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The Pseudopotential Approximation in Electronic Structure Theory

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Dedicated to Prof. Dr. Gernot Frenking on the occasion of his 65th birthday

A short review is presented on one of the most successful theories for electronic structure calculations, the pseudopotential approximation, originally introduced by Hans G. A. Hellmann in 1934. Recent developments in relativistic quantum theory allow for the accurate adjustment of pseudopotential parameters to valence spectra, producing results for properties of atoms, molecules, and the solid-state in excellent agreement with more accurate all-electron results if a small-core definition is used. Thus the relativistic pseudopotential approximation is now the most widely applied method for systems containing heavy elements.

1. Introduction

The general idea behind the pseudopotential approximation (PPA) is to replace complicated interactions between particles described by the (exact) Hamiltonian H_{exact} (if known) of a physical system by a pseudopotential operator V_{PP} (which often is of phenomenological nature), such that the (eigenvalue) spectrum of the resulting pseudo-Hamiltonian (or effective Hamiltonian), $\sigma(H_{PP})$, is as close as possible to $\sigma(H_{exact})$ [or a desired subset of $\sigma(H_{exact})$], and the corresponding pseudo-eigenfunctions, Ψ_{PP}, match the exact ones, Ψ_{exact}, as closely as possible for the region of interest. This more general definition for the pseudopotential approximation is applicable to all areas describing interactions between particles, that is, to electronic structure theory for atoms, molecules, and the solid state, to interactions in Bose–Einstein condensates, or to nuclear interactions and scattering processes, to name but a few.[1] The main motivation for such a procedure is that the eigenfunctions and eigenvectors of H_{PP} are more easily accessible through efficient computer codes than it would be through the formally exact Hamiltonian, H_{exact}, and that not all of the information that can be extracted from H_{exact} is relevant for the physical system of current interest.

One of the most important concepts in chemistry is that only the valence electrons are chemically active, that is, the core electrons remain inactive and act as spectators in chemical reactions (frozen-core approximation). As we are mostly interested in chemical properties coming from the valence space, we can try to replace the effect of the core electrons on a valence system in an atom, molecule or infinite system by a pseudopotential, which for this special case we call an effective core potential (ECP) (unfortunately, in electronic structure theory the term effective core potential and the more general term pseudopotential are used synonymously, the latter favoured by European theoretical chemists and the solid-state community, which we will adopt in the following). Core states are localized in the vicinity of the nucleus where valence states oscillate in order to maintain orthogonality with the core functions. This results in a large kinetic energy (kinetic energy pressure) for the valence electrons in the core region, which roughly cancels the large potential energy from the Coulomb interaction (this can nicely be seen in the work by Schwarz et al.[2]). Hans G. A. Hellmann[3] in 1934 therefore replaced these effects by a pseudopotential (which he called Zusatzpotential, that is, added-on potential),[4] which is repulsive in the core region and therefore keeps the electrons out of the core (Pauli repulsion). Around the same time, both Enrico Fermi (for the simulation of alkali atom spectra) and Pál Gombás (for the simulation of alkali metals) independently proposed the use of pseudopotentials.[5] It took, however, until 1959 when James C. Phillips and Leonard Kleinman from the solid-state community provided a more rigorous theoretical foundation for the pseudopotential theory for single valence-electron systems by replacing the core–valence orthogonalization terms by an effective repulsive (hard-core) potential in a very simple procedure.[6] Weeks and Rice later in 1968 extended this method to many-valence-electron systems.[7]

Without any doubt the pseudopotential approximation is the most widely used method in electronic structure theory dealing with heavy atoms where relativistic effects need to be considered: "Pseudopotential calculations are less accurate than all-electron calculations, but they simulate the results of the latter often surprisingly well, for substantially smaller expenses. It does therefore not astonish that in the chemistry of heavy atoms, relativistic pseudopotential theory is practically

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the method of choice. It is certainly the most successful of all approximate relativistic molecular theories", Werner Kutzelnigg, 1987[8]. The pseudopotential approximation saves valuable computer time in large molecular calculations (or in calculations for infinite systems) as the basis set is considerably reduced, that is, integrals arising from core orbitals are avoided and substituted by corresponding (one-electron) pseudopotential integrals, which can be treated in an efficient way. Moreover, relativistic contributions can be treated in a more efficient way compared to all-electron methods by including such effects directly into the pseudopotential. In the last two decades it became evident that the error inherent in the (ab initio) electron correlation or density functional procedure is almost always larger than the error produced by the pseudopotential approximation (if a small core definition is chosen and care has been taken in the adjustment procedure for the pseudopotential parameters). Despite the overwhelming success of the pseudopotential approximation, there have been some misunderstandings in the past concerning the validity of this approximation and the quality of the accompanying valence basis sets. One needs to understand that the use of smooth pseudo-valence orbitals is strictly for valence properties only (which need to be defined); in other words, using the pseudopotential approximation in electronic structure calculations requires some knowledge of its limits of applicability (as for any other approximate quantum chemical method).

Many excellent and comprehensive reviews on the pseudopotential approximation in electronic structure theory have been published over the last 20 years, mainly dealing with molecular systems (and a few for the solid state).[9–12] The accuracy of the pseudopotential approximation as compared to more accurate all-electron methods has been investigated intensively in the past, leading to a much better understanding of this useful theory.[13–16] Here we highlight some of the recent important developments in this area, and address some of the drawbacks of the pseudopotential approximation,[17–20] detailing where some care needs to be taken if this theory is applied in electronic structure calculations. It is hoped that this Minireview serves as a basic guide to computational chemists who want to apply this theory in quantum chemical applications from molecules to surfaces and the solid state, that is, it should serve as a beginners' guide to pseudopotential theory. A much more comprehensive and rigorous recent review on relativistic pseudopotentials is given by Dolg and Cao, and is highly recommended for further reading.[12]

2. Pseudopotential Theory

Electrons are indistinguishable and a separation into pure core, pure valence and mixed core–valence terms for the electronic Hamiltonian is therefore not possible. Nevertheless, it is convenient to write, for example, the molecular pseudo-Hamiltonian H_V for valence electrons in the form given by Equation (1):

$$H_V = -\frac{1}{2}\sum_i^{n_V}\nabla_i^2 + \sum_{i<j}^{n_V}\frac{1}{r_{ij}} + \sum_i^{n_V}\sum_a^{N_C}\left[V_{PP}^a(r_{ai}) - \frac{Q_a}{r_{ai}}\right] + \sum_{a<b}^{N_C}\frac{Q_aQ_b}{r_{ab}} \quad (1)$$

with n_V the valence electrons and N_C the cores (nuclei), and atomic units are used throughout. The indices a,b run over all cores (nuclei), i,j over all valences electrons, Q_a is the charge of core a ($Q_a=Z_a-N_a$, N_a being the number of core electrons of atom a, Z_a the nuclear charge, and for an all-electron atom we simply get $Q_a=Z_a$), and the last term in Equation (1) describes the classical (point charge) core–core repulsion. V_{PP} is the one-electron(!) pseudopotential operator, which keeps the valence electrons out of the core and in the valence space (therefore repulsive in the short-range and attractive in the long-range). Additional corrections may apply if non-frozen core effects are considered such as core-repulsion and core-polarization terms.[12,21] It is clear that we already made a choice in Equation (1) for the core of a specific atom in our molecule, which can only come from previous atomic Hartree–Fock (HF) or density functional Kohn–Sham (DFT-KS) calculations, where orbital energies and corresponding one-particle densities give us a clear indication of what is to be considered core or valence space. From a theoretical point of view it is therefore more appropriate to introduce the pseudopotential approximation within an orbital-based theory (mean-field theory or independent particle model).

