core electrons. It is usually an atom-centered, spherical Gaussian that is normalized to the charge of nucleus and core of that atom. In the pseudopotential approach,  $\tilde{Z}_R(\mathbf{r})$  it does not change with the potential. The pseudo density  $\tilde{n}(\mathbf{r}) = \sum_n f_n \tilde{\Psi}_n^*(\mathbf{r}) \tilde{\Psi}_n(\mathbf{r})$  is constructed from the pseudo wavefunctions.

In this way we obtain a different potential for each angular momentum channel. In order to apply these potentials to a given wavefunction, the wavefunction must first be decomposed into angular momenta. Then each component is applied to the pseudopotential  $v_{\ell}^{ps}$  for the corresponding angular momentum.

The pseudopotential defined in this way can be expressed in a semi-local form

$$v^{ps}(\mathbf{r}, \mathbf{r}') = \bar{v}(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}') + \sum_{\ell, m} \left[ Y_{\ell, m}(\mathbf{r}) [v_{\ell}^{ps}(\mathbf{r}) - \bar{v}(\mathbf{r})] \frac{\delta(|\mathbf{r}| - |\mathbf{r}'|)}{|\mathbf{r}|^2} Y_{\ell, m}^*(\mathbf{r}') \right] \quad (8)$$

The local potential  $\bar{v}(\mathbf{r})$  only acts on those angular momentum components, not included in the expansion of the pseudopotential construction. Typically it is chosen to cancel the most expensive nonlocal terms, the one corresponding to the highest physically relevant angular momentum.

The pseudopotential is non-local as it depends on two position arguments,  $\mathbf{r}$  and  $\mathbf{r}'$ . The expectation values are evaluated as a double integral

$$\langle \tilde{\Psi} | v_{ps} | \tilde{\Psi} \rangle = \int d^3r \int d^3r' \tilde{\Psi}^*(\mathbf{r}) v^{ps}(\mathbf{r}, \mathbf{r}') \tilde{\Psi}(\mathbf{r}')$$

The semi-local form of the pseudopotential given in Eq. 8 is computationally expensive. Therefore, in practice one uses a separable form of the pseudopotential<sup>8,28,55</sup>.

$$v^{ps} \approx \sum_{i, j} v^{ps} | \tilde{\phi}_i \rangle \left[ \langle \tilde{\phi}_j | v^{ps} | \tilde{\phi}_i \rangle \right]_{i, j}^{-1} \langle \tilde{\phi}_j | v^{ps} \quad (9)$$

Thus the projection onto spherical harmonics used in the semi-local form of Eq. 8 is replaced by a projection onto angular momentum dependent functions  $|v^{ps} \tilde{\phi}_i\rangle$ .

The indices  $i$  and  $j$  are composite indices containing the atomic-site index  $R$ , the angular momentum quantum numbers  $\ell, m$  and an additional index  $\alpha$ . The index  $\alpha$  distinguishes partial waves with otherwise identical indices  $R, \ell, m$ , as more than one partial wave per site and angular momentum is allowed. The partial waves may be constructed as eigenstates to the pseudopotential  $v_{\ell}^{ps}$  for a set of energies.

One can show that the identity of Eq. 9 holds by applying a wavefunction  $|\tilde{\Psi}\rangle = \sum_i |\tilde{\phi}_i\rangle c_i$  to both sides. If the set of pseudo partial waves  $|\tilde{\phi}_i\rangle$  in Eq. 9 is complete, the identity is exact. The advantage of the separable form is that  $\langle \tilde{\phi} | v^{ps} |$  is treated as one function, so that expectation values are reduced to combinations of simple scalar products  $\langle \tilde{\phi}_i | v^{ps} | \tilde{\Psi} \rangle$ .

## B. The Pseudopotential total energy

The total energy of the pseudopotential method can be written in the form

$$E = \sum_n f_n \langle \tilde{\Psi}_n | -\frac{\hbar^2}{2m_e} \nabla^2 | \tilde{\Psi}_n \rangle + E_{self} + \sum_n f_n \langle \tilde{\Psi}_n | v_{ps} | \tilde{\Psi}_n \rangle$$

$$+\frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{[\tilde{n}(\mathbf{r}) + \tilde{Z}(\mathbf{r})][\tilde{n}(\mathbf{r}') + \tilde{Z}(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\tilde{n}(\mathbf{r})] \quad (10)$$

The constant  $E_{self}$  is adjusted such that the total energy of the atom is the same for an all-electron calculation and the pseudopotential calculation.

For the atom, from which it has been constructed, this construction guarantees that the pseudopotential method produces the correct one-particle energies for the valence states and that the wave functions have the desired shape.

While pseudopotentials have proven to be accurate for a large variety of systems, there is no strict guarantee that they produce the same results as an all-electron calculation, if they are used in a molecule or solid. The error sources can be divided into two classes:

- Energy transferability problems: Even for the potential of the reference atom, the scattering properties are accurate only in given energy window.
- Charge transferability problems: In a molecule or crystal, the potential differs from that of the isolated atom. The pseudopotential, however, is strictly valid only for the isolated atom.

The plane-wave basis set for the pseudo wavefunctions is defined by the shortest wave length  $\lambda = 2\pi/|G|$  via the so-called plane wave cutoff  $E_{PW} = \frac{\hbar^2 G_{max}^2}{2m_e}$ . It is often specified in Rydberg (1 Ry= $\frac{1}{2}$  H $\approx$ 13.6 eV). The plane-wave cutoff is the highest kinetic energy of all basis functions. The basis-set convergence can systematically be controlled by increasing the plane-wave cutoff.

