# Filling the Gap between Pseudopotential and All-Electron Schemes: Frozen-Core Calculations with Efficient Use of Density-Fitting

Hermann Stoll*

Institut für Theoretische Chemie, Universität Stuttgart D-70550 Stuttgart, Germany

ABSTRACT: Pseudopotentials simulate the interaction of the valence-electron system with frozen atomic cores using radially nodeless pseudo-orbitals. This leads to computational simplifications absent in frozen-core all-electron calculations. It is argued here that applying density fitting allows for using essentially the same (reduced) auxiliary basis sets for the valence interaction in both pseudopotential and all-electron calculations. We furthermore show that reduced auxiliary basis sets may also be made use of for fitting core Coulomb and exchange operators beyond on-site matrix elements. This leads to efficient substitutes for pseudopotentials in frozen-core all-electron calculations. At some pilot examples (Au_n, HfO, RnF_6), we demonstrate the possibility to systematically improve the accuracy of standard pseudopotential calculations with limited additional computational effort.
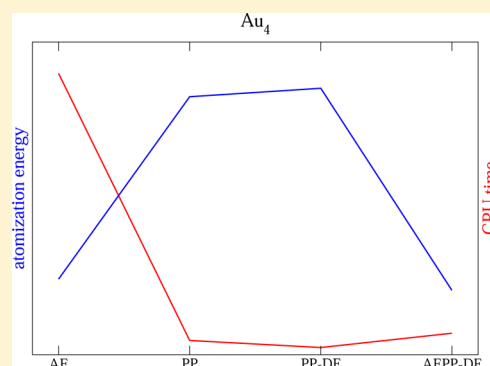
1. INTRODUCTION

Over the past decades, pseudopotentials (PP; also called effective core potentials, ECP) have been a valuable tool to extend ab initio calculations to the realm of heavy-atom compounds. Eliminating core orbitals and simulating their effect on the valence-electron system, they allow for treating atoms of a given group of the periodic table on the same footing and with the same computational effort. It is important, in this connection, that PPs are able to implicitly describe relativistic effects of the inner atomic region, so that the same formally nonrelativistic Hamiltonian can be used throughout the group. For a recent review on the variety of PP approaches, see ref 1.

For these advantages, a price has to be paid, of course. As with other computational schemes, approximations are involved in the PP treatment. Notable is the frozen-core approximation, that is, the neglect of core-orbital changes when transferring pseudopotentials from atoms to molecules. Second, the pseudo-orbital transformation, that is, the elimination of radial nodes of the valence orbitals in the core region, saves computational effort but brings about further (mostly even larger) transferability errors: the concomitant changes in valence interaction can be compensated by the PP for a limited number of (atomic) reference states only. Third, all-electron relativistic operators are not applicable in view of the changed orbital structure, and the implicit inclusion of relativistic effects into the PP by fitting to properties of selected atomic reference states is no guarantee for overall accuracy. It is fair to say that carefully adjusted PPs are often surprisingly accurate, with errors distinctly smaller than basis-set errors in ab initio calculations, but there is no systematic and controlled way of improvement.

Modern progress in computer hardware and software development influences both all-electron and PP calculations alike. In particular, density-fitting (DF) and explicitly correlated (F12) methods lead to higher efficiency and improved basis-set convergence of ab initio calculations, whether all-electron or valence-only, see for example refs 2−4. However, with increased accuracy of the treatment of valence-electron interaction, PP errors eventually become non-negligible. In the present paper, we address the question on how to improve on standard PPs while preserving the computational efficiency of this approach as far as possible.

As a first step toward a reduction of PP errors, avoidance of the pseudo-orbital transformation seems to be instrumental. At the first glance, this step does not seem to be possible without, at the same time, enlarging basis sets by core-like functions. Thus, the main computational advantages of the pseudopotential method would be lost, and the resulting scheme would bear close resemblance to model-potential and all-electron frozen-core approaches well established in literature (see, e.g., refs 5 and 6). However, DF approaches involve two kinds of basis sets, that is, orbital basis sets as well as auxiliary basis sets for density fitting, and we may well ask whether reduced PP-like basis sets can be retained at least for the latter ones. Thus, a scheme intermediate in efficiency between standard PP and all-electron treatment could be achieved. This possibility has, to the author's knowledge, not been discussed in the literature so far (see ref 7 for a preliminary account of some relevant aspects).