For the following it is useful to outline the Phillips–Kleinman procedure for a single valence-electron atom with a closed-shell core of $n_C/2$ core orbitals (for a more complicated many-valence electron treatment leading to the generalized Phillips–Kleinman form see ref. [7]). The Hartree–Fock equation for a valence orbital φ_V is given by Equation (2) (NB: $\varphi \equiv |\varphi\rangle$):

$$F\varphi_V = \varepsilon_V\varphi_V \quad \text{with} \quad \langle\varphi_V \mid \varphi_C\rangle = 0 \quad (2)$$

We now create a pseudo-valence orbital χ_V by mixing core orbitals into φ_V [the pseudo-valence orbital transformation or Phillips–Kleinman ansatz, Eq. (3)]:

$$\chi_V = \varphi_V + \sum_C a_{CV}\varphi_C \quad \text{with} \quad a_{CV} = \langle\varphi_C \mid \chi_V\rangle \quad (3)$$

and we obtain Equation (4):

$$\langle\chi_V|F|\chi_V\rangle = \varepsilon_V + \sum_C a_{CV}^2\varepsilon_C \quad (4)$$

As we have complete freedom for the choice of linear combination in Equation (3), we may select the pseudo-valence orbital χ_V to become nodeless (smooth) in the radial part of the region $[0,\infty)$. Our aim is to construct a new Fock operator F^{PK} for the valence orbital χ_V such that [Eq. (5)]:

$$F^{PK}\chi_V = \varepsilon_V\chi_V \quad (5)$$

In order to do this, we write down the original Hartree–Fock equation for χ_V [Eq. 6]:

$$F\chi_V = \varepsilon_V\varphi_V + \sum_C a_{CV}\varepsilon_C\varphi_C = \varepsilon_V\chi_V + \varepsilon_V(\varphi_V - \chi_V) + \sum_C a_{CV}\varepsilon_C\varphi_C$$
$$= \varepsilon_V\chi_V + \sum_C a_{CV}(\varepsilon_C - \varepsilon_V)\varphi_C = \varepsilon_V\chi_V + \sum_C \langle\chi_V \mid \varphi_C\rangle(\varepsilon_C - \varepsilon_V)\varphi_C \quad (6)$$

Rearranging Equation (6) gives Equation (7):

$$\left[F + \sum_C (\varepsilon_V - \varepsilon_C)|\varphi_C\rangle\langle\varphi_C|\right]\chi_V = [F + P_C]\chi_V = F^{PK}\chi_V = \varepsilon_V\chi_V \quad (7)$$

with P_C being a core-projection operator, which assures that the valence electrons cannot collapse into the core. We now split the original Fock operator F into a core and valence-only part [Eq. (8)]:

$$F = F_C + F_V \quad (8)$$

but remember that the core exchange operator also leads to core–valence contributions when acting on a valence orbital. We now define the non-local pseudopotential operator for a valence electron at position $\mathbf{r}$ [Eq. (9)]:

$$V_{PP}(\mathbf{r}) = F_C + P_C = -\frac{n_C}{r} + \sum_C (2J_C - K_C) + P_C \quad (9)$$

and obtain the expectation values for F^{PK}

$$\frac{\langle\chi_V|F^{PK}|\chi_V\rangle}{\langle\chi_V \mid \chi_V\rangle} = \frac{\langle\chi_V|F_V + V_{PP}|\chi_V\rangle}{\langle\chi_V \mid \chi_V\rangle} = \langle\varphi_V|F^{PK}|\varphi_V\rangle = \langle\varphi_C|F^{PK}|\varphi_C\rangle = \varepsilon_V \quad (10)$$

Equation (10) shows that all core energies ε_C are shifted up to the valence energy ε_V due to the shift operator P_C. If we use the Fock-operator F^{PK} instead of F, nothing would be gained for computational purposes. We therefore try to find suitable and computer-efficient approximations to V_{PP} leading to results close to all-electron calculations.

There are basically two current approaches in molecular applications for approximating V_{PP} (the terminology here is rather unfortunate, but is used throughout the theoretical chemistry community): 1) the model core potential (MCP) approximation, or its extension to the ab initio model potential (AIMP) approximation, originating from Huzinaga and Cantu in 1971 which directly models the non-local Hartree–Fock potential for a valence orbital,[22] where the inner nodes of the radial valence orbitals are maintained, but the core levels are shifted to higher energies into the virtual space in order to avoid occupation by electrons, and 2) the semi-local pseudopotential approximation of using orbitals that are smooth and nodeless in the short-range of the radial function and can be derived from the (generalized) Phillips–Kleinman procedure[6,7] as discussed above.

In the MCP approximation, V_{PP} is replaced by an adjustable local potential and a projection operator,[23] for example by Equation (11):

$$V_{PP}(r_i) = \sum_k A_k r_i^{n_k} e^{-\alpha_k r_i^2} + \sum_C B_C|\varphi_C(r_i)\rangle\langle\varphi_C(r_i)| \quad (11)$$

where A_k, n_k and α_k are adjustable parameters (k runs over the Gaussian expansion) and B_C is chosen such that $B_C \gg (\varepsilon_V - \varepsilon_C)$ (usually $B_C = -2\varepsilon_C$ is taken). The corresponding one-electron integrals over Gaussian functions are easy to implement [integrals over the local potential in Eq. (11) can be solved analytically except for the standard error and Dawson function, and the projection operator results in simple overlap integrals]. This approximation can be improved by considering also the non-local core–valence exchange K_C of the original all-electron Fock operator, giving raise to AIMPs.[24] The advantage of Equation (11) is that the inner nodal structure of the resulting pseudo-valence orbitals is conserved, thus closely approximating all-electron valence orbitals. As a result, relativistic operators, such as the scalar Douglas–Kroll operator, acting in the close proximity of the nucleus, can be applied directly to such pseudo-valence orbitals.[25] Spin–orbit effects can be included as well.[26] The parameters in Equation (11) can be adjusted to Hartree–Fock orbital energies and corresponding radial functions in [27]. MCPs and AIMPs have been implemented into molecular program packages like MOLCAS[28] or GAMESS-US[29] for most of the elements of the periodic table.