The charge transferability is substantially improved by including a nonlinear core correction<sup>36</sup> into the exchange-correlation term of Eq. 10. Hamann<sup>17</sup> showed, how to construct pseudopotentials also from unbound wavefunctions. Vanderbilt<sup>34,55</sup> generalized the pseudopotential method to non-normconserving pseudopotentials, so-called ultra-soft pseudopotentials, which dramatically improves the basis-set convergence. The formulation of ultra-soft pseudopotentials has already many similarities with the projector augmented wave method. Truncated separable pseudopotentials suffer sometimes from so-called ghost states. These are unphysical core-like states, which render the pseudopotential useless. These problems have been discussed by Gonze<sup>16</sup>. Quantities such as hyperfine parameters that depend on the full wavefunctions near the nucleus, can be extracted approximately<sup>54</sup>. A good review about pseudopotential methodology has been written by Payne<sup>41</sup> and Singh<sup>46</sup>.

In 1985 R. Car and M. Parrinello published the ab-initio molecular dynamics method<sup>14</sup>. Simulations of the atomic motion have become possible on the basis of state-of-the-art electronic structure methods. Besides making dynamical phenomena and finite temperature effects accessible to electronic structure calculations, the ab-initio molecular dynamics method also introduced a radically new way of thinking into electronic structure methods. Diagonalization of a Hamilton matrix has been replaced by classical equations of motion for the wavefunction coefficients. If one applies friction, the system is quenched to the ground state. Without friction truly dynamical simulations of the atomic structure are performed. Using thermostats<sup>12,13,24,39</sup> simulations at constant temperature can be performed. The Car-Parrinello method treats electronic wavefunctions and atomic positions on an equal footing.

#### IV. PROJECTOR AUGMENTED WAVE METHOD

The Car-Parrinello method had been implemented first for the pseudopotential approach. There seemed to be unsurmountable barriers against combining the new technique with augmented wave methods. The main problem was related to the potential dependent basis set used in augmented wave methods: the Car-Parrinello method requires a well defined and unique total energy functional of atomic positions and basis set coefficients. Furthermore the analytic evaluation of the first partial derivatives of the total energy with respect to wave functions,  $H|\Psi_n\rangle$ , and atomic position, the forces, must be possible. Therefore, it was one of the main goals of the PAW method to introduce energy and potential independent basis sets that were as accurate as the previously used augmented basis sets. Other requirements have been: (1) The method should at least match the efficiency of the pseudopotential approach for Car-Parrinello simulations. (2) It should become an exact theory when converged and (3) its convergence should be easily controlled. We believe that these criteria have been met, which explains why the PAW method becomes increasingly wide spread today.

##### A. Transformation theory

At the root of the PAW method lies a transformation, that maps the true wavefunctions with their complete nodal structure onto auxiliary wavefunctions, that are numerically convenient. We aim for smooth auxiliary wavefunctions, which have a rapidly convergent plane-

wave expansion. With such a transformation we can expand the auxiliary wave functions into a convenient basis set such as plane-waves, and evaluate all physical properties after reconstructing the related physical (true) wavefunctions.

Let us denote the physical one-particle wavefunctions as  $|\Psi_n\rangle$  and the auxiliary wavefunctions as  $|\tilde{\Psi}_n\rangle$ . Note that the tilde refers to the representation of smooth auxiliary wavefunctions and  $n$  is the label for a one-particle state and contains a band index, a  $k$ -point and a spin index. The transformation from the auxiliary to the physical wave functions is denoted by  $\mathcal{T}$ .

$$|\Psi_n\rangle = \mathcal{T}|\tilde{\Psi}_n\rangle \quad (11)$$

Now we express the constrained density functional  $F$  of Eq. 2 in terms of our auxiliary wavefunctions

$$F[\mathcal{T}\tilde{\Psi}_n, \Lambda_{m,n}] = E[\mathcal{T}\tilde{\Psi}_n] - \sum_{n,m} [\langle \tilde{\Psi}_n | \mathcal{T}^\dagger \mathcal{T} | \tilde{\Psi}_m \rangle - \delta_{n,m}] \Lambda_{m,n} \quad (12)$$

The variational principle with respect to the auxiliary wavefunctions yields

$$\mathcal{T}^\dagger H \mathcal{T} |\tilde{\Psi}_n\rangle = \mathcal{T}^\dagger \mathcal{T} |\tilde{\Psi}_n\rangle \epsilon_n. \quad (13)$$

Again we obtain a Schrödinger-like equation (see derivation of Eq. 4), but now the Hamilton operator has a different form,  $\tilde{H} = \mathcal{T}^\dagger H \mathcal{T}$ , an overlap operator  $\tilde{O} = \mathcal{T}^\dagger \mathcal{T}$  occurs, and the resulting auxiliary wavefunctions are smooth.

When we evaluate physical quantities we need to evaluate expectation values of an operator  $A$ , which can be expressed in terms of either the true or the auxiliary wavefunctions.

$$\langle A \rangle = \sum_n f_n \langle \Psi_n | A | \Psi_n \rangle = \sum_n f_n \langle \tilde{\Psi}_n | \mathcal{T}^\dagger A \mathcal{T} | \tilde{\Psi}_n \rangle \quad (14)$$

In the representation of auxiliary wavefunctions we need to use transformed operators  $\tilde{A} = \mathcal{T}^\dagger A \mathcal{T}$ . As it is, this equation only holds for the valence electrons. The core electrons are treated differently as will be shown below.