The main idea to be pursued in the present paper is 2-fold. First, as mentioned above, the retainment of radial nodes in the core region would necessitate, in principle, use of full all-electron basis sets. However, for the valence orbitals, the core orthogonalization tails are small corrections anyway, and for the

evaluation of valence electron interaction, reduced auxiliary DF basis sets can be expected to be sufficient. In fact, as will be shown below, essentially the same DF basis sets can be used in valence-only calculations whether or not the pseudo-orbital transformation is applied.

Second, the evaluation of the core−valence interaction involves intra-atomic and interatomic terms. For the former ones full all-electron basis sets are certainly needed, but these terms can be determined in atomic calculations and transferred unchanged to molecules. The evaluation of interatomic terms, on the other hand, can be expected to be less basis-set dependent. In fact, it will be shown that only slight extension of the PP valence DF auxiliary basis sets is needed when abandoning the pseudo-orbital transformation. This way, it is possible to cast the PP method into a truly ab initio form: no predetermined PPs are needed any more, all necessary integrals can be evaluated on-the-fly.

In the next section (section 2), we describe this new all-electron derived PP (AEPP) scheme in some detail. Section 3 contains first benchmark examples: the results for Au, Au_2, and Au_4 are used for an assessment of accuracy and efficiency of the AEPPs vs results from standard all-electron and PP calculations; HfO[8] and RnF_6[9] are examples from literature where standard PPs are known to have difficulties and where a systematic improvement with AEPPs might be especially useful. Section 4, finally, gives conclusions.

2. ALL-ELECTRON DERIVED PSEUDOPOTENTIALS (AEPP)

A common approximation for the treatment of chemically inactive groups in ab initio all-electron (AE) calculations is the use of frozen orbitals for these groups. This involves the neglect of changes of these orbitals when going from some reference system (usually an atom) to systems of interest with a different chemical environment; it also involves the neglect of electron correlation effects for these groups. Thus, the choice of the inactive groups (size of atomic cores, e.g.) is a critical issue. However, a controlled improvement is always possible by reducing the size of the groups, that is, by relaxation of some frontier orbital shells.

Using the frozen-core (FC) approximation, the AE calculation can be restricted to the valence-electron system, with the valence Hamiltonian

$$H_v = \sum_i^{n_v} \left(h_i + \sum_c V_i^c \right) + \sum_{i,j}^{n_v} \frac{1}{r_{ij}} \tag{1}$$

$$V^c = \sum_{k_c} (2J_{k_c} - K_{k_c}) \tag{2}$$

Here, the electron indices i, j run over the valence electrons only (n_v being the number of valence electrons), and h_i and $1/r_{ij}$ are the usual one-electron and two-electron operators. The impact of the frozen groups c on the valence electrons is contained in the Coulomb and exchange operators, J_{k_c} and K_{k_c}, where the sum runs over the orbitals of the frozen groups which are assumed to be doubly occupied.

In order to keep the valence-electron system (strongly) orthogonal to the frozen groups, one can either use valence basis functions explicitly orthogonalized to the frozen groups,[6] or one uses the full basis set together with level shifts

$$H_v \rightarrow H_v + \sum_c P^c \tag{3}$$

$$P^c = \sum_{k_c} \lambda_{k_c} |\phi_{k_c}\rangle\langle\phi_{k_c}| \tag{4}$$

moving the frozen orbitals ϕ_{k_c} to high energies.[5]

In view of the strong-orthogonality requirement, computational advantages over a standard AE calculation are limited. The same primitive basis set is needed in both cases. It is possible to reduce the number of contractions for the valence-only calculation by orthogonalization to the cores, but at the expense of contracting basis functions over different atoms. Such a contraction pattern is not normally possible in quantum-chemical codes and requires a transformation of the two-electron integrals.

However, even when using the same orbital basis set in the frozen-core calculation as in the AE one, computational simplifications over a full AE calculation are possible. Standard generally contracted AE basis sets contain fixed linear combinations for core orbitals. The valence orbitals in the frozen-core calculation have only small (orthogonalization) tails with respect to these core basis functions. An explicit description of the orthogonalization tails is important especially for the kinetic energy (Pauli repulsion) and also for relativistic effects arising in the core region. For two-electron valence Coulomb and exchange interactions, on the other hand, their contribution is less significant. Therefore, a reduction of the auxiliary basis set for density fitting (DF) of valence two-electron integrals in the FC calculation seems to be possible:

$$(pq|rs) \approx (\widetilde{pr|rs})_v = \sum_{A_v,B_v} (pq|A_v)[J^{-1}]_{A_v,B_v}(B_v|rs) \tag{5}$$