In the pseudopotential (or effective core potential) approximation, V_{PP} is replaced by a semi-local (local in the coordinate r but non-local in spherical angle coordinates θ and ϕ) potential,[30,31] for example by splitting it into a local V_{local} and an angular-momentum-dependent semi-local term V_l [Eq. (12)]:

$$V_{PP}(r_i) = V_{local}(r_i) + \sum_{l=0}^{l_{max}} V_l(r_i)P_{l,i}$$
$$= \sum_k A_k r_i^{n_k} e^{-\alpha_k r_i^2} + \sum_{l=0}^{l_{max}} \sum_k B_{lk} r_i^{n_{lk}} e^{-\beta_{lk} r_i^2} \sum_{m=-l}^{l} |lm\rangle_i\langle lm|_i \quad (12)$$

where A_k, B_{lk}, n_k, n_{lk}, α_{lk} and β_{lk} are adjustable parameters, and the last term in Equation (12) contains a projection operator P_l (containing spherical harmonics) which projects onto the Hilbert sub-space with angular momentum l. Note that if l_{max} is taken large enough, the local term can be avoided. Unlike in Equation (11), there are no core functions and the pseudo-valence orbitals belonging to the lowest Hartree–Fock (or Kohn–Sham) solutions for each angular momentum l are therefore nodeless for the radial part. The integrals over the semi-local part over the Gaussian basis functions (and its derivatives) in Equation (12) are more complicated than in the AIMP approach, but efficient algorithms have been developed in the past.[32] One can also use a transformation from a semi-local to a non-local form to speed up the integration.[33] Scalar relativistic effects are included directly into V_{PP} by the adjustment pro-

cedure,[34] as relativistic perturbation operators originating, for example, from the Breit–Pauli or Douglas–Kroll Hamiltonian are short-to-medium range in nature[2] and should not be used for smooth pseudo-valence orbitals. However, this shift of relativistic effects into the valence region seems to work perfectly well (we come back to this problem in the next section). Therefore, one- and two-electron spin–orbit effects are also treated by a relativistic (R) one-electron pseudopotential of the form [Eq. (13)]:[35]

$$V_{PP}^{R}(r_i) = \sum_{l=0}^{l_{max}} \sum_{j=|l-1/2|}^{l+1/2} V_{PP}^{lj}(r_i) \sum_{m_j=-j}^{j} |ljm_j\rangle_i\langle ljm_j|_i$$
$$= \sum_{l=0}^{l_{max}} \sum_{j=|l-1/2|}^{l+1/2} \sum_{k} C_{ljk} r_i^{n_{ljk}} e^{-\gamma_{ljk} r_i^2} \sum_{m_j=-j}^{j} |ljm_j\rangle_i\langle ljm_j|_i \quad (13)$$

Pitzer and Winter split this equation in a convenient scalar relativistic (SR) and pure spin–orbit (SO) part for efficient integral evaluation to be used in configuration interaction (CI) treatments [Eq. (14)]:[36]

$$V_{PP}^{R}(r_i) = V_{PP}^{SR}(r_i) + V_{PP}^{SO}(r_i)$$
$$= \sum_{l=0}^{l_{max}} (2l+1)^{-1} \left[l V_{PP}^{l,l-1/2}(r_i) + (l+1) V_{PP}^{l,l+1/2}(r_i) \right] \sum_{m=-l}^{l} |lm\rangle_i\langle lm|_i$$
$$+ \vec{s}_i \cdot \sum_{l=0}^{l_{max}} \left(l+\tfrac{1}{2}\right)^{-1} \left[V_{PP}^{l,l+1/2}(r_i) - V_{PP}^{l,l-1/2}(r_i) \right] \sum_{m'=-l}^{l} \sum_{m=-l}^{l} |lm\rangle_i\langle lm|\vec{l}_i|lm'\rangle_i\langle lm'|_i \quad (14)$$

which is useful for extracting the scalar relativistic part if Equation (13) is solely for the adjustment procedure including both spin–orbit and scalar relativistic effects [except for a local potential as shown in Eq. (12) which can be included as well]. Spin–orbit effects are usually treated at the post-HF level of theory (e.g. in a multi-reference configuration interaction procedure), but have recently been implemented in a two-component form into the program system DIRAC[37] by Lee and coworkers.[38] Here we mention that a four-component treatment of pseudopotentials perhaps "overstretches" that method, as the small component of the Dirac orbital has most of its density in the vicinity of the nucleus and the kinetic-balance condition loses its meaning as pseudo-valence orbitals neglect important core-like contributions. To phrase it differently, if core states are shifted to higher energies or are eliminated, there is no need to account for the negative energy states. Moreover, the advantage of the relativistic pseudopotential approach is that the pseudo-Hamiltonian is bound from below, thus causing no difficulties for the variational principle of the Rayleigh–Schrödinger term.

Relativistic pseudopotentials of the form of Equations (12) or (13) are implemented in most program packages, including Gaussian 09,[39] Molpro,[40] MOLCAS[28] or Turbomole,[41] but is also found in the solid-state program CRYSTAL,[42] which uses Cartesian Gaussian functions as basis sets. The pseudopotential shown in Equation (12) (with or without the local form) is the most widely applied approximation for valence electrons in heavy-element-containing systems (most notably but in different functional form for the solid state using plane-wave basis sets for reasons which will be explained below), and we therefore give a short overview over the two main adjustment techniques used to produce either energy- or shape-consistent pseudopotentials.

The energy-consistent pseudopotentials originated from the Stuttgart group (Preuss, Stoll, Dolg, Schwerdtfeger and others), anticipated originally for the development of semi-empirical pseudopotentials. Here the adjustable pseudopotential parameters in Equation (12) or (13) are determined in a least-squares fitting procedure to a large number of precalculated atomic transitions in the valence space (including ionization potentials and the electron affinity of the neutral atom) obtained, for example, from relativistic Dirac–Fock calculations including Breit interactions [and if necessary even quantum electrodynamic (QED) effects[43]]. This fitting technique has been developed and perfected over more than three decades now by the Stuttgart group, and more recently by Dolg and coworkers.[44] Only up to two or three Gaussians [$k_{max}=2$ or 3 in Eqs. (12) or (13)] per angular symmetry l are required. These energy-consistent relativistic pseudopotentials are available for almost all elements of the periodic table and can be downloaded from the Stuttgart or Cologne websites.[45] These pseudopotentials are usually adjusted to (multi-reference) Hartree–Fock or Dirac–Hartree–Fock energies, but they seem to be easily transferable to the density functional domain without much loss of accuracy, as errors produced by the density functional approximation far outweighs the error inherent in the pseudopotential approximation for valence properties. Figure 1 shows the performance of various pseudopotentials using a large-core three-valence-electron ([Pd]-core) definition for indium. It is clear that the improved multi-electron

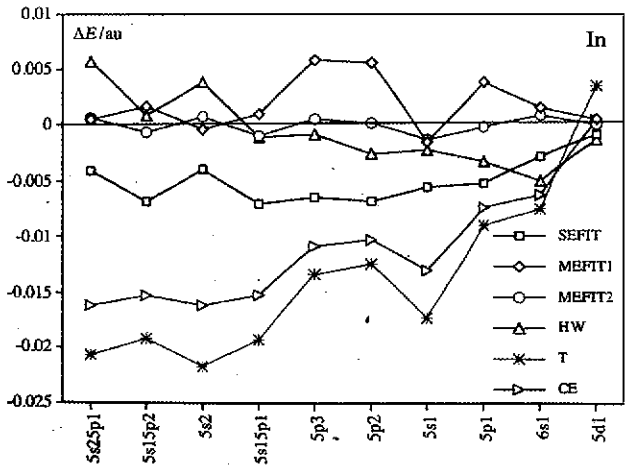

Figure 1. Comparison of the performance of various pseudopotentials for indium using a [Pd] core. Difference in total electronic energies for various valence configurations. Data taken from ref. [14]. SEFIT: Single valence electron energy-consistent pseudopotential (ref. [46]); MEFIT1: Multi-electron energy-consistent pseudopotential (ref. [47]); MEFIT2: Multi-electron energy-consistent pseudopotential (ref. [14]); HW: Hay–Wadt shape-consistent pseudopotential (refs. [48, 49]; T: Toulouse shape-consistent PP (ref. [52]); CE: Christiansen–Ermler shape-consistent pseudopotential (ref. [50]). All values are in atomic units.

energy-consistent pseudopotential (MEFIT2) is performing extremely well compared to the other fitting techniques, which is discussed in the following.