The transformation takes us conceptionally from the world of pseudopotentials to that of augmented wave methods, which deal with the full wavefunctions. We will see that our auxiliary wavefunctions, which are simply the plane-wave parts of the full wavefunctions, translate into the wavefunctions of the pseudopotential approach. In the PAW method the

auxiliary wavefunctions are used to construct the true wavefunctions and the total energy functional is evaluated from the latter. Thus it provides the missing link between augmented wave methods and the pseudopotential method, which can be derived as a well-defined approximation of the PAW method.

In the original paper<sup>9</sup>, the auxiliary wavefunctions have been termed pseudo wavefunctions and the true wavefunctions have been termed all-electron wavefunctions, in order to make the connection more evident. We avoid this notation here, because it resulted in confusion in cases, where the correspondence is not clear-cut.

## B. Transformation operator

Sofar, we have described how we can determine the auxiliary wave functions of the ground state and how to obtain physical information from them. What is missing, is a definition of the transformation operator  $\mathcal{T}$ .

The operator  $\mathcal{T}$  has to modify the smooth auxiliary wave function in each atomic region, so that the resulting wavefunction has the correct nodal structure. Therefore, it makes sense to write the transformation as identity plus a sum of atomic contributions  $\mathcal{S}_R$

$$\mathcal{T} = 1 + \sum_R \mathcal{S}_R. \quad (15)$$

For every atom,  $\mathcal{S}_R$  adds the difference between the true and the auxiliary wavefunction.

The local terms  $\mathcal{S}_R$  are defined in terms of solutions  $|\phi_i\rangle$  of the Schrödinger equation for the isolated atoms. This set of partial waves  $|\phi_i\rangle$  will serve as a basis set so that, near the nucleus, all relevant valence wavefunctions can be expressed as superposition of the partial waves with yet unknown coefficients.

$$\Psi(\mathbf{r}) = \sum_{i \in R} \phi_i(\mathbf{r}) c_i \quad \text{for } |\mathbf{r} - \mathbf{R}_R| < r_{c,R} \quad (16)$$

With  $i \in R$  we indicate those partial waves that belong to site  $R$ .

Since the core wavefunctions do not spread out into the neighboring atoms, we will treat them differently. Currently we use the frozen-core approximation, which imports the density and the energy of the core electrons from the corresponding isolated atoms. The transformation  $\mathcal{T}$  shall produce only wavefunctions orthogonal to the core electrons, while the core electrons are treated separately. Therefore, the set of atomic partial waves  $|\phi_i\rangle$  includes only valence states that are orthogonal to the core wavefunctions of the atom.

For each of the partial waves we choose an auxiliary partial wave  $|\tilde{\phi}_i\rangle$ . The identity

$$\begin{aligned} |\phi_i\rangle &= (1 + \mathcal{S}_R)|\tilde{\phi}_i\rangle \quad \text{for } i \in R \\ \mathcal{S}_R|\tilde{\phi}_i\rangle &= |\phi_i\rangle - |\tilde{\phi}_i\rangle \end{aligned} \quad (17)$$

defines the local contribution  $\mathcal{S}_R$  to the transformation operator. Since  $1 + \mathcal{S}_R$  shall change the wavefunction only locally, we require that the partial waves  $|\phi_i\rangle$  and their auxiliary counter parts  $|\tilde{\phi}_i\rangle$  are pairwise identical beyond a certain radius  $r_{c,R}$ .

$$\phi_i(\mathbf{r}) = \tilde{\phi}_i(\mathbf{r}) \quad \text{for } i \in R \quad \text{and} \quad |\mathbf{r} - \mathbf{R}_R| > r_{c,R} \quad (18)$$

Note that the partial waves are not necessarily bound states and are therefore not normalizable, unless we truncate them beyond a certain radius  $r_{c,R}$ . The PAW method is formulated such that the final results do not depend on the location where the partial waves are truncated, as long as this is not done too close to the nucleus and identical for auxiliary and all-electron partial waves.

In order to be able to apply the transformation operator to an arbitrary auxiliary wavefunction, we need to be able to expand the auxiliary wavefunction locally into the auxiliary partial waves.

$$\tilde{\Psi}(\mathbf{r}) = \sum_{i \in R} \tilde{\phi}_i(\mathbf{r}) c_i = \sum_{i \in R} \tilde{\phi}_i(\mathbf{r}) \langle \tilde{p}_i | \tilde{\Psi} \rangle \quad \text{for } |\mathbf{r} - \mathbf{R}_R| < r_{c,R} \quad (19)$$

which defines the projector functions  $|\tilde{p}_i\rangle$ . The projector functions probe the local character of the auxiliary wave function in the atomic region. Examples of projector functions are shown in Figure 2. From Eq. 19 we can derive  $\sum_{i \in R} |\tilde{\phi}_i\rangle \langle \tilde{p}_i| = 1$ , which is valid within  $r_{c,R}$ . It can be shown by insertion, that the identity Eq. 19 holds for any auxiliary wavefunction  $|\tilde{\Psi}\rangle$  that can be expanded locally into auxiliary partial waves  $|\tilde{\phi}_i\rangle$ , if

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{i,j} \quad \text{for } i, j \in R \quad (20)$$

Note that neither the projector functions nor the partial waves need to be orthogonal among themselves. The projector functions are fully determined with the above conditions and a closure relation, which is related to the unscreening of the pseudopotentials (see Eq. 90 in<sup>9</sup>).