Here, the $(pq|rs)$ are 2-electron integrals over orbital basis functions used to describe valence orbitals. The $(pq|A_v)$ and $J_{A_v,B_v} = (A_v|B_v)$ are 3-index and 2-index electron-repulsion integrals involving auxiliary basis functions. The formula is the standard one for density fitting in Coulomb metric,[10−14] except that the DF auxiliary basis functions A_v, B_v are restricted to a 'valence' subset of those needed for an AE calculation—for example, those optimized for a corresponding PP calculation. Still, with respect to a full PP calculation, the orbital basis set $\{p\}$ is larger, but the enhancement factor for the FC calculation over the PP one becomes proportional to the square of the ratio between the sizes of AE and PP basis set (instead to the fourth power). As an additional advantage, high angular momentum auxiliary basis functions that would be needed for high-l core orbitals in the AE calculation are no longer needed in the FC one. From the viewpoint of accuracy, on the other hand, it is to be noted that density fitting within a Coulomb metric is known to be a robust fitting, that is, deviations of the fitted basis function product distributions pq or rs lead to second order errors in their self-interactions. Thus, neglect of the small orthogonalization tails in the fitting basis can be expected to be small if not negligible.

Let us now turn our consideration from the treatment of valence interaction to core contributions. Clearly, in a frozen-core formalism, calculation of intracore contributions is not needed since they are fixed and only add a constant shift to the total energy. The geometry-dependent intercore contributions cannot be neglected but are liable to a simplified treatment: for spherically symmetric nonoverlapping cores a point-charge

approximation has been proven to be sufficiently accurate in PP work.[1] On the other hand, core−valence interaction, that is, the action of the core Coulomb and exchange operators on the valence system, requires a more sophisticated treatment. However, because of the frozen-core assumption, these operators do not change during the SCF optimization and need to be evaluated only once. Moreover, the important part of core−valence interaction is of intra-atomic origin, while it can be modeled by a simple point-charge potential in the long-range limit. This suggests the following approximate treatment: use precomputed intra-atomic matrix elements of core Coulomb and exchange, for each given core, and apply density fitting for all the rest of the matrix elements:

$$\langle p| \sum_{k_c} (J_{k_c} - K_{k_c}) |q\rangle$$

$$\approx \sum_{r_c,s_c} D^c_{r_c s_c} \begin{cases} [2(pq|r_c s_c) - (pr_c|qs_c)] & \text{for} \quad \{p, q\} \equiv \{p_{[c]}, q_{[c]}\} \\ [2\overline{(pq|r_c s_c)}_{v'} - \overline{(pr_c|qs_c)}_{v'}] & \text{otherwise} \end{cases}$$

(6)

Here, $D^c_{r_c s_c}$ is the density matrix of the frozen group (core) c; r_c and s_c are core-like basis functions for this group, and $p_{[c]}$, $q_{[c]}$ are basis functions of the atom carrying core c; the integrals $\overline{(pq|r_c s_c)}_{v'}$, $\overline{(pr_c|qs_c)}_{v'}$ are density fitted integrals as above but use an auxiliary basis set $\{A_{v'}, B_{v'},...\}$ not necessarily identical to that of eq 5. The transfer of atomic matrix elements for a given core (upper line of eq 6) from the atom to the molecule is certainly consistent with the basic ideas of pseudopotential theory. With respect to the DF integrals (lower line of eq 6), it is seen that the exchange matrix elements involve at least one orbital product of a core basis function with a basis function centered at another atom—these products are small. For the DF Coulomb matrix elements this is not necessarily the case; however, the 'large' matrix elements describe the Coulomb interaction of a spherically symmetric core with surrounding atoms and do not present much difficulty for the DF auxiliary basis set. Thus, due to the use of exact intra-atomic terms, the need for overly tight and high-l functions $A_{v'}$, $B_{v'}$ in the auxiliary basis can be avoided. In fact, as will be shown below, valence auxiliary basis sets designed for PPs need to be only slightly extended for the present purpose, for example, by adding a few tight low-l functions in an even-tempered way. The treatment of core−valence interaction described in this paragraph has the advantage that it bypasses pseudopotential fits altogether and can be improved in a systematic and transparent way, just by enlarging the core−valence auxiliary basis.

