



Pseudopotentials and modelpotentials

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The basic assumptions of quantum chemical *ab initio* valence-only (VO) schemes, i.e., pseudopotential and modelpotential approaches, are briefly discussed. Both effective core potential schemes lead to a reduction of the computational effort for wavefunction-based as well as density functional theory electronic structure calculations in comparison to corresponding all-electron treatments and allow to include the most important relativistic contributions implicitly into formally nonrelativistic calculations by means of a suitable parameterization of the VO model Hamiltonian. © 2011 John Wiley & Sons, Ltd. *WIREs Comput Mol Sci* 2011 1 200–210 DOI: 10.1002/wcms.28

INTRODUCTION

It is well known that relativistic effects increase roughly with the fourth power of the nuclear charge and thus become important, quantitatively as well as often even qualitatively, in the chemistry of heavy elements.¹ Rigorous relativistic all-electron (AE) electronic structure calculations are feasible for atoms and small molecules but usually become computationally by far too demanding for larger systems. Fortunately, for many problems in chemistry and also in physics, approximate schemes already yield sufficiently accurate results. The computational effort arising from the presence of heavy atoms with chemically inert core shells can be considerably lowered by restricting the explicit quantum chemical treatment in a valence-only (VO) approach to the valence electron system, i.e., by replacing the effect of the compact and atomic-like core shells by so-called effective core potentials (ECPs). Significant savings arise due to the possibility of using smaller basis sets during the integral evaluation, the self-consistent solution of the Hartree–Fock (HF) or Kohn–Sham (KS) equations as well as the integral transformation prior to wavefunction-based electron correlation calculations or in quantum Monte Carlo studies. In addition ECPs can incorporate relativistic contributions implicitly by means of a suitable adjustment of free parameters in the VO model Hamiltonian to relativistic AE reference data. The ECPs fall into two categories, i.e.,

modelpotentials (MPs), which aim to retain the original valence orbitals with the correct nodal structure in the calculations, and pseudopotentials (PPs), which after a formal transformation to pseudo-valence orbitals with a simplified radial nodal structure require even smaller basis sets. The following paragraphs provide a brief overview of MPs and PPs currently used in molecular electronic structure theory. Due to limitations of space only the most popular variants are mentioned and a few representative articles are cited. For additional references, also pointing to other approaches, the reader is referred to the reviews listed under *Further Reading*.

CHOICE OF THE CORE

The choice of the core is a fundamental decision for all ECPs and results from a compromise between accuracy and computational effort, which may depend on the problem to tackle. Figure 1 shows that, e.g., for Ti, one has essentially two choices for the core, i.e., the large Ar core following chemical intuition (four valence electrons) and the small Ne core (12 valence electrons). AE frozen-core (FC) calculations provide information how accurate an ECP for a specific core can be at best. Table 1 lists FC errors for various atomic energy differences of Ti from relativistic Dirac–Hartree–Fock (DHF) AE calculations with the Dirac–Coulomb (DC) Hamiltonian and reveals that the smaller Ne core yields a significantly higher accuracy than the larger Ar core. Small cores in general lead to a better transferability of the ECPs from the atom to molecules and thus usually are the preferred selection.

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TABLE 1 | Energies relative to the ground state configuration of selected configurations of Ti from all-electron Dirac-Hartree-Fock calculations using the Dirac-Coulomb-Hamiltonian (DHF/DC), contributions of the Breit interaction (+B), frozen-core errors (FCE) for Ne and Ar cores, relativistic contributions (Rel. Contr.) as well as errors for a shape-consistent (SC; wrt DHF/DC)²⁸ and an energy-consistent (EC; wrt DHF/DC + B)¹⁷ small-core pseudopotential (PP) in one- and two-component (1-c, 2-c) calculations. Mean absolute errors/deviations (m.a.e./m.a.d) are listed in the last line (eV).

Configuration	DHF/DC	+B	FCE Ne	FCE Ar	Rel. Contr.	SC-PP 1-c	EC-PP 1-c	EC-PP 2-c
Ti 3d ² 4s ²	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3d ³ 4s ¹	1.743	−0.007	0.000	0.116	0.152	−0.022	−0.014	−0.007
3d ⁴	5.477	−0.010	0.000	0.206	0.164	−0.050	−0.031	−0.022
Ti ¹⁺ 3d ¹ 4s ²	8.319	0.011	0.000	0.356	−0.187	0.024	0.006	−0.006
3d ² 4s ¹	5.838	−0.001	0.000	0.003	0.064	−0.007	−0.002	−0.002
3d ³	6.952	−0.009	0.000	0.152	0.193	−0.036	−0.015	−0.007
Ti ²⁺ 4s ²	18.558	0.025	0.000	0.018	0.137	0.052	0.023	−0.007
3d ¹ 4s ¹	22.131	0.010	0.000	0.474	−0.109	0.010	0.003	−0.011
3d ²	30.370	−0.003	0.001	1.972	−0.457	−0.021	−0.005	−0.005
Ti ³⁺ 4s ¹	53.741	0.023	0.001	2.498	−0.353	0.033	0.023	−0.009
3d ¹	44.064	0.008	0.000	0.702	−0.002	−0.011	0.000	−0.015
Ti ⁴⁺	86.261	0.021	0.001	3.320	−0.209	0.012	0.027	−0.009
m.a.d./m.a.e.		0.012	0.000	0.893	0.184	0.025	0.013	0.009