By combining Eq. 17 and Eq. 19, we can apply  $\mathcal{S}_R$  to any auxiliary wavefunction.

$$\mathcal{S}_R|\tilde{\Psi}\rangle = \sum_{i \in R} \mathcal{S}_R|\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi} \rangle = \sum_{i \in R} (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi} \rangle \quad (21)$$

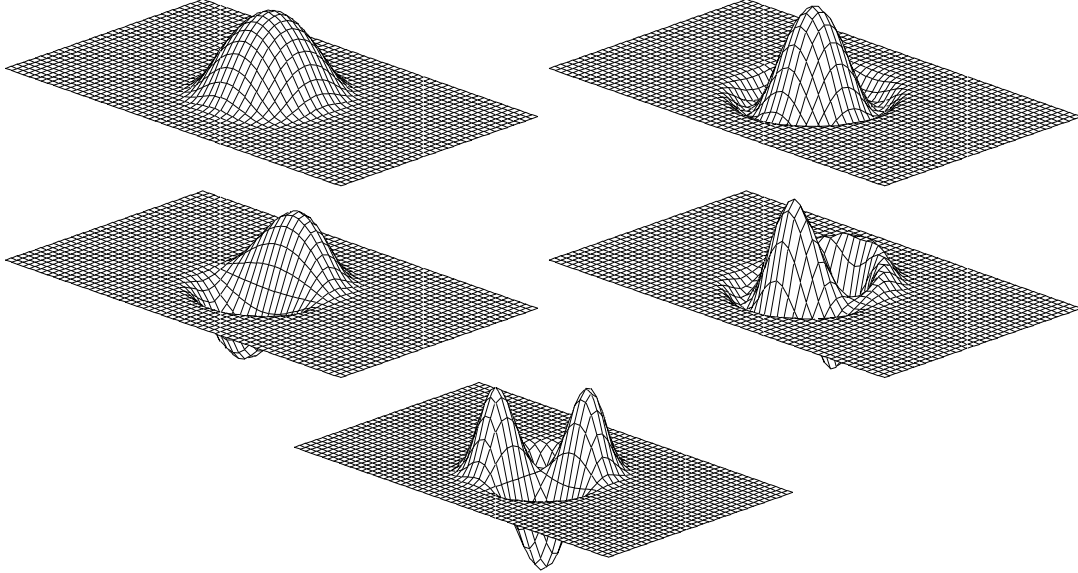


FIG. 2: Projector functions of the chlorine atom. Top: two s-type projector functions, middle: p-type, bottom: d-type.

Hence the transformation operator is

$$\mathcal{T} = 1 + \sum_i \left( |\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i | \quad (22)$$

where the sum runs over all partial waves of all atoms. The true wave function can be expressed as

$$|\Psi\rangle = |\tilde{\Psi}\rangle + \sum_i \left( |\phi_i\rangle - |\tilde{\phi}_i\rangle \right) \langle \tilde{p}_i | \tilde{\Psi}\rangle = |\tilde{\Psi}\rangle + \sum_R \left( |\Psi_R^1\rangle - |\tilde{\Psi}_R^1\rangle \right) \quad (23)$$

with

$$|\Psi_R^1\rangle = \sum_{i \in R} |\phi_i\rangle \langle \tilde{p}_i | \tilde{\Psi}\rangle \quad (24)$$

$$|\tilde{\Psi}_R^1\rangle = \sum_{i \in R} |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \tilde{\Psi}\rangle \quad (25)$$

In Fig. 3 the decomposition of Eq. 23 is shown for the example of the bonding p- $\sigma$  state of the Cl<sub>2</sub> molecule.

To understand the expression Eq. 23 for the true wave function, let us concentrate on different regions in space. (1) Far from the atoms, the partial waves are, according to Eq. 18, pairwise identical so that the auxiliary wavefunction is identical to the true wavefunction, that is  $\Psi(\mathbf{r}) = \tilde{\Psi}(\mathbf{r})$ . (2) Close to an atom  $R$ , however, the auxiliary wavefunction is, according to Eq. 19, identical to its one-center expansion, that is  $\tilde{\Psi}(\mathbf{r}) = \tilde{\Psi}_R^1(\mathbf{r})$ . Hence