3. TESTS AND APPLICATIONS

Within the present section, all-electron (AE) calculations use the third order Douglas−Kroll−Hess (DKH3) operator[15] for taking scalar-relativistic effects into account. Pseudopotential (PP) calculations use the scalar-relativistic energy-consistent PPs of the Stuttgart−Cologne groups.[1,16] Valence-only calculations with the AE-derived PPs (AEPP) are performed at the DKH3 level, using projectors P^c (eq 4) in order to prevent occupation of core orbitals. We use large prefactors of $\lambda_{k_c} > 10^4$ E$_h$, in order to make the results independent of these parameters.

All calculations are performed using the Molpro ab initio suite of programs.[17,18] CPU times in the tables refer to calculations in C_1 symmetry on a Intel I5-3550 (3.3 GHz) workstation. For the (integral-direct) DF calculations, the CPU

times include integral evaluation; otherwise, the time for integral evaluation is included in t_{SCF}. In the open-shell case, SCF calculations are done as RHF ones, and RMP2 energies are extracted from the RCCSD or DF-RMP2 modules of Molpro, respectively.

3.1. Au$_n$. The Au atom is a good showcase for pseudopotential application, since it is a heavy atom with large relativistic effects. The pseudopotential[19] replaces a core with 60 electrons including high-l shells (up to 4f) while the 19 valence electrons occupy orbitals with lower angular momentum quantum numbers (5spd, 6s). We use basis sets of triple-ζ quality, the cc-pVTZ-DK3 set[20] in the all-electron case (93 contractions per atom), and the comparable cc-pVTZ-PP set[21] in the pseudopotential case (63 contractions). When applying density fitting, we invoke the def2-TZVPP-JKfit[22] and cc-pVTZ-MP2fit[23] auxiliary basis sets for SCF and MP2 calculations, respectively, both of them derived for use with energy-consistent PP. We present valence energies (total minus core energies) at the SCF level and MP2 correlation contributions obtained when correlating the Au 5d6s shells, together with corresponding CPU times.

Results for the Au atom are listed in Table 1. It turns out that the PP energies considerably deviate from the all-electron

Table 1. AEPP Results for the Au Atom, in Comparison to Reference All-Electron (AE) and Pseudopotential (PP) Ones[a]

	E_{SCF}	ΔE^{MP2}_{corr}	t_{SCF}	t_{MP2}
AE reference[b]	−136.122138	−0.364258	15.6	1.28
PP[c]	−134.780779	−0.383855	0.3	0.41
PP-DF[d]	−134.780776	−0.383861	0.7 (8 iter.[f])	0.12
AEPP-DF(v)[e]	−136.128915	−0.364027	4.2 (14 iter.[f])	0.41

[a]Valence SCF energy, E_{SCF}, and MP2 correlation energy (active space: 5d6s), ΔE^{MP2}_{corr}, in E$_h$, CPU times t (C$_1$ symmetry) in seconds. [b]Scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis (93 contractions).[20] [c]Scalar-relativistic PP from ref 19, cc-pVTZ-PP basis (63 contractions).[21] [d]As footnote c, density fitting (DF): JKfit def2-TZVPP,[22] MP2fit cc-pVTZ-PP.[23] [e]AEPP calculation, scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis (93 contractions), density fitting for valence interaction DF(v): JKfit def2-TZVPP, MP2fit cc-pVTZ-PP. [f]Number of SCF iterations.

reference values, by 1.3 E$_h$ and 0.02 E$_h$ at the SCF and MP2 levels, respectively. While the SCF deviation is caused by the fact that the PP reference energies are extracted from spin−orbit averaged Dirac−Hartree−Fock rather than scalar-relativistic DKH3 calculations, the MP2 deviation is mainly caused by the elimination of radial nodes in the pseudo-orbitals,[24] which leads to a typical overestimation of the PP correlation energy (5% in the present case). On the other hand, CPU times are much lower in the PP case, by a factor of 50 for SCF, due to the considerably smaller basis set. Density fitting (DF) in the PP calculation turns out to be rather accurate, with energy changes of <10^{-5} E$_h$, but an efficiency gain does not yet show up in the atomic case (since DF calculations are done as direct SCF/MP2 ones).

Turning now to the AEPP approach of the present paper, it can be seen that the resulting atomic energies closely mimic the full all-electron ones, with deviations of 0.007 E$_h$ and 2 × 10^{-4} E$_h$ at the SCF and MP2 levels, respectively. The price to pay for this advantage is an increase of the CPU time by a factor of 3−4 with respect to the PP-DF one (when the time per iteration is compared in the SCF case). The increase in CPU time is

roughly proportional to the square of the ratio of the number of orbital basis functions in the AE and PP calculations, respectively; see section 2.