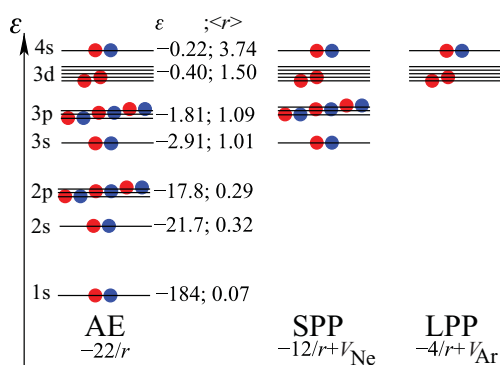


FIGURE 1 | Valence electron systems for Ti small-core (Ne core) and large-core (Ar core) pseudopotentials in comparison to the all-electron treatment. The energetic and spatial separation of core and valence can be judged from the orbital energies ϵ and radial expectation values $\langle r \rangle$ (a.u.).

PSEUDOPOTENTIALS

Theoretical Basis

Generalized Phillips–Kleinman Equation

One of the first PPs was published by Hellmann² already in 1935 for semi-empirical treatments of the valence electron of K together with applications to KH and K₂. Early applications in chemistry were performed in the 1950s by Preuss.³ A rigorous theoretical foundation of PPs was provided by Phillips and Kleinman⁴ in 1959 within an effective one-electron

ab initio framework for solids, and later generalized by Weeks and Rice⁵ in 1968 to many-valence-electron cases. In the generalized Phillips–Kleinman (GPK) equation

$$(\hat{H}_v + \hat{V}^{\text{GPK}})|\Phi_p\rangle = E_v|\Phi_p\rangle, \quad (1)$$

where \hat{H}_v stands for the valence (v) electron Hamiltonian, E_v denotes the total valence energy, and $|\Phi_p\rangle$ is a many-electron pseudo-valence eigenfunction. The so-called generalized GPK PP \hat{V}^{GPK} is a nonlocal, energy-dependent many-electron operator,

$$\hat{V}^{\text{GPK}} = -\hat{H}_v \hat{P} - \hat{P} \hat{H}_v + \hat{P} \hat{H}_v \hat{P} + E_v \hat{P}. \quad (2)$$

The projection operator \hat{P} projects out from $|\Phi_p\rangle$ any core components, thus yielding the original valence eigenfunction $|\Phi_v\rangle$ of \hat{H}_v for the eigenvalue E_v , i.e.,

$$|\Phi_v\rangle = (1 - \hat{P})|\Phi_p\rangle. \quad (3)$$

Equations (1)–(3) are formidable and essentially useless for practical applications, but they provide a formal theoretical basis for the development of PPs. The equations prove that in principle it is possible to find a ‘potential’ which, when added to a VO-Hamiltonian, allows the variational solution of the corresponding Schrödinger equation without collapse to core-like energies. The pseudo-valence wavefunction does not need to be orthogonal to the core wavefunction. In order to construct an ECP, one formally has to perform

a core–valence separation, apply the FC approximation, and finally eliminate all explicit reference to the core electron system by introducing for \hat{V}^{GPK} a suitable approximation. The first step corresponds to the neglect of core and core–valence correlation effects, the second requires the assumption of a core electron system, which is unaffected by any changes in the valence electron system, and the third is only possible if an accurate parameterization efficiently reduces the corresponding errors.

Valence-Only Model Hamiltonian for an Atom

For an atom with n_v valence electrons the VO-Hamiltonian is given by

$$\hat{H}_v = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \sum_{j>i}^{n_v-1} \frac{1}{r_{ij}} + \sum_i \hat{V}_{\text{cv}}(i). \quad (4)$$

The first two terms stand for the electron kinetic energy and the electron–electron interaction. $\hat{V}_{\text{cv}}(i)$ is an effective one-electron potential which accounts for all interactions of the valence electron i with the nucleus and the (removed) core (c) electron system, i.e.,

$$\hat{V}_{\text{cv}}(i) = -\frac{Q}{r_i} + \Delta \hat{V}_{\text{cv}}(i), \quad (5)$$

where Q denotes the core charge, i.e., $Q = Z - n_c$ when n_c electrons and a nucleus with charge Z form the core. $\Delta \hat{V}_{\text{cv}}(i)$ is often referred to as a PP. At the nonrelativistic level the most frequently used semilocal PP ansatz, initially proposed by Abarenkov and Heine⁶ in the framework of solid state physics and later introduced to quantum chemistry by Schwarz⁷ as well as Kahn and Goddard,⁸ consists of a sum of radial (local) potentials $V_l(r_i) - V_L(r_i)$ acting on each angular momentum symmetry $0 \leq l \leq L-1$ separately up to the maximum angular momentum $L-1$ present in the core. A common (local) potential $V_L(r_i)$ acts on all angular momentum symmetries $l \geq L$, i.e.,

$$\Delta \hat{V}_{\text{cv}}(i) \cong V_L(r_i) + \sum_{l=0}^{L-1} (V_l(r_i) - V_L(r_i)) \hat{P}_l(i), \quad (6)$$

where $\hat{P}_l(i)$ represents the angular momentum projection operator based on spherical harmonics $|lm\rangle$

$$\hat{P}_l(i) = \sum_{m=-l}^{m=l} |lm\rangle \langle lm|. \quad (7)$$

The need for an l -dependency of the PP arises, e.g., from the different number of core shells for each l for which implicitly orthogonalization effects have