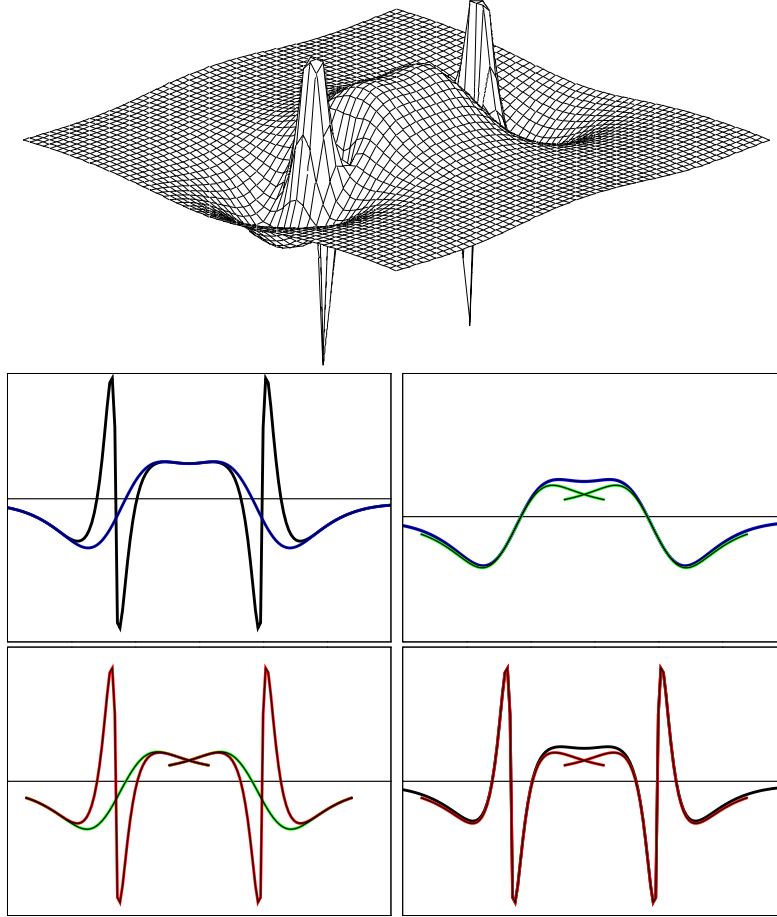


FIG. 3: Bonding  $p\text{-}\sigma$  orbital of the  $\text{Cl}_2$  molecule and its decomposition of the wavefunction into auxiliary wavefunction and the two one-center expansions. Top-left: True and auxiliary wave function; top-right: auxiliary wavefunction and its partial wave expansion; bottom-left: the two partial wave expansions; bottom-right: true wavefunction and its partial wave expansion.

the true wavefunction  $\Psi(\mathbf{r})$  is identical to  $\Psi_R^1(\mathbf{r})$ , which is built up from partial waves that contain the proper nodal structure.

In practice, the partial wave expansions are truncated. Therefore, the identity of Eq. 19 does not hold strictly. As a result the plane-waves also contribute to the true wavefunction inside the atomic region. This has the advantage that the missing terms in a truncated partial wave expansion are partly accounted for by plane-waves, which explains the rapid convergence of the partial wave expansions. This idea is related to the additive augmentation of the LAPW method of Soler<sup>50</sup>.

Frequently, the question comes up, whether the transformation Eq. 22 of the auxiliary wave-

functions indeed provides the true wavefunction. The transformation should be considered merely as a change of representation analogous to a coordinate transform. If the total energy functional is transformed consistently, its minimum will yield auxiliary wavefunctions that produce the correct wave functions  $|\Psi\rangle$ .

### C. Expectation values

Expectation values can be obtained either from the reconstructed true wavefunctions or directly from the auxiliary wave functions

$$\begin{aligned} \langle A \rangle &= \sum_n f_n \langle \Psi_n | A | \Psi_n \rangle + \sum_{n=1}^{N_c} \langle \phi_n^c | A | \phi_n^c \rangle \\ &= \sum_n f_n \langle \tilde{\Psi}_n | \mathcal{T}^\dagger A \mathcal{T} | \tilde{\Psi}_n \rangle + \sum_{n=1}^{N_c} \langle \phi_n^c | A | \phi_n^c \rangle \end{aligned} \quad (26)$$

where  $f_n$  are the occupations of the valence states and  $N_c$  is the number of core states. The first sum runs over the valence states, and second over the core states  $|\phi_n^c\rangle$ .

Now we can decompose the matrix element for a wavefunction  $\Psi$  into its individual contributions according to Eq. 23.

$$\begin{aligned} \langle \Psi | A | \Psi \rangle &= \langle \tilde{\Psi} + \sum_R (\Psi_R^1 - \tilde{\Psi}_R^1) | A | \tilde{\Psi} + \sum_{R'} (\Psi_{R'}^1 - \tilde{\Psi}_{R'}^1) \rangle \\ &= \underbrace{\langle \tilde{\Psi} | A | \tilde{\Psi} \rangle + \sum_R \left( \langle \Psi_R^1 | A | \Psi_R^1 \rangle - \langle \tilde{\Psi}_R^1 | A | \tilde{\Psi}_R^1 \rangle \right)}_{\text{part 1}} \\ &\quad + \underbrace{\sum_R \left( \langle \Psi_R^1 - \tilde{\Psi}_R^1 | A | \tilde{\Psi} - \tilde{\Psi}_R^1 \rangle + \langle \tilde{\Psi} - \tilde{\Psi}_R^1 | A | \Psi_R^1 - \tilde{\Psi}_R^1 \rangle \right)}_{\text{part 2}} \\ &\quad + \underbrace{\sum_{R \neq R'} \langle \Psi_R^1 - \tilde{\Psi}_R^1 | A | \Psi_{R'}^1 - \tilde{\Psi}_{R'}^1 \rangle}_{\text{part 3}} \end{aligned} \quad (27)$$

Only the first part of Eq. 27, is evaluated explicitly, while the second and third parts of Eq. 27 are neglected, because they vanish for sufficiently local operators as long as the partial wave expansion is converged: The function  $\Psi_R^1 - \tilde{\Psi}_R^1$  vanishes per construction beyond its augmentation region, because the partial waves are pairwise identical beyond that region. The function  $\tilde{\Psi} - \tilde{\Psi}_R^1$  vanishes inside its augmentation region, if the partial wave expansion

is sufficiently converged. In no region of space both functions  $\Psi_R^1 - \tilde{\Psi}_R^1$  and  $\tilde{\Psi} - \tilde{\Psi}_R^1$  are simultaneously nonzero. Similarly the functions  $\Psi_R^1 - \tilde{\Psi}_R^1$  from different sites are never nonzero in the same region in space. Hence, the second and third parts of Eq. 27 vanish for operators such as the kinetic energy  $\frac{-\hbar^2}{2m_e}\nabla^2$  and the real space projection operator  $|r\rangle\langle r|$ , which produces the electron density. For truly nonlocal operators the parts 2 and 3 of Eq. 27 would have to be considered explicitly.