If the pseudopotential parameters are fitted in such a way that the valence orbitals of different symmetries reproduce to a high accuracy the corresponding all-electron orbitals from a certain cut-off (valence) radius r_c onwards with matching orbital energies, we obtain shape-consistent pseudopotentials. This method was favoured by a number of research groups in the United States, in particular by Hay and Wadt[48,49] as well as Kahn,[31] Christiansen, Ermler and co-workers[50] and Cundari and Stevens.[51] This technique has the disadvantage that it requires inversion of the Fock equation to produce angular-momentum-dependent pseudopotentials, resulting in a large number of Gaussian fitting functions. The Toulouse group elegantly avoided this by using a direct fit to the shape of the valence orbital,[52,53] which was also adopted later by Stevens et al., who accordingly named their pseudopotentials compact effective core potentials (CEPs).[54] Shape-consistent pseudopotentials have the advantage that the fitting technique used is fast and efficient. However, energy-consistent pseudopotentials choosing a rather large valence spectrum in the fit procedure fulfil the shape-consistent requirement extremely well (not necessarily vice versa) if the spectrum is accurately adjusted.[55] Here we note that, because of historical reasons, the definition of the pseudopotential used by these groups may differ slightly for the local potential[48–51] (as implemented for example in programs like Gaussian 09[39]), that is, V_{PP} is often defined according to the original paper by Kahn and Goddard[31] as [Eq. (15)]:

$$V_{PP}(r_i) = V_{local}(r_i) + \sum_{l=0}^{l_{max}} [V_l(r_i) - V_{local}(r_i)]P_{l,i} \qquad (15)$$

This implies that the local potential only acts on symmetries $l_{max}+1$ and higher up [if the local potential is set to zero, the definitions in Eqs. (12) and (15) are trivially the same].

Titov expanded the pseudopotential approximation of Equation (12) by dividing the valence space into an outer core part and a valence part,[56] which he calls the generalized relativistic effective core potential (GRECP) approximation. This introduces an extra degree of freedom (non-locality) and in principle, if a small core definition is used, should be more accurate in the fit procedure compared to Equation (12). However, the fit technique used for these GRECPs is identical to the way shape-consistent pseudopotentials are produced, which, as experience shows, is less accurate than the corresponding procedure for the energy-consistent pseudopotentials (see Figure 1). Moreover, as pseudopotential parameters are not available for all elements of the periodic table, and additional projection operators are required, the method is not widely used. It therefore remains to be seen if the GRECP approximation finds wider acceptance.

In electronic structure theory for 1D, 2D or 3D infinite systems (polymers, surfaces and the bulk), plane waves are ideally suited as Bloch basis functions. There are only few exceptions such as the CRYSTAL[42] or Gaussian 09[39] program suites, where Gaussian basis sets are applied. In this case, pseudopotentials of the form shown in Equation (12) can be used. Localized functions such as Gaussians are generally better suited to describe the large oscillations of the valence orbitals in the core region in all-electron calculations, and the corresponding one- and two-electron integrals in the Hartree–Fock (or in post-Hartree–Fock) procedures are easily evaluated. On the other hand, plane waves have many advantages over such localized basis functions for infinite systems (for a review on this subject see ref. [57]). However, the expansion of wavefunctions in plane waves converges rather slowly for the description of large oscillations in the core region, and pseudopotentials are therefore ideally suited, for example in solid-state calculations. The norm-conserving pseudopotential (NC-PP or NC-ECP) developed by Hamann and Schlüter and others,[58] originated from the orthogonalized plane-wave (OPW) approximation,[59] and is identical to (or a slight modification of) the shape-consistent pseudopotential method adopted for plane-wave codes within the density-functional formalism. It enforces the condition that up to a certain cut-off radius, the norm of each pseudo-valence orbital is identical to the corresponding all-electron orbital. The norm-conserving pseudopotentials are constructed from Kohn–Sham rather than Hartree–Fock equations, and thus are dependent on the functional used. For example, the Troullier and Martins approach[60] is a refinement of Kerker's procedure[61] and uses the following condition for the construction of radial (shape-consistent) pseudo-valence orbitals [Eq. (16)]:

$$\varphi_l^{PP}(r) = \begin{cases} \exp\left(\sum_{n=0}^{m+2} c_{nl} r^{2n}\right) & \text{for } r \le r_c \\ \varphi_l(r) & r \ge r_c \end{cases} \qquad (16)$$

The coefficients c_{nl} are obtained from the following conditions [Eq. (17)]:

$$\begin{aligned} &\frac{d^n}{dr^n}\varphi_l^{PP}(r_c) = \frac{d^n}{dr^n}\varphi_l(r_c) \quad \forall n = 0, \ldots, m \quad \text{(match first } m \text{ derivatives)} \\ &\int_0^{r_c} dr\, r^2 \left[\varphi_l^{PP}(r) - \varphi_l(r)\right]^2 = 0 \quad \text{(norm conservation)} \\ &\frac{d^2}{dr^2} V_l^{PP/scr}(0) = 0 \end{aligned} \qquad (17)$$

The cut-off radius r_c needs to be larger than the outermost node of the valence orbital to obtain nodeless pseudo-valence orbitals. Using the pseudo-valence orbitals generated through the conditions given in Equation (17), the Kohn–Sham equations can be inverted while avoiding singularities (except for the origin) because of the nodeless character of the $\varphi^{PP}(r)$. Figure 2 shows a comparison between all-electron and nodeless pseudo-valence orbitals for sulphur. The smoothness condition in Equation (17) ensures rapid convergence of the total energy (and system properties) with increasing plane-wave basis set. Here $V^{PP,scr}$ is the screened pseudopotential derived from inverting the radial Schrödinger equation for an atom [Eq. (18)]:[60]

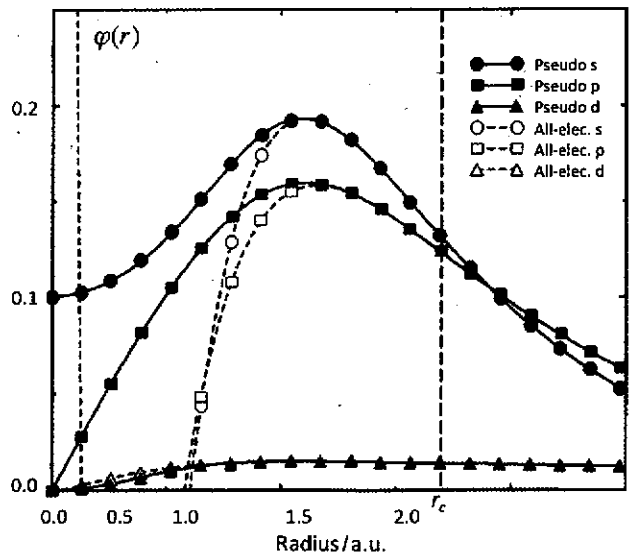

Figure 2. Pseudo- and all-electron valence wavefunctions for sulphur of Troulliers–Martin type (data taken from ref. [15]).

$$V_l^{PP,scr}(r) = \varepsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2r\varphi_l^{PP}(r)}\frac{d^2}{dr^2}r\varphi_l^{PP}(r) \tag{18}$$