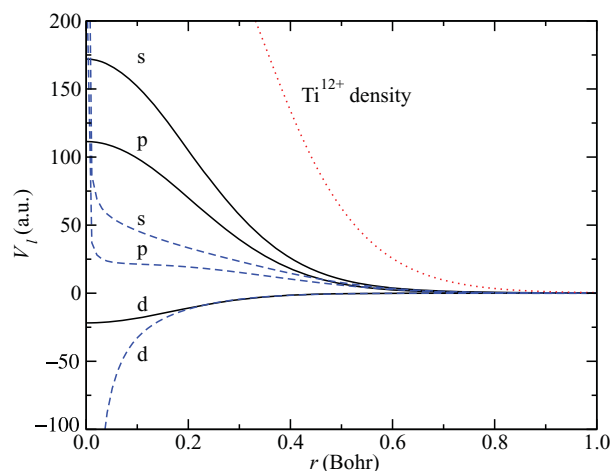


FIGURE 2 | Scalar-relativistic radial potentials V_l of an energy-consistent¹⁷ (solid lines) and a shape-consistent²⁸ (dashed lines) Ti small-core (Ne core) pseudopotential. The Ti^{12+} core electron density (dotted line, arbitrary units) is given for orientation.

to be accounted for by the PP. Another reason is the implicit inclusion of exchange effects, which depend on the l -value of the (pseudo-)valence orbital. The radial potentials V_l of two Ti small-core PPs are plotted in Figure 2 together with the Ti^{12+} core electron density. It can be seen that the PPs act essentially only inside the core, are strongly l -dependent and differ in shape between the two approaches, despite their similar good performance, cf. Table 1.

At the relativistic level, besides the main quantum number n and angular momentum quantum number l , the orbitals (or spinors) also depend on the total angular momentum j . The corresponding semilocal PP may be written as a lj -dependent effective one-electron operator^{9,10}

$$\Delta \hat{V}_{\text{cv}}(i) \cong V_{Lj}(r_i) + \sum_{l=0}^{L-1} \sum_{j=|l-\frac{1}{2}}^{j=l+\frac{1}{2}} (V_{lj}(r_i) - V_{Lj}(r_i)) \hat{P}_{lj}(i), \quad (8)$$

and can be decomposed in a spin-free averaged (av) and a spin-dependent (so) term¹¹

$$\Delta \hat{V}_{\text{cv}}(i) = \Delta \hat{V}_{\text{cv,av}}(i) + \Delta \hat{V}_{\text{cv,so}}(i), \quad (9)$$

where $\Delta \hat{V}_{\text{cv,av}}(i)$ corresponds to $\Delta \hat{V}_{\text{cv}}(i)$ defined in Eq. (6), whereas the spin–orbit term may be written as¹²

$$\Delta \hat{V}_{\text{cv,so}}(i) = \sum_{l=1}^{L-1} \frac{2\Delta V_l(r_i)}{2l+1} \hat{P}_l(i) \hat{l}_i \cdot \hat{s}_i \hat{P}_l(i), \quad (10)$$

where $\hat{l}_i = \hat{r}_i \times \hat{p}_i$ and \hat{s}_i stand for the operators of orbital angular momentum and spin, respectively.

Molecular Pseudopotentials

The VO-Hamiltonian for a molecule with n_v valence electrons reads as

$$\hat{H}_v = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \sum_{j>i}^{n_v-1} \frac{1}{r_{ij}} + \sum_i^{n_v} \hat{V}_{cv}(i) + V_{cc}. \quad (11)$$

The last two terms represent the core/nucleus–electron and core/nucleus–core/nucleus interactions of a molecular PP. $\hat{V}_{cv}(i)$ is usually approximated as a superposition of atomic PPs/potentials centered at the cores λ , with the electron–core/nucleus point charge Coulomb attraction as the leading term and an additional correction taking care of, e.g., the deviations from the point charge approximation, the Pauli-repulsion, and implicitly also relativistic contributions

$$\hat{V}_{cv}(i) = \sum_{\lambda} \hat{V}_{cv}^{\lambda}(i) = -\sum_{\lambda} \frac{Q_{\lambda}}{r_{\lambda i}} + \sum_{\lambda} \Delta \hat{V}_{cv}^{\lambda}(i). \quad (12)$$

V_{cc} can be written as a sum over pairwise-additive Coulomb repulsions between point charge cores/nuclei and additional corrections accounting for deviations from the point charge model as well as for the Pauli-repulsion between the cores

$$V_{cc} = \sum_{\lambda<\mu} \left(\frac{Q_{\lambda} Q_{\mu}}{r_{\lambda\mu}} + \Delta V_{cc}^{\lambda\mu}(r_{\lambda\mu}) \right). \quad (13)$$

The sums in Eqs (12) and (13) run over all centers λ, μ with core/nuclear charges Q_{λ}, Q_{μ} . Mutual penetration effects between small cores are not significant and the leading point-charge repulsion is a good approximation for V_{cc} . For large cores additional core–core/nucleus repulsive corrections have to be accounted for, e.g., by a Born–Mayer-type ansatz¹³

$$\Delta V_{cc}^{\lambda\mu}(r_{\lambda\mu}) = B_{\lambda\mu} \exp(-b_{\lambda\mu} r_{\lambda\mu}). \quad (14)$$

The free parameters can be determined, e.g., from FC HF calculations on core–core/nucleus pairs. We note that it is possible to mix AE (for lighter elements) and PP (for heavier elements) treatments in one calculation, i.e., to neglect the PP in Eq. (12) for the centers treated at the AE level, and to include the correction Eq. (13) only for core–core repulsion and in cases where a nucleus noticeably penetrates a core electron system.