The expression, Eq. 26, for the expectation value can therefore be written with the help of Eq. 27 as

$$\begin{aligned}
\langle A \rangle &= \sum_n f_n \left( \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle + \langle \Psi_n^1 | A | \Psi_n^1 \rangle - \langle \tilde{\Psi}_n^1 | A | \tilde{\Psi}_n^1 \rangle \right) + \sum_{n=1}^{N_c} \langle \phi_n^c | A | \phi_n^c \rangle \\
&= \sum_n f_n \langle \tilde{\Psi}_n | A | \tilde{\Psi}_n \rangle + \sum_{n=1}^{N_c} \langle \tilde{\phi}_n^c | A | \tilde{\phi}_n^c \rangle \\
&+ \sum_R \left( \sum_{i,j \in R} D_{i,j} \langle \phi_j | A | \phi_i \rangle + \sum_{n \in R}^{N_{c,R}} \langle \phi_n^c | A | \phi_n^c \rangle \right) \\
&- \sum_R \left( \sum_{i,j \in R} D_{i,j} \langle \tilde{\phi}_j | A | \tilde{\phi}_i \rangle + \sum_{n \in R}^{N_{c,R}} \langle \tilde{\phi}_n^c | A | \tilde{\phi}_n^c \rangle \right) \tag{28}
\end{aligned}$$

where  $D_{i,j}$  is the one-center density matrix defined as

$$D_{i,j} = \sum_n f_n \langle \tilde{\Psi}_n | \tilde{p}_j \rangle \langle \tilde{p}_i | \tilde{\Psi}_n \rangle = \sum_n \langle \tilde{p}_i | \tilde{\Psi}_n \rangle f_n \langle \tilde{\Psi}_n | \tilde{p}_j \rangle \tag{29}$$

The auxiliary core states,  $|\tilde{\phi}_n^c\rangle$  allow to incorporate the tails of the core wavefunction into the plane-wave part, and therefore assure, that the integrations of partial wave contributions cancel strictly beyond  $r_c$ . They are identical to the true core states in the tails, but are a smooth continuation inside the atomic sphere. It is not required that the auxiliary wave functions are normalized.

Following this scheme, the electron density is given by

$$\begin{aligned}
n(\mathbf{r}) &= \tilde{n}(\mathbf{r}) + \sum_R \left( n_R^1(\mathbf{r}) - \tilde{n}_R^1(\mathbf{r}) \right) \tag{30} \\
\tilde{n}(\mathbf{r}) &= \sum_n f_n \tilde{\Psi}_n^*(\mathbf{r}) \tilde{\Psi}_n(\mathbf{r}) + \tilde{n}_c \\
n_R^1(\mathbf{r}) &= \sum_{i,j \in R} D_{i,j} \phi_j^*(\mathbf{r}) \phi_i(\mathbf{r}) + n_{c,R} \\
\tilde{n}_R^1(\mathbf{r}) &= \sum_{i,j \in R} D_{i,j} \tilde{\phi}_j^*(\mathbf{r}) \tilde{\phi}_i(\mathbf{r}) + \tilde{n}_{c,R} \tag{31}
\end{aligned}$$

where  $n_{c,R}$  is the core density of the corresponding atom and  $\tilde{n}_{c,R}$  is the auxiliary core density that is identical to  $n_{c,R}$  outside the atomic region, but smooth inside.

Before we continue, let us discuss a special point: The matrix element of a general operator with the auxiliary wavefunctions may be slowly converging with the plane-wave expansion, because the operator  $A$  may not be well behaved. An example for such an operator is the singular electrostatic potential of a nucleus. This problem can be alleviated by adding an “intelligent zero”: If an operator  $B$  is purely localized within an atomic region, we can use the identity between the auxiliary wavefunction and its own partial wave expansion

$$0 = \langle \tilde{\Psi}_n | B | \tilde{\Psi}_n \rangle - \langle \tilde{\Psi}_n^1 | B | \tilde{\Psi}_n^1 \rangle \quad (32)$$

Now we choose an operator  $B$  so that it cancels the problematic behavior of the operator  $A$ , but is localized in a single atomic region. By adding  $B$  to the plane-wave part and the matrix elements with its one-center expansions, the plane-wave convergence can be improved without affecting the converged result. A term of this type, namely  $\bar{v}$  will be introduced in the next section to cancel the Coulomb singularity of the potential at the nucleus.

#### D. Total Energy

Like wavefunctions and expectation values also the total energy can be divided into three parts.

$$E[\tilde{\Psi}_n, R_R] = \tilde{E} + \sum_R (E_R^1 - \tilde{E}_R^1) \quad (33)$$

The plane-wave part  $\tilde{E}$  involves only smooth functions and is evaluated on equi-spaced grids in real and reciprocal space. This part is computationally most demanding, and is similar to the expressions in the pseudopotential approach.

$$\begin{aligned} \tilde{E} = & \sum_n \langle \tilde{\Psi}_n | \frac{-\hbar^2}{2m_e} \nabla^2 | \tilde{\Psi}_n \rangle \\ & + \frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{[\tilde{n}(\mathbf{r}) + \tilde{Z}(\mathbf{r})][\tilde{n}(\mathbf{r}') + \tilde{Z}(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|} \\ & + \int d^3r \bar{v}(\mathbf{r}) \tilde{n}(\mathbf{r}) + E_{xc}[\tilde{n}(\mathbf{r})] \end{aligned} \quad (34)$$