From this equation it is clear that if $V_l^{PP,scr}$ is to be continuous then $\varphi_l^{PP}(r)$ must be continuous up to (and including) the second derivative. Moreover, if we want to avoid a hard-core pseudopotential (singularity at the origin), the pseudo-valence orbitals must behave as r^l at the origin.[60] The screened pseudopotential includes the Hartree and exchange–correlation contributions from the valence electrons, and in order to obtain the pure ionic core part we must correct for these terms, giving Equation (19):

$$\begin{aligned} V_l^{PP,ion}(r) &= V_l^{PP,scr}(r) - V_{Hartree}^{PP}(r) - V_{xc}^{PP}(r) \\ &= V_{local}^{PP,ion}(r) + \sum_l V_l^{PP,semi-local}(r)P_l \end{aligned} \tag{19}$$

Equation (19) is identical to the general form of Equation (12), but obtained by a different procedure. Note that this implies that different pseudopotentials are produced for different exchange–correlation functionals. The integrals over plane-wave functions are easily solved,[62] or treated in a non-local form (Kleinman–Bylander transformation[33]). As in Equation (12) the local potential can be derived in an arbitrary procedure, for example, accounting for the high-angular momentum terms not covered by the semi-local potential $V_l^{PP,semi-local}$. Note that the construction of this soft-core pseudopotential $V_l^{PP,ion}(r)$ is a simple procedure and, as in the case of the shape-consistent pseudopotentials used in molecular applications, can perhaps not compete in accuracy with a more elaborate adjustment for the multi-electron energy-consistent pseudopotentials of the Stuttgart group, where the fit procedure leads to a good representation for the valence spectrum as well. However, a fair comparison between the different pseudopotentials used in molecular and in solid-state applications is still missing. Nevertheless, the plane-wave expansion in the Troullier–Martins scheme is significantly reduced compared to all-electron or to hard-core pseudopotential calculations. For example, Troullier and Martins required only about 850 plane waves for metallic copper to converge the energy to within 100 meV with respect to the basis size,[60] while for the pseudopotential of Hamann–Schlüter and Chiang[58] ~1800 plane waves were needed, for the Kerker pseudopotential[61] ~3000, and for the ultra-soft pseudopotential by Vanderbilt[63] ~1550. In the latter approach by Vanderbilt and co-workers, the norm-conservation is not enforced and there is greater flexibility for choosing the cut-off radius r_c to ensure better smoothness and transferability (see Figure 2). However, this implies dealing with charge augmentation and a generalized eigenvalue problem. The Fourier transform of $V_l^{PP,ion}(r)$ shows that these ultra-soft Vanderbilt pseudopotentials decay much faster in reciprocal space (which according to Troullier and Martins does not necessarily imply a faster convergence of the total energy with increasing plane-wave basis size[60]). Especially for transition metals, this results in a significant saving of computer time. For a general discussion on softening pseudopotentials for plane wave applications see Furthmüller et al.[64] The Troullier–Martins[60] and the Vanderbilt[63,65] -type pseudopotentials are the most widely used in solid-state and surface-science applications and lead to excellent results. Soft or ultra-soft pseudopotentials are available on a numerical grid base or fitted to standard functions, or can be easily generated through various atomic program codes.[66] Although different pseudopotentials are used for different functionals, the error inherent in the density functional approximation itself is much larger than that caused by the variation in the pseudopotential parameters due to different functionals.[67] Apart from the pseudopotentials already mentioned, there are also the ones by Delley,[68] Hutter, and coworkers,[69] or Krack[70] and others, all varying in the smoothness conditions and adjustment techniques. Norm-conserving and ultrasoft pseudopotentials are implemented in almost all plane-wave packages for infinite systems like VASP[71] or ESPRESSO,[72] or in programs like SIESTA, which uses numerical methods for the radial part of the basis functions.[73] Spin–orbit coupling can be included within the pseudopotential approximation for example in the usual way through Equation (13).[74]

3. Electronic Properties from Pseudopotentials

There are so many applications for molecules and the solid state that we restrict our discussion to very few examples in order to critically analyze the validity (transferability) of the pseudopotential approximation to molecules and infinite systems (for the latter we solely focus on the solid state). Figure 3 clearly highlights the enormous success of the pseudopotential approximation in electronic structure theory (the survey is by no means complete, but demonstrates the sudden increase in popularity since about 1990, mainly due to the immense increase in activity in solid-state physics, materials science and nanoscience).

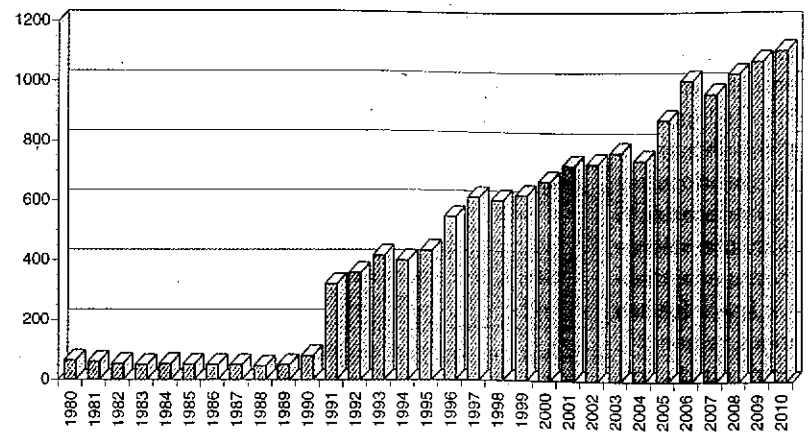

Figure 3. Number of papers published per year over the last 25 years using the pseudopotential approximation for atoms, molecules or infinite systems (from a Web-of-Science search with no guarantee of completeness).

3.1. Atoms

Atoms are better dealt with using all-electron methods at the four-component relativistic Dirac–Coulomb–Breit level together with accurate electron-correlation methods like Fock-space coupled-cluster theory.[75] Nevertheless, for certain atomic properties, such as electric dipole polarizabilities, the pseudopotential approximation has been quite useful in the past.[76] Studies on atomic properties are also useful to evaluate the accuracy of the core chosen, that is, the use of small vs large core pseudopotentials, and some of the short-comings of the pseudopotential approximation for certain properties (for a detailed discussion see ref. [12]). Table 1 shows a comparison between all-electron and pseudopotential results for various valence properties of neutral gold at the nonrelativistic and scalar relativistic Hartree–Fock level of theory obtained with an uncontracted all-electron (29s/25p/17d/12f) basis set.[20]