Core-Polarization Potentials

Static and dynamic core polarization effects, i.e., core polarization at the HF level and core–valence corre-

lation, can be included in VO treatments by adding a so-called core-polarization potential (CPP) \hat{V}_{CPP} to the valence electron model Hamiltonian \hat{H}_v Eq. (11)

$$\hat{V}_{CPP} = -\frac{1}{2} \sum_{\lambda} \hat{\mu}_{\lambda} \cdot \hat{f}_{\lambda} = -\frac{1}{2} \sum_{\lambda} \alpha_{\lambda} \hat{f}_{\lambda}^2, \quad (15)$$

where $\hat{\mu}_{\lambda}$ is the dipole moment of core λ with dipole polarizability α_{λ} induced by the external electric field \hat{f}_{λ} at a core λ . The electric field is generated by all other cores and nuclei as well as all valence electrons in the system. Eq. (15) strictly applies only to large distance(s) of the polarizing charge(s) from the polarized core(s) and even diverges in the limit of vanishing distances. Therefore a cutoff function F was suggested, e.g., by Müller et al.,¹⁴ multiplying the contributions to \hat{f}_{λ} and removing such singularities

$$\hat{f}_{\lambda} = -\sum_i \frac{\vec{r}_{i\lambda}}{r_{i\lambda}^3} F(r_{i\lambda}, \delta_e^{\lambda}) + \sum_{\mu \neq \lambda} Q_{\mu} \frac{\vec{r}_{\mu\lambda}}{r_{\mu\lambda}^3} F(r_{\mu\lambda}, \delta_c^{\lambda}). \quad (16)$$

The cutoff functions can be chosen, e.g., as

$$F(r, \delta) = (1 - \exp(-\delta r^2))^n, \quad (17)$$

with n being usually 1 or 2. The cutoff parameters δ_e^{λ} and δ_c^{λ} are adjusted to suitable reference data. CPPs of the type described here often accompany large-core PPs for main group elements as well as group 11 and 12 transition metals.¹³

Form of Radial Potentials

The radial potentials $V^{\lambda}(r_{\lambda i})$ for a core λ , i.e., $V_I^{\lambda}(r_{\lambda i})$ and $V_L^{\lambda}(r_{\lambda i})$ in Eq. (6), $V_{ij}^{\lambda}(r_{\lambda i})$ and $V_{Lj}^{\lambda}(r_{\lambda i})$ in Eq. (8), and $\Delta V_I^{\lambda}(r_{\lambda i})$ in Eq. (10), are generally written as linear combinations of Gaussian type functions multiplied by powers of $r_{\lambda i}$

$$V^{\lambda}(r_{\lambda i}) = \sum_k A_k^{\lambda} r_{\lambda i}^{n_k^{\lambda}} \exp(-a_k^{\lambda} r_{\lambda i}^2) \quad \text{with} \quad n_k^{\lambda} \geq -2. \quad (18)$$

This choice was made mainly because of computational convenience and efficiency for molecular calculations, i.e., matrix elements over PP operators may then be readily evaluated in a cartesian Gaussian basis.¹⁵ The determination of the exponents a_k^{λ} and coefficients A_k^{λ} differs for energy-consistent and shape-consistent PPs as described below.

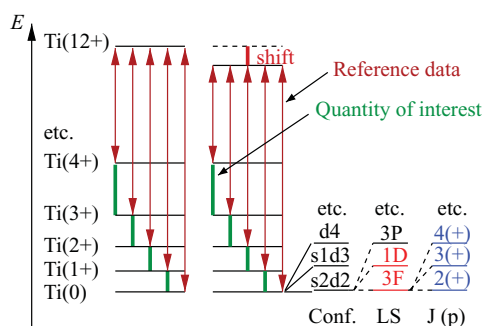


FIGURE 3 | Reference data to be used in the adjustment of a Ti small-core (Ne core) energy-consistent pseudopotential.¹⁷

Energy-Consistent Pseudopotentials

Energy-consistent PPs are based on quantum mechanical observables as reference data, i.e., total valence energies of a multitude of configurations, LS states or J levels for the neutral atom and its ions of a specific element, *cf.* Figure 3. The selection should cover all relevant charge states and electron configurations for the species to be treated with the resulting PP. Usually the ground state of the neutral atom, of low-charged cations and the anion, if it exists, as well as low-energy excited states are included. The selection may be also motivated by experimentally observed low-lying atomic states and typically comprises about 10–100 reference configurations or LS states, corresponding to a few hundred or thousand J levels.

Older energy-consistent scalar-relativistic PPs used reference energies of configurations or LS states from scalar-relativistic HF calculations applying the Wood–Boring (WB) Hamiltonian,¹⁶ which is very similar to the Cowan–Griffin (CG) approach underlying, e.g., the shape-consistent PPs of Hay and Wadt. Newer energy-consistent PPs are based on reference energies from intermediate coupling four-component multi-configuration DHF calculations with the DC Hamiltonian including a perturbative estimate of the Breit interaction (MCDHF/DC + B).