$\tilde{Z}(\mathbf{r})$  is an angular-momentum dependent core-like density that will be described in detail below. The remaining parts can be evaluated on radial grids in a spherical harmonics expan-

sion. The nodal structure of the wavefunctions can be properly described on a logarithmic radial grid that becomes very fine near nucleus,

$$\begin{aligned}
E_R^1 &= \sum_{i,j \in R} D_{i,j} \langle \phi_j | \frac{-\hbar^2}{2m_e} \nabla^2 | \phi_i \rangle + \sum_{n \in R}^{N_{e,R}} \langle \phi_n^c | \frac{-\hbar^2}{2m_e} \nabla^2 | \phi_n^c \rangle \\
&+ \frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{[n^1(\mathbf{r}) + Z(\mathbf{r})][n^1(\mathbf{r}') + Z(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|} \\
&+ E_{xc}[n^1(\mathbf{r})]
\end{aligned} \tag{35}$$

$$\begin{aligned}
\tilde{E}_R^1 &= \sum_{i,j \in R} D_{i,j} \langle \tilde{\phi}_j | \frac{-\hbar^2}{2m_e} \nabla^2 | \tilde{\phi}_i \rangle \\
&+ \frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \int d^3r \int d^3r' \frac{[\tilde{n}^1(\mathbf{r}) + \tilde{Z}(\mathbf{r})][\tilde{n}^1(\mathbf{r}') + \tilde{Z}(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|} \\
&+ \int d^3r \bar{v}(\mathbf{r}) \tilde{n}^1(\mathbf{r}) + E_{xc}[\tilde{n}^1(\mathbf{r})]
\end{aligned} \tag{36}$$

The compensation charge density  $\tilde{Z}(\mathbf{r}) = \sum_R \tilde{Z}_R(\mathbf{r})$  is given as a sum of angular momentum dependent Gauss functions, which have an analytical plane-wave expansion. A similar term occurs also in the pseudopotential approach. In contrast to the norm-conserving pseudopotential approach, however, the compensation charge of an atom  $\tilde{Z}_R$  is non-spherical and constantly adapts to the instantaneous environment. It is constructed such that

$$n_R^1(\mathbf{r}) + Z_R(\mathbf{r}) - \tilde{n}_R^1(\mathbf{r}) - \tilde{Z}_R(\mathbf{r}) \tag{37}$$

has vanishing electrostatic multi-pole moments for each atomic site. With this choice, the electrostatic potentials of the augmentation densities vanish outside their spheres. This is the reason that there is no electrostatic interaction of the one-center parts between different sites.

The compensation charge density as given here is still localized within the atomic regions. A technique similar to an Ewald summation, however, allows to replace it by a very extended charge density. Thus we can achieve, that the plane-wave convergence of the total energy is not affected by the auxiliary density.

The potential  $\bar{v} = \sum_R \bar{v}_R$ , which occurs in Eqs. 34 and 36 enters the total energy in the form of “intelligent zeros” described in Eq. 32

$$0 = \sum_n f_n \left( \langle \tilde{\Psi}_n | \bar{v}_R | \tilde{\Psi}_n \rangle - \langle \tilde{\Psi}_n^1 | \bar{v}_R | \tilde{\Psi}_n^1 \rangle \right) = \sum_n f_n \langle \tilde{\Psi}_n | \bar{v}_R | \tilde{\Psi}_n \rangle - \sum_{i,j \in R} D_{i,j} \langle \tilde{\phi}_i | \bar{v}_R | \tilde{\phi}_j \rangle \tag{38}$$

The main reason for introducing this potential is to cancel the Coulomb singularity of the potential in the plane-wave part. The potential  $\bar{v}$  allows to influence the plane-wave

convergence beneficially, without changing the converged result.  $\bar{v}$  must be localized within the augmentation region, where Eq. 19 holds.

### E. Approximations

Once the total energy functional provided in the previous section has been defined, everything else follows: Forces are partial derivatives with respect to atomic positions. The potential is the derivative of the non-kinetic energy contributions to the total energy with respect to the density, and the auxiliary Hamiltonian follows from derivatives  $\tilde{H}|\tilde{\Psi}_n\rangle$  with respect to auxiliary wave functions. The fictitious Lagrangian approach of Car and Parrinello<sup>14</sup> does not allow any freedom in the way these derivatives are obtained. Anything else than analytic derivatives will violate energy conservation in a dynamical simulation. Since the expressions are straightforward, even though rather involved, we will not discuss them here. All approximations are incorporated already in the total energy functional of the PAW method. What are those approximations?

- Firstly we use the frozen-core approximation. In principle this approximation can be overcome.
- The plane-wave expansion for the auxiliary wavefunctions must be complete. The plane-wave expansion is controlled easily by increasing the plane-wave cutoff defined as  $E_{PW} = \frac{1}{2}\hbar^2 G_{max}^2$ . Typically we use a plane-wave cutoff of 30 Ry.
- The partial wave expansions must be converged. Typically we use one or two partial waves per angular momentum  $(\ell, m)$  and site. It should be noted that the partial wave expansion is not variational, because it changes the total energy functional and not the basis set for the auxiliary wavefunctions.

We do not discuss here numerical approximations such as the choice of the radial grid, since those are easily controlled.

### F. Relation to the Pseudopotentials

We mentioned earlier that the pseudopotential approach can be derived as a well defined approximation from the PAW method: The augmentation part of the total energy  $\Delta E =$

$E^1 - \tilde{E}^1$  for one atom is a functional of the one-center density matrix  $D_{i,j \in R}$  defined in Eq. 29. The pseudopotential approach can be recovered if we truncate a Taylor expansion of  $\Delta E$  about the atomic density matrix after the linear term. The term linear to  $D_{i,j}$  is the energy related to the nonlocal pseudopotential.