Table 1 shows that both the ionization potential and electron affinity are well reproduced by the pseudopotential approximation, even for the large-core Hay–Wadt pseudopotential,[48] which only takes the ($5d^{10}6s^1$) electrons of Au into the valence space. The same is true for the static dipole polarizability, which is a typical valence property. Note that the multi-electron adjusted energy-consistent nonrelativistic pseudopotential for gold is from 1982[79] and could be improved considerably using modern adjustment procedures.[44] Second we note that relativistic effects, which have been successfully transferred into the valence space, are nicely reproduced. Moreover, there are many different procedures to transform the Dirac Hamiltonian to the two-component or one-component (scalar-relativistic) form,[80] and one expects slight differences between scalar-relativistic pseudopotential and all-electron results if different relativistic Hamiltonians are used. If we want to compare to experimental results we need to include electron correlation. Relativistic Fock-space coupled cluster calculations including Breit interactions by Kaldor and co-workers give (nonrelativistic values are given in parentheses) 9.197 (7.057) eV for the ionization potential and 2.295 (1.283) eV for the electron affinity.[81] This compares to 9.22554(2) and 2.30861(3) eV respectively from experiment.[82] Pseudopotential results give 9.14 (7.04) eV for the ionization potential and 2.13 (1.16) eV for the electron affinity[16] A fairer comparison using the same basis sets and electron correlation procedure needs to be made, however. Zeng and Klobukowski recently presented different ab initio model potentials [see Eq. (11)] for various core definitions.[27] For a similar core (5s5p5d6s valence space) compared to the Stuttgart pseudopotentials they obtained 9.324 eV for the ionization potential and 2.190 eV for the electron affinity at the multi-configuration quasi-degenerate perturbation theory (MC-QDPT) level of theory.[27] These results clearly demonstrate that the errors inherent in the pseudopotential approximation for valence properties are quite small (of chemical accuracy), and expected to be much smaller compared to the density functional approximation widely used in quantum chemical applications, or to limitations in the electron-correlation procedure. Moreover, quantum electrodynamic corrections for the ionization potential and electron affinity of neutral gold at the Dirac–Hartree–Fock level are −0.0211 and −0.009 eV respectively and already of the size of the pseudopotential error.[43] Such effects become rather sizable for the 7s or 8s shell of the superheavy elements and need to be included in the pseudopotential adjustment procedure.[43,83] Concerning the electric dipole polarizability for neutral gold, experimental values are not available, but pseudopotential coupled-cluster calculations give 35.1 a.u., in good agreement with an all-electron Douglas–Kroll coupled-cluster value of 36.1 a.u.[84]

The other properties shown in Table 1 are given to illustrate the (obvious) limitations of the pseudopotential approximation. Apart from (small) errors in the pseudopotential adjust-

Table 1. Selected properties for the neutral gold atom (except for the field gradient) in a comparison between nonrelativistic (NR) and scalar relativistic (SR) Douglas–Kroll–Hess second-order (DK2)[77] all-electron (AE) and small-core (SC) Stuttgart (5s5p5d6s valence space), and Hay–Wadt[48] large-core (LC) (5d6s valence space) pseudopotential calculations at the Hartree–Fock level of theory. Properties: ionization potential, IP, electron affinity, EA, static dipole polarizability, α_D, electric quadrupole moment, Q, and potential to kinetic energy virial ratio, $-\langle V\rangle/\langle T\rangle$ (see ref. [20] for details). The electric field gradient q at the nucleus is for the ^3D state of Au^+ (d^9s^1).

Property	NR-AE	NR-SCPP	DK2-AE	SR-SCPP	SR-LCPP
IP [eV][b]	5.92	5.93	7.66	7.68	7.60
EA [eV][b]	0.085	0.088	0.61	0.63	0.59
α_D [a.u.]	109	103	50.1	49.7	53.0
Q [DÅ]	−28.8	−25.0	−26.9	−23.1	−18.5
$-\langle V\rangle/\langle T\rangle$	2.00	3.91	1.68	3.93	2.32
q_{Au^+} [a.u.]	8.53	0.32	9.07	0.31	0.37

[a] Not corrected for the relativistic picture change effect.[78] [b] This work.

ment procedure, further errors arise from the neglect of core contributions, core-polarization and core–valence correlation, and from the use of nodeless pseudo-valence orbitals. It is clear that typical core properties like the electric field gradient at the nucleus (see Table 1), NMR chemical shifts, Mössbauer shifts, and so forth, cannot be described by the pseudopotential approximation without reintroducing the core orbitals.[85] From the missing kinetic and potential core and core–valence contributions it is also clear that the nonrelativistic virial theorem is not fulfilled[20,86] (although in this form it is not fulfilled for the relativistic Douglas–Kroll case for various reasons[87]). What is perhaps more surprising is that the electric quadrupole moment Q contains a rather sizeable error, which seems to increase with increasing core size. It is well known that radial pseudo-valence orbitals lead to expectation values for $<r^n>$ $(n>0)$ in very good agreement with all-electron orbitals (which contain all their nodes), thus $<r^n>$ is regarded as a typical valence property (and is the reason why dipole polarizabilities are well described by the pseudopotential approximation).[9] Indeed, it was found recently that even for multipole moments (and especially for the quadrupole moment), contributions arising from the core orbitals cannot be neglected anymore.[20] As quadrupole moments enter, for example, the equation for the calculation of magnetizabilities (response to an external magnetic field), such properties cannot be regarded anymore as typical valence properties (for a detailed discussion, see ref. [20]). Hence, *one needs to be aware which properties are well described by the pseudopotential approximation and which are not.* As a general rule, property operators containing inverse coordinate powers or derivatives, that is, operators of the type $r^{-n}\partial^m/\partial r^m$ $(n+m>0)$, are not well suited for nodeless pseudo-valence orbitals, and may give rather large contributions from core orbitals—the electric field gradient operator at a nucleus is of such type.

There are many other studies that deal with the accuracy of the pseudopotential methods for atoms.[13–19] We only mention a more recent paper by Pitzer and coworkers on the ground and low-lying excited states of U^{4+} and U^{5+}, where a 24 valence-electron shape-consistent relativistic pseudopotential including spin–orbit coupling yields low relative and rms errors for the electronic valence states, and correctly predicts the ordering of these states.[88]

3.2. Molecules

The pseudopotential approximation has become an invaluable tool in the electronic structure treatment of molecules,[89] especially for large molecules containing heavy elements. Considerable computational savings are made in the Hartree–Fock procedure and subsequent integral transformation for an electron-correlation treatment compared to an all-electron treatment. Moreover, the basis set superposition error is often reduced compared to all-electron calculations, which is an advantage for the treatment of weakly interacting systems such as Hg_2.[90] Of course, what has been described in the previous section concerning core properties also applies for molecules or the solid state. In this section we focus on a prime molecular example to discuss the accuracy of the relativistic pseudopotential approximation, on the diatomic AuH, discussing the quality of calculated spectroscopic constants, such as the bond distance, dissociation energy and vibrational constants. Table 2 contains the collected results from various correlated calculations.

Table 2. Spectroscopic constants for AuH at various levels of theory: bond distance r_e, dissociation energy D_e, harmonic vibrational energy ω_e, and anharmonicity constant $\omega_e x_e$. Terminology as in Table 1. DK3: third-order Douglas–Kroll–Hess. SC1: 5spd6s valence space. SC2: 4f5spd6s valence space.

Method	r_e [Å]	D_0 [eV][a]	ω_e [cm^{-1}]	$\omega_e x_e$ [cm^{-1}]
Experimental[b]	1.524	3.22	2305	43.1
DK3-AE-CCSD(T)[c]	1.526	3.05	2328	–
DK-AE-CASPT2[d]	1.522	2.95	2315	–
SCPP-CCSD(T)[e]	1.527	2.980	2306	45.6
SC1-AIMP-CASPT2[d]	1.523	2.95	2312	–
SC2-AIMP-CASPT2[d]	1.518	2.97	2328	–
NR-AE-CCSD(T)[c]	1.743	1.99	1587	–
NR-SCPP-CCSD(T)[e]	1.747	1.987	1575	30.3

[a] D_0 is D_e corrected for zero-point vibrational effects using ω_e and $\omega_e x_e$ (the latter if available). [b] Experimental values from ref. [91]. [c] All-electron values from ref. [92]. [d] Ab-Initio Model Potential and all-electron results from ref. [27]. [e] From ref. [16].