In order to determine the free parameters in Eq. (18) atomic finite-difference PP calculations for all reference configurations, LS states or J levels are performed for an initial guess of parameters using essentially the same machinery as for the AE reference calculations. The sum over squared deviations of the PP total valence energies E_I^{PP} from the AE reference values E_I^{AE} is evaluated and iteratively minimized with respect to the free parameters.

$$S = \sum_I \left(w_I [E_I^{\text{PP}} - E_I^{\text{AE}} + \Delta E_{\text{shift}}]^2 \right) = \min. \quad (19)$$

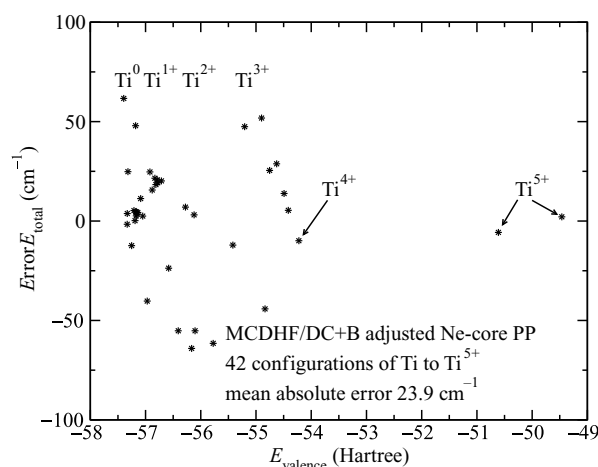


FIGURE 4 | Errors wrt AE data in valence energies of configurational averages for a DHF/DC + B-adjusted Ne-core PP for Ti.¹⁷

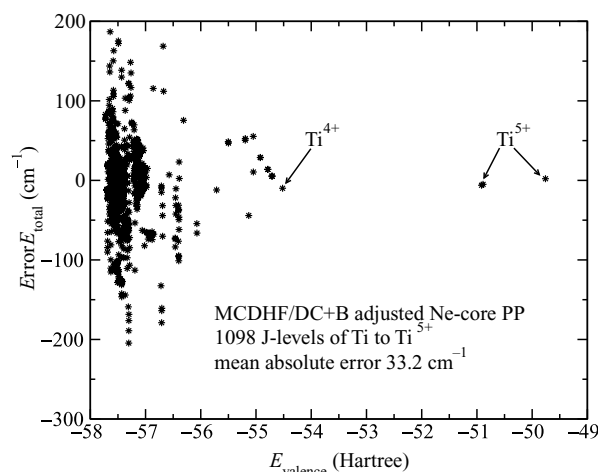


FIGURE 5 | Errors wrt AE data in valence energies of J-levels for a DHF/DC + B-adjusted Ne-core PP for Ti.¹⁷

Usually an accuracy of at least 0.1 eV is required for the total valence energies of many-electron configurations or LS states with one or two Gaussian functions per radial potential of each *l*- or *lj*-value, *cf.*, e.g., Figures 4 and 5. The global shift ΔE_{shift} (*cf.* Figure 3) is typically of the order of 1% or less of the ground state total valence energy, but it improves the accuracy of the fit by one or two orders of magnitude.

Table 1 demonstrates the accuracy of an energy-consistent DHF/DC + B-adjusted Ne-core PP for Ti in atomic calculations.¹⁷ It is noteworthy that already for a light element like Ti relativistic contributions are larger than the errors introduced by a PP. Errors in total valence energies of 42 configurations of Ti to

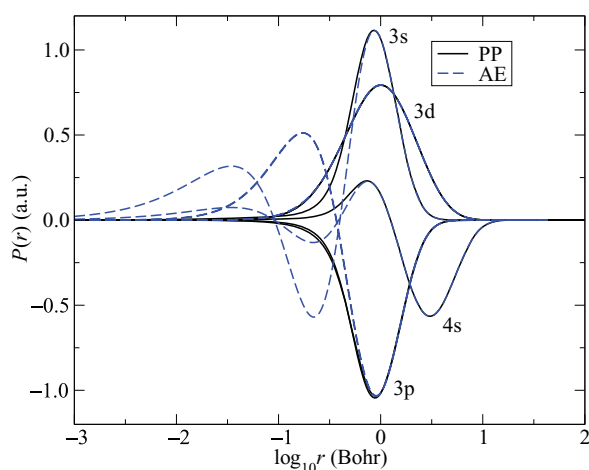


FIGURE 6 | Pseudo-valence orbitals for a Ti DHF/DC + B-adjusted Ne core pseudopotential¹⁷ in comparison to relativistic AE DHF/DC orbitals.

Ti⁵⁺ with respect to AE results are below 0.01 eV (80 cm⁻¹) and only 0.003 eV (24 cm⁻¹) on average (Figure 4). For the corresponding 1098 J-levels the errors are below 0.025 eV (200 cm⁻¹) and only 0.004 eV (32 cm⁻¹) on average (Figure 5). Figure 6 shows that the pseudo-valence orbitals agree very well with the true valence orbitals in the spatial valence region, whereas their structure is more simple in the spatial core region.