$$\begin{aligned} \Delta E(D_{i,j}) &= \Delta E(D_{i,j}^{at}) + \sum_{i,j} (D_{i,j} - D_{i,j}^{at}) \frac{\partial \Delta E}{\partial D_{i,j}} + O(D_{i,j} - D_{i,j}^{at})^2 \\ &= E_{self} + \sum_n f_n \langle \tilde{\Psi}_n | v^{ps} | \tilde{\Psi}_n \rangle - \int d^3r \bar{v}(\mathbf{r}) \tilde{n}(\mathbf{r}) + O(D_{i,j} - D_{i,j}^{at})^2 \end{aligned} \quad (39)$$

which can directly be compared to the total energy expression Eq. 10 of the pseudopotential method. The local potential  $\bar{v}(\mathbf{r})$  of the pseudopotential approach is identical to the corresponding potential of the projector augmented wave method. The remaining contributions in the PAW total energy, namely  $\tilde{E}$ , differ from the corresponding terms in Eq. 10 only in two features: our auxiliary density also contains an auxiliary core density, reflecting the nonlinear core correction of the pseudopotential approach, and the compensation density  $\tilde{Z}(\mathbf{r})$  is non-spherical and depends on the wave function. Thus we can look at the PAW method also as a pseudopotential method with a pseudopotential that adapts to the instantaneous electronic environment. In the PAW method, the explicit nonlinear dependence of the total energy on the one-center density matrix is properly taken into account.

What are the main advantages of the PAW method compared to the pseudopotential approach?

Firstly all errors can be systematically controlled so that there are no transferability errors. As shown by Watson<sup>56</sup> and Kresse<sup>33</sup>, most pseudopotentials fail for high spin atoms such as Cr. While it is probably true that pseudopotentials can be constructed that cope even with this situation, a failure can not be known beforehand, so that some empiricism remains in practice: A pseudopotential constructed from an isolated atom is not guaranteed to be accurate for a molecule. In contrast, the converged results of the PAW method do not depend on a reference system such as an isolated atom, because PAW uses the full density and potential.

Like other all-electron methods, the PAW method provides access to the full charge and spin density, which is relevant, for example, for hyperfine parameters. Hyperfine parameters are sensitive probes of the electron density near the nucleus. In many situations they are the only information available that allows to deduce atomic structure and chemical environment

of an atom from experiment.

The plane-wave convergence is more rapid than in norm-conserving pseudopotentials and should in principle be equivalent to that of ultra-soft pseudopotentials<sup>55</sup>. Compared to the ultra-soft pseudopotentials, however, the PAW method has the advantage that the total energy expression is less complex and can therefore be expected to be more efficient.

The construction of pseudopotentials requires to determine a number of parameters. As they influence the results, their choice is critical. Also the PAW methods provides some flexibility in the choice of auxiliary partial waves. However, this choice does not influence the converged results.

### G. Recent Developments

Since the first implementation of the PAW method in the CP-PAW code, a number of groups have adopted the PAW method. The second implementation was done by the group of Holzwarth<sup>23</sup>. The resulting PWPAW code is freely available<sup>51</sup>. This code is also used as a basis for the PAW implementation in the AbInit project. An independent PAW code has been developed by Valiev and Weare<sup>53</sup>. Recently the PAW method has been implemented into the VASP code<sup>33</sup>. The PAW method has also been implemented by W. Kromen into the ESTCoMPP code of Blügel and Schröder.

Another branch of methods uses the reconstruction of the PAW method, without taking into account the full wavefunctions in the energy minimization. Following chemist notation this approach could be termed “post-pseudopotential PAW”. This development began with the evaluation for hyperfine parameters from a pseudopotential calculation using the PAW reconstruction operator<sup>54</sup> and is now used in the pseudopotential approach to calculate properties that require the correct wavefunctions such as hyperfine parameters.

The implementation by Kresse and Joubert<sup>33</sup> has been particularly useful as they had an implementation of PAW in the same code as the ultra-soft pseudopotentials, so that they could critically compare the two approaches with each other. Their conclusion is that both methods compare well in most cases, but they found that magnetic energies are seriously – by a factor two – in error in the pseudopotential approach, while the results of the PAW method were in line with other all-electron calculations using the linear augmented plane-wave method. As a short note, Kresse and Joubert incorrectly claim that their implemen-



tation is superior as it includes a term that is analogous to the non-linear core correction of pseudopotentials<sup>36</sup>: this term however is already included in the original version in the form of the pseudized core density.

Several extensions of the PAW have been done in the recent years: For applications in chemistry truly isolated systems are often of great interest. As any plane-wave based method introduces periodic images, the electrostatic interaction between these images can cause serious errors. The problem has been solved by mapping the charge density onto a point charge model, so that the electrostatic interaction could be subtracted out in a self-consistent manner<sup>10</sup>. In order to include the influence of the environment, the latter was simulated by simpler force fields using the molecular-mechanics-quantum-mechanics (QM-MM) approach<sup>57</sup>.

In order to overcome the limitations of the density functional theory several extensions have been performed. Bengone<sup>7</sup> implemented the LDA+U approach into the CP-PAW code. Soon after this, Arnaud<sup>5</sup> accomplished the implementation of the GW approximation into the CP-PAW code. The VASP-version of PAW<sup>21</sup> and the CP-PAW code have now been extended to include a non-collinear description of the magnetic moments. In a non-collinear description the Schrödinger equation is replaced by the Pauli equation with two-component spinor wavefunctions

The PAW method has proven useful to evaluate electric field gradients<sup>42</sup> and magnetic hyperfine parameters with high accuracy<sup>11</sup>. Invaluable will be the prediction of NMR chemical shifts using the GIPAW method of Pickard and Mauri<sup>44</sup>, which is based on their earlier work<sup>38</sup>. While the GIPAW is implemented in a post-pseudopotential manner, the extension to a self-consistent PAW calculation should be straightforward. An post-pseudopotential approach has also been used to evaluate core level spectra<sup>25</sup> and momentum matrix elements<sup>26</sup>.

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