Note that the AEPP data for the Au atom refer to the valence-only calculation with given (fixed) core−valence potential; the DF approximation is only applied to the valence interaction. If one would apply the DF approximation with the reduced PP-optimized auxiliary basis set also to the calculation of the core−valence potential, a large error of the order of 4 E_h would result. It is for this reason that we recommend to precalculate atomic core−valence potentials in the atomic basis sets, for the purpose of using them in molecular calculations.

Note also that we need level shifts, in the valence-only AEPP calculation, in order to prevent occupation of core orbitals. As mentioned above, we use large prefactors, but even a Huzinaga-type level-shift of $\lambda_{k_c} = -2\epsilon_{k_c}$ (where ϵ_{k_c} is the orbital energy of core orbital ϕ_{k_c}) would be reasonably accurate: the valence SCF energy does not change, the MP2 correlation energy increases by $\approx 1\%$.

As a next step, we consider SCF atomization energies and MP2 correlation contributions to atomization energies of Au$_2$ and Au$_4$; see Tables 2 and 3. For Au$_2$, we use the experimental

Table 2. AEPP Results for the Au$_2$ Molecule ($r_{Au-Au} = 2.4715$ Å), in Comparison to Reference All-Electron (AE) and Pseudopotential (PP) Ones[a]

	$E_{at,SCF}$	$\Delta E_{at,corr}^{MP2}$	t_{SCF}	t_{MP2}
AE reference[b]	−0.028050	−0.058959	238	2.8
AE-fc[c]	−0.028012	−0.058904		
PP[d]	−0.026499	−0.059641	6.8	0.6
PP-DF[e]	−0.026471	−0.059616	5.4 (9 iter.[h])	0.3
AEPP-DF(v)[f]	−0.028102	−0.058936	23.6 (14 iter.[h])	1.1
AEPP-DF(v+cv)[g]	−0.028077	−0.059030	+2[i]	

[a]SCF atomization energy, $E_{at,SCF}$, and MP2 correlation contribution (active space: Au 5d6s) to the atomization energy, $\Delta E_{at,corr}^{MP2}$, in E_h, CPU times t (C$_1$ symmetry) in seconds. [b]Scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis (186 contractions).[20] [c]Frozen-core ($1s - 4f$) AE calculation. [d]Scalar-relativistic PP from ref 19, cc-pVTZ-PP basis (126 contractions).[21] [e]As footnote d, density fitting (DF): JKfit def2-TZVPP,[22] MP2fit cc-pVTZ-PP.[23] [f]AEPP calculation, scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis (186 contractions), density fitting for valence interaction DF(v): JKfit def2-TZVPP, MP2fit cc-pVTZ-PP. [g]AEPP calculation with density fitting also for core−valence interaction: JKfit def2-TZVPP uncontracted +3s1p1d (exponents s, 26, 52, 104; p, 124; d, 74). [h]Number of SCF iterations. [i]Additional CPU time for setting up the molecular core−valence potential.

bond length of 2.472 Å;[25] for Au$_4$, the D$_{2h}$ rhombus is taken, with side length 2.725 Å and a short diagonal of 2.648 Å optimized in density functional calculations (B3LYP functional).

Let us first discuss results for Au$_2$. It is seen that the atomization energies virtually coincide in all-electron reference and frozen-core calculations, both for the (rather weak) SCF bond and the (dominating) correlation contribution; deviations are of the order of 5×10^{-5} E_h. Although the frozen-core approximation is so well satisfied, PP calculations yield atomization energies off the all-electron values by 0.001−0.002 E_h (5% of the total SCF value). While the source of the SCF deviation is unclear (it could be due to shortcomings of the AE DKH3 relativistic treatment as well as to PP shortcomings), the MP2 correlation contribution is probably

Table 3. AEPP Results for Au$_4$ (D$_{2h}$ Structure[a]), in Comparison to Reference All-Electron (AE) and Pseudopotential (PP) Ones[b]

	$E_{at,SCF}$	$\Delta E_{at,corr}^{MP2}$	t_{SCF}	t_{MP2}
AE reference[c]	−0.075033	−0.163939	2249	84.4
PP[d]	−0.072700	−0.163710	114.1	18.0
PP-DF[e]	−0.072592	−0.163650	57.4 (9 iter.[h])	2.7
AEPP-DF(v)[f]	−0.075176	−0.163890	171.7 (17 iter.[h])	8.5
AEPP-DF(v+cv)[g]	−0.075243	−0.164108	+14.5[i]	