A convenient source for energy-consistent PPs and corresponding valence basis sets is, beside the original publications, the www-pages of the Stuttgart/Cologne group.¹⁸ These offer input formats for the quantum chemistry codes MOLPRO, GAUSSIAN, and TURBOMOLE and the solid state code CRYSTAL. Energy-consistent PPs without singularity at the core constructed for quantum Monte Carlo calculations are also available from the www-pages of the Cologne group.¹⁹

Shape-Consistent Pseudopotentials

In contrast to the energy-consistent *ab initio* PP approach which relies only on quantum mechanical observables as reference data, i.e., total valence energies, the method of shape-consistent PPs uses AE valence orbitals ($\varphi_{v,lj}$) and orbital energies ($\varepsilon_{v,lj}$) as reference data,^{20,21} i.e., quantities defined within an effective one-electron picture. The pseudo-valence orbital $\varphi_{p,lj}$ is required to retain the shape of the AE valence orbital $\varphi_{v,lj}$ in the valence region outside a critical radius r_c , whereas in the core region ($r < r_c$) $\varphi_{p,lj}$ is chosen

as a function f_{lj} being radially nodeless and smooth.

$$\varphi_{p,lj}(r) = \begin{cases} \varphi_{v,lj}(r) & \text{for } r \geq r_c \\ f_{lj}(r) & \text{for } r < r_c \end{cases} \quad (20)$$

The choice of r_c and f_{lj} is in certain limits arbitrary and a matter of experience. Usually, a polynomial is used for f_{lj} , e.g.,

$$f_l(r) = r^b (a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4), \quad (21)$$

where b is a constant depending on the l value. The free parameters a_i are determined, e.g., by requiring that $\varphi_p(r)$ remains normalized and that $f_l(r)$ and its first three derivatives match φ_v and its first three derivatives at r_c .

After constructing nodeless pseudo-valence orbitals for each lj -set a radial Fock equation can be set up

$$\begin{aligned} & \left(-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} - \frac{Q}{r} + \Delta V_{cv,lj}(r) \right. \\ & \quad \left. + \hat{W}_{p,lj}[\{\varphi_{p',lj'}\}] \right) |\varphi_{p,lj}(r)\rangle \\ & = \varepsilon_{v,lj} |\varphi_{p,lj}(r)\rangle. \end{aligned} \quad (22)$$

The first two terms in the parentheses are the radial kinetic-energy operator and $\hat{W}_{p,lj}$ stands for an effective valence Coulomb and exchange operator for $\varphi_{p,lj}$. With a given nodeless $\varphi_{p,lj}$ and $\varepsilon_{v,lj}$, the radial potential $\Delta V_{cv,lj}(r)$ can be determined pointwise by inversion and tabulated on a grid. By repeating this procedure for each lj -combination up to LJ , one can construct the semilocal PP of Eq. (8). For applications in subsequent calculations with basis sets, the pointwise given potentials are usually fitted by means of a least-squares criterion to a linear combination of Gaussian functions according to Eq. (18). When based on a scalar-relativistic AE HF scheme, e.g., the CG approach,²² the described procedure can also be carried out to determine scalar-relativistic PPs according to Eq. (6). The shape-consistent adjustment has been extended by Titov and Mosyagin²³ in order to allow also the extraction of radial potentials from pseudoorbitals with nodes, which improves the quality especially of small-core PPs. The authors also propose a combination of the semi-local and nonlocal ansatz for the PP, so that different operators may act on valence and semi-core orbitals. A disadvantage of the approach is the more complicated VO-Hamiltonian with a quite large number of parameters, which are determined for a single reference state.

A very popular set of PPs for main group and transition elements based on scalar-relativistic CG AE calculations was published by Hay and Wadt.^{24–26} Other less frequently used sets based on DHF/DC AE reference data were published by Christiansen and coworkers²⁷ and Stevens et al.²⁸ Table 1 demonstrates that the accuracy of a shape-consistent small-core PP²⁸ for Ti is comparable to the one of an energy-consistent PP¹⁷.

Valence Basis Sets

As important as the PP parameterization itself is the optimization of reliable valence basis sets. Therefore, most PPs are published together with corresponding valence basis sets, which are available from the original publications, PP and basis set libraries of many standard quantum chemistry codes or, e.g., the EMSL basis set exchange www-pages²⁹. The main advantage of the PP approach over the MP approach is the reduction of the size of the valence basis sets as well as relatively small basis set superposition errors due to the simplified radial nodal structure of the pseudo-valence orbitals. These advantages might be lost when large unoptimized basis sets, e.g., even-tempered basis sets, are applied. It should also be noted that due to the different radial shapes of the pseudo-valence orbitals in the core region for different PPs of a specific element only the usage of basis sets optimized for the PP under consideration will provide a reliable description. If a more extended basis set than provided for a specific PP is desired, it is thus recommended to augment the basis set coming with the PP.

For several popular PPs additional basis sets have been published separately. Weigend and Ahlrichs³⁰ optimized split-valence, triple- and quadruple-zeta valence basis sets for energy-consistent PPs for Rb to Rn excluding the lanthanides. Martin and Sundermann³¹ published correlation consistent valence basis sets for the Ga to Kr and In to Xe energy-consistent PPs. Peterson constructed correlation consistent basis sets of various sizes for all modern energy-consistent small-core PPs.^{32,33} Hay and coworkers³⁴ recently presented revised basis sets for their shape-consistent PPs which are especially suitable for density functional theory (DFT) investigations.