The results shown in Table 2 clearly demonstrate that errors for typical valence properties caused by the small-core pseudopotential approximation are small compared to errors originating from the incomplete treatment of electron correlation or basis set incompleteness. Further, relativistic effects are correctly reproduced by the pseudopotential method. A more detailed analysis can be found in ref. [16], where similar basis sets were used for both all-electron and pseudopotential MP2 (second-order Møller-Plesset) calculations in order to make the performance of the pseudopotential approximation more transparent, see Table 3. The results clearly demonstrate that a small-core pseudopotential for gold leads to negligible deviations to all-electron results for typical valence properties, while a large-core definition can lead to substantial errors, especially for the dissociation energy of AuH. At the same time, Han and Hirao carried out test calculations for the ground states of AuH, AuCl, and Au_2, and pointed out that a small-core relativistic pseudopotential can safely be used in density functional calculations with little loss of accuracy.[93] Previous claims that pseudopotentials yield rather large errors in structural or electronic valence properties compared to all-electron calculations are unfounded, and either due to insufficient valence basis sets or low-quality pseudopotentials used. However, as explained above, special care needs to be taken to define the correct core size in the pseudopotential adjustment procedure. For example, a one-valence electron pseudopotential for gold is not acceptable and leads to very large errors in valence properties, as core repulsion, core polarization and core–valence correlation effects become very large.[11] Even for copper in the higher oxidation state, a compound like CuF_4^- involves strong bonding participation by the Cu(3d) orbitals as Figure 4

Table 3. A comparison between small-core (SC, 19 valence electrons for Au) and large-core (LC, 11 valence electrons for Au) pseudopotential (PP) and all-electron (AE) results for AuH at the MP2-level of theory: bond distance r_e, dissociation energy D_e, harmonic vibrational energy ω_e, anharmonicity constant $\omega_e x_e$, and dipole moment μ_e. Terminology as in Table 2. The PP valence basis set for Au used is a subset of the all-electron basis set.

Method	r_e [Å]	D_e [eV][a]	ω_e [cm^{-1}]	$\omega_e x_e$[cm^{-1}]	μ_e [D]
NR-AE	1.694	1.955	1716	27.1	3.43
NR-SCPP-St[b]	1.689	1.955	1726	30.0	3.40
DC-AE[c]	1.484	3.208	2521	–	1.03
DK2-AE	1.486	3.034	2517	48.4	1.07
SCPP-St[d]	1.480	3.161	2523	44.6	1.01
SCPP-CE[e]	1.477	3.193	2524	44.5	0.99
SCPP-HW[f]	1.472	3.307	2587	44.7	0.87
SCPP-SK[g]	1.484	3.144	2518	44.5	1.04
LCPP-CE[h]	1.519	2.520	2303	40.7	1.08
LCPP-HW[i]	1.547	2.450	2156	37.1	1.20

[a] D_e is not corrected for zero-point vibrational effects for better comparison. [b] Nonrelativistic energy-consistent SCPP from the Stuttgart group. [c] Dirac–Coulomb all-electron. [d] Scalar relativistic energy-consistent SCPP from the Stuttgart group. [e] Scalar relativistic shape-consistent SCPP of Christiansen and Ermler. [f] Scalar relativistic shape-consistent SCPP of Hay and Wadt. [g] Scalar relativistic shape-consistent SCPP of Stevens et al. [h] Scalar relativistic shape-consistent LCPP of Christiansen and Ermler. [i] Scalar relativistic shape-consistent LCPP of Hay and Wadt. For details and references see ref. [16].

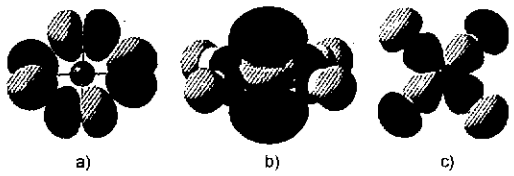

Figure 4. Selected valence molecular orbitals for CuF_4^- showing large contributions from the Cu(3d) in some lower lying "valence" orbitals (b and c) with orbital energies close to the highest occupied molecular orbital (HOMO). a) HOMO (−0.11 a.u.) b) MO (−0.17 a.u.) c) MO (−0.29 a.u.).

shows, and thus a one-valence electron pseudopotential for copper is also inappropriate. Placing just the 5d electrons into the valence space for Au to give an 11 valence-electron pseudopotential can lead to sizeable errors as well as the results in Table 3 show.[13,16]

As pointed out before for the atomic case, one needs to be aware which properties are well described by the pseudopotential approximation and which are not. For example, the dynamic or static dipole (hyper)polarizability of an atom or molecule is considered as a typical valence property, and results for atoms, molecules or atomic clusters indeed show very good agreement with all-electron results or experimental measurements.[94] However, one might naively expect that the response to an external magnetic field is equally well described by the pseudopotential approximation. This is however not the case, as recent test calculations on diamagnetic and paramagnetic contributions to the magnetizability of AuF and clusters of tin up to Sn_{20} show.[20] Here the pseudopotential approximation carries rather large errors from missing core contributions and the missing correct inner nodal structure of the pseudo-valence orbitals, which can be corrected for the diamagnetic part, but not so easily for the paramagnetic component of the magnetizability.[20] It is obvious that typical core properties like the electric field gradient or the NMR chemical shift cannot be accurately obtained if a pseudopotential is used at the center considered. Here one needs to either reintroduce the core and nodal structure of the valence orbitals,[85] or carry out a single-point all-electron calculations (at the optimized pseudopotential geometry).

3.3. Infinite Systems

The pseudopotential approximation is the method of choice for the treatment of infinite systems, including heavy elements, and has become invaluable in the electronic structure calculation of surfaces and the solid state. In a careful analysis, Yin and Cohen pointed out that the pseudopotential approximation is an accurate and viable method for the study of structural properties of solids.[95] Barth and Gelatt came to similar results.[86] Table 4 shows a comparison of pseudopotential with

Table 4. A comparison of different solid-state approaches by Holzwarth et al.[96] using the local density approximation parametrized by Perdew and Wang[97] for the lattice constant a_0, cohesive energy E_{coh}, and bulk modulus B_0. PP: Pseudopotential of Vanderbilt type,[98] PAW: projector augmented wave method of Blöchl,[99] LAPW: All-electron linearized augmented-plane-wave method.[100] Experimental values from ref. [100].

solid	Method	a_0 [Å]	E_{coh} [eV]	B_0 [GPa]
Si *dia*[a]	Exp.	5.43	4.63	99
	PP	5.39	5.99	98
	PAW	5.38	6.03	98
	LAPW	5.41	5.92	98
Ca *fcc*	Exp.	5.58	1.84	15
	PP	5.37	2.14	20
	PAW	5.32	2.24	19
	LAPW	5.33	2.20	19
V *bcc*	Exp.	3.03	5.31	162
	PP	2.94	9.46	210
	PAW	2.94	9.39	200
	LAPW	2.94	9.27	200

[a] Diamond structure for silicon.

all-electron results for various solids carried out by Holzwarth et al.[96] The large deviations to experimental values are clearly caused by the density functional method used and not by the pseudopotential approximation, that is, the local density approximation (LDA) severely overestimates cohesive energies. Nevertheless, the all-electron linearized augmented-plane-wave (LAPW) results are in good agreement with the pseudopotential values.