[a]Side length of the rhombus $r_{Au-Au} = 2.725$ Å, short diagonal 2.648 Å (optimized at B3LYP level). [b]SCF atomization energy, $E_{at,SCF}$, and MP2 correlation contribution (active space: Au 5d6s) to the atomization energy, $\Delta E_{at,corr}^{MP2}$, in E_h, CPU times t (C$_1$ symmetry) in seconds. [c]Scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis (372 contractions).[20] [d]Scalar-relativistic PP from ref 19, cc-pVTZ-PP basis (252 contractions).[21] [e]As footnote d, density fitting: JKfit def2-TZVPP,[22] MP2fit cc-pVTZ-PP.[23] [f]AEPP calculation, scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis (372 contractions), density fitting for valence interaction DF(v): JKfit def2-TZVPP, MP2fit cc-pVTZ-PP. [g]AEPP calculation with density fitting also for core−valence interaction: JKfit def2-TZVPP uncontracted +3s1p1d (exponents s, 26, 52, 104; p, 124; d, 74). [h]Number of SCF iterations. [i]Additional CPU time for setting up the molecular core−valence potential.

slightly overestimated with the PP due to the elimination of radial nodes in the valence orbitals. On the other hand, the efficiency of PP calculations is clearly apparent from the very favorable CPU times, which show reductions by factors of 35 and 5 for SCF and MP2, respectively; with density fitting, the situation even becomes slightly better, especially for MP2 (reduction by another factor of 2).

With the new AEPP, results are intermediate: the atomization energies are definitively closer to the all-electron than to the PP ones—the AEPP accuracy is in the range of 0.1 mE$_h$. However, CPU times increase by a factor of $\approx 3-4$ with respect to the PP ones (comparing CPU times per iteration, in the SCF case). Concerning density fitting in the AEPP calculation, it turns out that the PP-derived auxiliary JKfit basis is sufficient for describing valence interaction, but for the fitting of the core Coulomb and exchange terms decontraction of the $(13s12p11d9f5g3h2i)/[13s11p10d8f4g3h2i]$ auxiliary basis set[22] and addition of a few tight low-l basis functions (we used an even-tempered extension by a $3s1p1d$ set) is required to match the accuracy of the valence interaction.

As a corollary, I would like to stress that level-shifting of the core orbitals to high energies is vital for the AEPP calculation, not only to avoid swapping of core and valence orbitals in the valence-only calculation but also to remove any spurious admixture of core orbitals to valence ones. Orthogonalization of valence basis functions to core orbitals for each atom separately, as suggested in ref 6, is not sufficient; mixture of core AOs at one atom to valence basis functions of the other atom leads (in conjunction with Huzinaga-like level shifts) to unacceptable results for Au$_2$, with an SCF atomization energies too low by a factor of more than 2.

Turning finally to Au$_4$, it is seen that CPU times become substantial now in the all-electron case (>2000 s and ~100 s, for SCF and MP2, respectively), and that pseudopotentials tend to become the method of choice (reducing the CPU times by factors of 20 and 5, for SCF and MP2, even without density fitting; with density fitting, reduction factors of 40 and 30, respectively, can be achieved). The new AEPP formalism

requires CPU times higher than the PP ones by factors 2–3 (and the cost for setting up the core–valence operators amounts to around 1–2 additional SCF cycles), but the results are significantly closer to the AE reference values than the PP ones and could easily be made even more accurate.

3.2. HfO. Early $5d$ transition-metal compounds are critical cases for pseudopotentials: the $4f$ shell is usually attributed to the pseudopotential core, since it is spatially localized in the inner atomic region, but it is still energetically high-lying at the beginning of the row. Indeed, it has been shown for HfO[8] that pseudopotential errors with respect to all-electron calculations are unusually large, of the order of 5 kcal/mol for the dissociation energy and 2 pm for the bond length. For comparison, basis-set errors beyond triple-ζ level are between 4 and 5 kcal/mol and between 0 and 1 pm, respectively. Note that, in addition, correlation of the $4f$ shell is not negligible: it contributes with 2 kcal/mol to D_e and 1 pm to r_e. This means that for an accurate treatment of HfO, the $4f$ shell has to be either included in the valence space or simulated by a core-polarization potential.