Integral Evaluation

The efficient evaluation of Cartesian Gaussian function multicenter integrals over PP and possibly CPP operators is an important aspect of VO calculations. McMurchie and Davidson³⁵ showed that the ma-

trix elements reduce to sums over products of angular and radial integrals and presented an algorithm without inherent limitation with respect to the angular momenta of either basis functions or PPs. Following partly their work Pitzer and Winter³⁶ presented integrals over PPs including the spin-orbit operators. Formulas for multicenter integrals over CPPs have been published by Schwerdtfeger and Silberbach³⁷ who used a Laplace transformation, and by Smit³⁸ who applied the McMurchie and Davidson scheme.

Calibration

Calibration studies are mandatory in order to check the reliability of the developed PPs and corresponding basis sets, e.g., the transferability from the atomic reference states to other states of interest, from the atom to molecules as well as uncorrelated to correlated calculations. Usually theoretically and/or experimentally accurately studied atoms and small molecules are chosen for this purpose.

Figure 7 shows that DHF/DC + B-adjusted Ne-core PPs for Sc to Ni perform as well as the AE DKH approach for basis set extrapolated CCSD(T) atomic excitation/ionization energies when compared to experimental data.¹⁷ Going to much heavier elements, a recently published relativistic energy-consistent small core (60 core electrons) PP for U was adjusted to four-component AE MCDHF/DC + B reference data with mean absolute errors (m.a.e.) of 12.3 and 196.5 cm⁻¹ for 100 reference configurations from U to U⁷⁺ and 30190 corresponding J-levels (energy range 4.7 × 10⁶ cm⁻¹), respectively.³⁹ Both atomic (U⁵⁺ 5f¹, U⁴⁺ 5f²) and molecular (UH) calibration studies have been performed.^{39,40} For U⁵⁺ both PP spin-orbit configuration interaction (SO-CI) and intermediate Hamiltonian Fock-Space Coupled-Cluster (IH-FSCC) results are in excellent agreement with experiment ($\Delta E = 7608$ cm⁻¹), i.e., deviations of 183 cm⁻¹ (2.4%) and 0 cm⁻¹, respectively, were found. For the U⁴⁺ spectrum up to 50 000 cm⁻¹ the corresponding m.a.e. with respect to the experimental data amounts to 948 and 420 cm⁻¹, respectively, whereas the best AE DCB IH-FSCC calculations exhibit a m.a.e. of 357 cm⁻¹. Finally, in case of the lowest Ω -levels of UH the bond distances, vibrational constants, and term energies from correlated AE DKH and PP calculations agree within 0.006 Å, 8 cm⁻¹, and 0.005 eV, despite the fact that the PP models DHF/DC + B calculations, whereas the DKH Hamiltonian does not include the Breit correction.

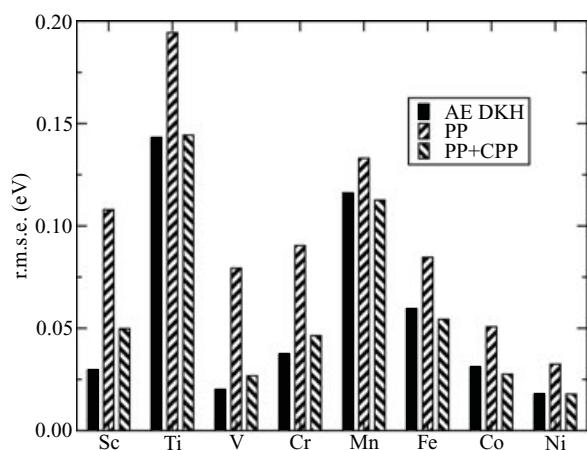


FIGURE 7 | Errors wrt experimental data in CCSD(T) $1/\beta$ basis set extrapolated $3d^n 4s^2 \rightarrow 3d^{n+1} 4s^1$, $3d^{n+2}$, $3d^n 4s^1$, $3d^{n+1}$ excitation/ionization energies for DHF/DC + B-adjusted Ne-core PPs¹⁷ and AE DKH calculations for Sc – Ni. Basis sets: DKH 25s20p15d13f11g9h, PP 15s15d13f11g9h.

MODELPOTENTIALS

The MP approach is another important, although less widely used category of ECP methods. It originates from the so-called Huzinaga–Cantu equation⁴¹

$$\left(\hat{F} + \sum_c (-2\varepsilon_c) |\varphi_c\rangle \langle \varphi_c| \right) |\varphi_v\rangle = \varepsilon_v |\varphi_v\rangle. \quad (23)$$

By adding a shift operator, i.e., the second term in parenthesis, to the Fock operator \hat{F} the energies of the core orbitals φ_c are shifted upwards from ε_c (<0) to $-\varepsilon_c$ (>0). In other words, the shift term models the repulsive effects acting on a valence electron preventing it from collapsing into the core. The valence orbital φ_v in the Huzinaga–Cantu equation keeps its correct nodal structure. Consequently, the basis sets used in MP calculations usually have to be larger than the basis sets used in PP calculations.