Troullier and Martins showed that the pseudopotential functions $V_l(r)$ for a specific angular momentum l (including the local part if not absent) can differ substantially between the different adjustment techniques (see for example Figure 7 for Cu in ref. [60]). The same was found for pseudopotentials used in molecular calculations.[14] However, they all lead to very simi-

lar structural and electronic properties. Table 5 shows a comparison of results for bulk copper, obtained with a Troullier-Martins pseudopotential, with other calculations,[60] demonstrating that the pseudopotential approximation performs extremely well compared to the LAPW method. It also shows that relativistic effects are successfully transferred into the valence region.

Table 5. Lattice constants a_0, cohesive energies E_{coh}, and bulk moduli B_0 for fcc copper at the LDA level of theory. SR: Scalar relativistic. NR: Nonrelativistic. PP: Pseudopotential. TM: Troullier-Martins. K: Kerker. BHS: Bachelet-Hamann-Schlüter. LAPW: Linearized augmented-plane-wave method.[99] Experimental values from ref. [100]. For details see ref. [60].

Method	a_0 [Å]	E_{coh} [eV]	B_0 [GPa]
Exp.	3.61	3.50	142
SR-TM-PP	3.57	4.38	174
SR-BHS-PP	3.62	3.35	150
LAPW	3.56	4.42	183
NR-TM-PP	3.60	4.19	160
NR-K-PP	3.62	3.83	188
NR-LAPW	3.61	4.14	163

Luppi et al. showed that the pseudopotential approximation can safely be applied to excited electronic states for solids.[101] This is perhaps not surprising, as this has been known for decades within the molecular quantum chemistry community.[9–12] Nevertheless, band gaps and optical spectra are well reproduced compared to all-electron results, and large errors compared to experiment come from the density functional approximation. However, it was recently shown that the magnetic moment of the V(100) surface obtained from pseudopotentials deviates significantly from all-electron full-potential linearized augmented plane-wave (FLAPW) calculations.[17,102] Thus, while the magnetization in the top layer vanishes after surface relaxation (in agreement with experiment), the pseudopotential value for the surface magnetization is $0.75\mu_B$ for the relaxed and $1.77\mu_B$ for the bulk truncated surface. A careful analysis by Kresse and coworkers showed that these results are sensitive to the cut-off radius r_c chosen, and a large value of r_c leads to erroneous results.[18] They further argued that for softer potentials (large r_c) the maximum in the V(3d) pseudo wavefunction is shifted significantly outward, thus causing a reduction of the core–valence overlap, and subsequently a too large value for the spin-enhancement factor in the region where the magnetization density reaches its maximum. They advise to perform careful convergence studies on the pseudopotential cut-offs before applying it to such calculations.[18]

Cocula and Carter showed that the problem of correctly describing the magnetic behaviour of surfaces (or the solid state) can be corrected by using spin-dependent pseudopotentials.[19] However, the transferability of such an approach to other systems needs to be tested. In such problematic cases where the pseudopotential approximation breaks down (see the recent discussion on the electric quadrupole moment and corresponding magnetizability for atoms and molecules[20]), one may be better served to carry out an all-electron calculation. One way to avoid pseudopotentials for infinite systems and at the same time a very large plane-wave expansion, is by using mixed basis sets, for example, Gaussian-type functions for the short-range and plane waves for the long-range.[103] However, currently a more popular method seems to be the projector augmented-wave (PAW) approximation as suggested by Blöchl,[98] which combines ideas from both the pseudopotential and the LAPW methods. Here one takes advantage of the pseudopotential approximation, that is, the smooth pseudo-valence orbitals are used in the variational calculations, but the correct inner nodal structure is retained through all-electron and projector functions using the frozen-core approximation. Blöchl achieves this by introducing a linear transformation connecting the true orbitals, which retain all their inner nodes, to pseudo-valence orbitals (for details see ref. [98]). This technique saves significantly in computational costs and gives results close to fully variational all-electron methods. Hence, the PAW procedure can be used to reconstruct all-electron orbitals from pseudo-orbitals useful for typical core properties, where the inner nodes of the valences orbitals are required. A formal relationship between Vanderbilt's ultrasoft pseudopotential approximation and the PAW method has been derived by Kresse and Joubert, showing that the total energy functional for ultrasoft pseudopotential pseudopotentials can be obtained by linearization of two terms in a slightly modified PAW total energy functional.[104] Thus programs that use norm-conserving or ultrasoft pseudopotentials can easily be modified for the PAW method. Spin–orbit coupling can also be treated in an efficient way within the PAW method.[105]

4. Outlook

The pseudopotential approximation remains an invaluable tool in the theoretical treatment of the electronic structure for large molecules and infinite systems such as surfaces or the solid state. For structural and electronic valence properties, the accuracy of this method (if the core is chosen appropriately, that is, not too large to avoid frozen-core errors) is high enough compared to other errors caused for example by insufficient treatment of electron correlation or by the density-functional approximation, except perhaps for atoms and small molecules where large scale configuration-interaction or coupled-cluster techniques can achieve spectroscopic accuracy. Relativistic effects are well incorporated into the valence space by the pseudopotential approximation and are successfully transferred to molecules or the solid state, despite the fact that relativistic perturbation operators act in the close vicinity of the nucleus. Care needs to be taken in applying this method to properties where the (polarized) core-density, the nodal structure of the valence orbitals, core–valence correlation or core-overlap effects become important. For example, in high-pressure simulations of materials one needs to be sure that the valence densities of the neighbouring atoms do not penetrate significantly into the core region of the atom carrying a pseudopotential. More recently we have also learned that external magnetic field properties contain large contributions from the core region.[20] In such cases, single-point all-electron calcula-

tions at the optimized pseudopotential geometry are advisable.

Herein we did not discuss Gaussian basis sets in detail. Like all-electron basis sets used in atomic or molecular calculations, the accompanying valence basis sets can be obtained from various sources like the basis set exchange service at the Environmental Molecular Sciences Laboratory (EMSL).[106] Most noteworthy here is the development of Dunning-type[107] correlation-consistent valence basis sets by Peterson and coworkers.[108] We also did not reflect on pseudopotentials used in quantum Monte Carlo applications and refer here to the work by Dolg and coworkers.[109] In the last 50 years the development of accurate pseudopotentials happened independently in two different communities, the molecular (chemistry) and the solid-state (physics) community. What perhaps is missing is a fair comparison of the pseudopotentials obtained from both communities, as they can learn from each other.

Hellmann's very basic idea of the well known fact that only valence electrons are important for the understanding of chemical bonding and processes, can be brought into a rigorous quantum mechanical framework and has been refined to such perfection and high accuracy[12] that the pseudopotential approximation is the method of choice in most structural and electronic properties of systems containing heavy elements. When Pekka Pyykkö was asked in an interview what difference the increased computing power has made to his work, he replied: *You can do far more complex calculations. One very good philosophy is that if you push your calculations to the currently available limit, more often than not, you find new science. Another thing that made relativistic quantum chemistry available to anyone was pseudopotentials. There have been other approximate methods, but the market share of pseudopotentials is perhaps the largest one.*[110]

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