However, for the purpose of comparing AE and PP calculations of HfO to corresponding ones with our new AEPP, we use the 12-valence-electron energy-consistent PP[20] with its standard core definition. Frozen-core orbitals are the Hf $1s$–$4f$ ones, and for the construction of the AEPP we extracted them from an atomic calculation for Hf^{2+}. In Table 4, we

Table 4. AEPP Results for HfO, in Comparison to Reference All-Electron (AE) and Pseudopotential (PP) Ones[a]

	$r_{e,SCF}$	$r_{e,MP2}$	$D_{e,SCF}$	$D_{e,MP2}$
AE reference[b]	1.7091	1.7557	0.1858	0.3389
AE-fc[c]	1.7133	1.7620	0.1849	0.3373
PP[d]	1.6949	1.7431	0.1923	0.3427
PP-DF[e]	1.6949	1.7431	0.1923	0.3424
AEPP-DF(v)[f]	1.7135	1.7623	0.1849	0.3370
AEPP-DF(v+cv)[g]	1.7134		0.1849	

[a]Counterpoise-corrected SCF and MP2 (valence correlation only, excluding the $5s5p$ shells of Hf) values for bond length r_e in Å, and dissociation energy D_e in E_h. [b]Scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis for Hf,[20] aug-cc-pVTZ for O.[26,27] [c]Frozen-core AE calculation, $1s$–$4f$ core from $Hf^{2+}(6s^2)$. [d]Scalar-relativistic PP from ref 20, cc-pVTZ-PP basis for Hf,[20] aug-cc-pVTZ for O. [e]As footnote d, density fitting: JKfit def2-TZVPP for Hf,[22] aug-cc-pVTZ for O;[28] MP2fit cc-pVTZ-PP for Hf,[29] aug-cc-pVTZ for O.[13] [f]AEPP calculation, scalar-relativistic effects at DKH3 level, cc-pVTZ-DK3 basis for Hf, aug-cc-pVTZ for O, density fitting for valence interaction DF(v): JKfit def2-TZVPP for Hf, aug-cc-pVTZ for O; MP2fit cc-pVTZ-PP for Hf, aug-cc-pVTZ for O. [g]AEPP calculation with density fitting also for core–valence interaction: JKfit def2-TZVPP uncontracted $+2s1p$ (exponents s, 60, 120; p, 100) for Hf.

present counterpoise-corrected values for r_e and D_e of HfO, both at the SCF and the MP2 level. For MP2, where we correlated only the genuine valence orbitals ($5d$ and $6s$ for Hf), we eliminated mixing of the Hf $4f_0$ orbital with the lowest valence sigma one by means of a localization in the space of these two orbitals, in the AE case, in order to get a meaningful comparison with PP and AEPP. Basis sets used are cc-pVTZ-DK3 (93 contractions)[20] and cc-pVTZ-PP (63 contractions)[20] for Hf, in the AE and PP cases, respectively, while aug-cc-pVTZ[26,27] was used for O. Auxiliary basis sets for density fitting are def2-TZVPP[22] for Hf, aug-cc-pVTZ[28] for O (JKfit), and cc-pVTZ-PP[29] for Hf, aug-cc-pVTZ[13] for O (MP2fit). Note that

the Hf auxiliary basis sets were optimized for PP calculations again.

The results show that, as judged from the all-electron reference calculation, the introduction of the frozen-core approximation leads, as expected, to a slight increase of the bond length and decrease of the dissociation energy, by 0.4 (0.6) pm and 0.9 (1.6) mE_h at the SCF (MP2) level, respectively. The standard PP should simulate the frozen-core results, from the theoretical point of view, but in practice, the results deviate from the fully variational all-electron reference to the other side, leading to a decrease of bond length by 1.4 (1.3) pm and an increase of D_e by 7 (4) mE_h. The new AEPP approach, on the other hand, closely reproduces the frozen-core results, as it should, with negligible deviations if the density-fitting approximation is involved for valence interaction only. If the density-fitting approximation is also invoked for the (intermolecular part of) core–valence interaction, it turns out to be necessary again, to decontract the Hf JKfit auxiliary basis set and add a few tight sp functions (we used an even-tempered $2s1p$ extension), in order to preserve the high accuracy.

3.3. RnF$_6$. As another example of a case where standard energy-consistent pseudopotentials lead to larger errors than usual, let me mention bonding in rare-gas hexafluorides. Bonding here is to a large extent a correlation effect: at the CCSD(T) equilibrium geometry of the O_h structure of RnF_6 (r(Rn–F) = 1.977 Å), for example, SCF is antibonding by 34 kcal/mol. Peterson and co-workers[9] found that pseudopotentials overestimate bonding in RnF_6 by around 3–4 kcal/mol. It turns out that this error has little to due with correlation: the antibonding effect at the SCF level is reduced by 4 kcal/mol with PPs.