The molecular valence electron model Hamiltonian for the probably most successful and widely used variant of the MP method, i.e., *ab initio* model potentials (AIMPs) of Huzinaga et al.,⁴² may be written as

$$\hat{H}_v^{\text{MP}} = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \sum_{\lambda<\mu} \frac{Q_\lambda Q_\mu}{r_{\lambda\mu}} + \sum_i \sum_\lambda \left(-\frac{Q_\lambda}{r_{\lambda i}} + \hat{V}_{\text{MP},\lambda}(i) \right). \quad (24)$$

The MP $\hat{V}_{\text{MP},\lambda}(i)$ for electron i originating from core λ is defined as

$$\hat{V}_{\text{MP},\lambda}(i) = \Delta \hat{V}_{\text{C},\lambda}(i) + \Delta \hat{V}_{\text{X},\lambda}(i) + \hat{P}_\lambda(i), \quad (25)$$

where $\Delta \hat{V}_{\text{C},\lambda}(i)$ denotes the Coulomb (C) interaction between core λ and valence electron i , where the Coulomb operators $\hat{f}_{\text{C},\lambda}(i)$ are usually approximated by a linear combination of Gaussians with prefactors $1/r$

$$\begin{aligned} \Delta \hat{V}_{\text{C},\lambda}(i) &= -\frac{n_{\text{C},\lambda}}{r_{i\lambda}} + 2 \sum_c \hat{f}_{\text{C},\lambda}(i) \\ &= \frac{1}{r_{i\lambda}} \sum_k C_k^\lambda e^{-\alpha_k^2 r_{i\lambda}^2}. \end{aligned} \quad (26)$$

The exponents α_k^λ and coefficients C_k^λ are adjusted to the AE Coulomb potential in a least-squares sense under the constraint that $\sum_k C_k^\lambda = -n_{\text{C},\lambda}$ in order to enforce for $\Delta \hat{V}_{\text{C},\lambda}(i)$ the correct asymptotic behavior. $\Delta \hat{V}_{\text{X},\lambda}(i)$ represents the core–valence exchange (X) interaction with the exchange operators $\hat{K}_{\text{C},\lambda}(i)$ approximated as their spectral representation in the space defined by a set of functions χ_p^λ centered on core λ

$$\begin{aligned} \Delta \hat{V}_{\text{X},\lambda}(i) &= - \sum_c \hat{K}_{\text{C},\lambda}(i) \\ &= \sum_{p,q} |\chi_p^\lambda(i)\rangle A_{pq}^\lambda \langle \chi_q^\lambda(i)|. \end{aligned} \quad (27)$$

Since the exchange part is short ranged, only a moderate number of functions χ_p^λ is needed. In practical applications, the basis used in the spectral representation is chosen to be identical to the primitive functions of the valence basis set used for the atom under consideration and the A_{pq}^λ are calculated during the input processing of each AIMP calculation. Relativistic contributions, usually evaluated using a WB HF scheme, are also incorporated in this term. $\hat{P}_\lambda(i)$ is the shift operator associated to core λ where the core orbitals $\varphi_{\text{C},\lambda}$ are represented by sufficiently large (AE) basis set

$$\hat{P}_\lambda(i) = \sum_c (-2\varepsilon_c^\lambda) |\varphi_{\text{C},\lambda}(i)\rangle \langle \varphi_{\text{C},\lambda}(i)|. \quad (28)$$

SO coupling can be taken into account by adding to the AIMPs an effective one-electron SO operator,⁴³ similar to Eq. (10) used in PP calculations, where the parameters are determined by means of a least-squares fit to the radial components of the WB SO term¹⁶.

A related, although simpler, MP approach is the model core potential (MCP) method of Zheng and

Klobukowski.⁴⁴ Here Coulomb, exchange and relativistic contributions are all folded into a local radial potential similar to Eq. (26) and the shift operator Eq. (28) prevents the valence orbitals from collapsing to the core space.

The primary source for AIMP and corresponding valence basis sets is, besides the original publications, the www-pages of the group of Seijo.⁴⁵

SOLIDS

The use of PPs in solid state physics was initiated by the work of Phillips and Kleinman⁴ in 1959. Most of the PPs used in this very active field are constructed for DFT calculations using plane wave basis sets and thus use a large core approximation. Whereas the PPs for use in molecules are usually derived in the framework of wavefunction-based calculations (e.g., HF or DHF), the PPs for solids mainly use DFT reference data. It is beyond the scope of the current brief overview of PPs used for molecular studies to review the PP approaches designed for solids. We therefore refer the reader to a few articles describing sets of intensively used PPs for solids, e.g., scalar-relativistic PPs by Bachelet et al.,⁴⁶ soft (non-normconserving)

self-consistent PPs of Vanderbilt,⁴⁷ norm-conserving PPs of Troullier and Martins⁴⁸ or relativistic separable dual-space Gaussian PPs of Hartwigsen et al.⁴⁹ We finally note that PPs constructed for molecular applications with Gaussian basis sets can also be used in corresponding periodic DFT, HF, and post-HF calculations.

CONCLUSION

Despite the impressive development of rigorous relativistic AE approaches to electronic structure theory for systems containing heavy elements, the PP and MP approximate schemes still remain a useful workhorse in relativistic quantum chemistry. The gain in computational efficiency by restricting the explicit quantum chemical treatment to the valence electron system can hardly be denied. Moreover, modern VO approaches reach an accuracy, which allows to model accurately effects such as e.g., the full Breit interaction or even contributions from quantum electrodynamics, which are very difficult to take into account in routine calculations. PPs can even be derived for cores with e.g., open 4f- or 5f-shells, making computational lanthanide and actinide model chemistry much easier.

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