We reproduced Peterson's results, comparing DKH3 all-electron reference calculations to PP calculations with the scalar-relativistic energy-consistent PP of ref 30 and the new AEPP approach (also relying on a DKH3 scalar-relativistic treatment). As orbital basis sets, we used aug-cc-pwCVTZ-DK3 (125 contractions) for Rn[9] and aug-cc-pVTZ-DK for F,[26,27,31] in the AE and AEPP cases; in the PP case, we used aug-cc-pwCVTZ-PP (96 contractions) for Rn[32] and aug-cc-pVTZ for F.[26,27] As auxiliary basis sets, we applied def2-ATZVPP sets throughout.[22] For the purpose of setting up the Rn core Coulomb and exchange operators, we used the Rn def2-ATZVPP set uncontracted.

The results, cf. Table 5, clearly show that the above-mentioned PP defect does not originate from the frozen-core approximation. The SCF dissociation energies are very nearly the same, with and without this approximation. With PP, the antibonding effect becomes lower by 4 kcal/mol as mentioned above. Note that this is a case where the introduction of the PP does not alleviate the computational effort very much as compared to the AE case; however, in conjunction with the DF approximation, the CPU time is reduced by an order of magnitude with respect to the AE calculation. With our new AEPP approach, the CPU time per SCF iteration is practically the same as in the PP-DF case, but the SCF energy difference is now within half a kcal/mol of the AE reference result. Note that this accuracy is achieved independently on whether the DF approximation is only applied to the valence interaction or also to the setting up of the core–valence potential.

4. CONCLUSIONS

All-electron derived PP (AEPP) have been introduced in the present paper, as a computational scheme intermediate

Table 5. AEPP Results for RnF$_6$, O$_h$ Structure^b, in Comparison to Reference All-Electron (AE) and Pseudopotential (PP) Ones^a

	$E_{at,SCF}$	t_{SCF}
AE reference^c	34.36	705
AE-fc^d	34.37	
PP^e	30.42	356
PP-DF^f	30.47	49 (9 iter.^{i})
AEPP-DF(v)^g	34.79	5 (per iter.)
AEPP-DF(v+cv)^h	34.93	

^{a}SCF atomization energy, $E_{at,SCF}$, in kcal/mol, CPU times t (C$_1$ symmetry) in seconds. $^b r$(Rn−F) = 1.9770 Å.^{9} ^{c}Scalar-relativistic effects at DKH3 level, aug-cc-pwCVTZ-DK3 basis^9 for Rn, aug-cc-pVTZ-DK^{26,27,31} for F. ^{d}Frozen-core AE calculation. ^{e}Scalar-relativistic PP from ref 30, aug-cc-pwCVTZ-PP basis^{32} for Rn, aug-cc-pVTZ^{26,27} for F. ^{f}As footnote e, density fitting: JKfit def2-ATZVPP,^{22} with additional diffuse functions as described in the Molpro basis set library.^{18} ^{g}AEPP calculation, scalar-relativistic effects at DKH3 level, aug-cc-pwCVTZ-DK3 basis for Rn, aug-cc-pVTZ-DK for F, density fitting for valence interaction DF(v): JKfit def2-ATZVPP. ^{h}AEPP calculation with density fitting also for core−valence interaction: JKfit def2-ATZVPP uncontracted. ^{i}Number of SCF iterations.

between standard pseudopotential calculations and frozen-core all-electron ones. No prefitted potentials are needed any more, all necessary quantities are evaluated on-the-fly, in atomic and molecular calculations. Approximations with respect to the frozen-core all-electron approach are contained within the density-fitting basis sets chosen (one for the valence interaction and one for the long-range [beyond intra-atomic] field of the cores). Test calculations seem to indicate that PP-derived valence-only auxiliary basis sets (or only slightly enlarged versions) are sufficient for reaching an accuracy surpassing that of standard PP calculations. More extensive and systematic studies are underway to corroborate these findings.

In contrast to standard PPs, the AEPP approach can easily be extended, in essentially unchanged form, to the modelization of frozen orbital groups around an active center in a complex. This may be a promising field for future applications of the AEPP.

■ AUTHOR INFORMATION

Corresponding Author
*Email: stoll@theochem.uni-stuttgart.de.

Notes
The authors declare no competing financial interest.

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