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Improved relativistic energy-consistent pseudopotentials for 3d-transition metals

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Abstract Energy-consistent relativistic pseudopotentials for 3d-transition metals Sc to Ni based on modified valence energies are proposed. The pseudopotentials are adjusted at the finite difference level within the intermediate coupling scheme with respect to multi-configuration Dirac–Hartree–Fock data based on the Dirac–Coulomb Hamiltonian with an estimate of the Breit contributions in quasidegenerate perturbation theory. Typically a few hundred to thousand J levels arising from about 35 to 40 configurations ranging from the anion down to the highly charged cation are considered as references. It is shown that introducing a small common energetic shift of all valence energies reduces the errors in the parameter adjustment considerably. Results of highly correlated atomic and molecular test calculations using large basis sets and basis set extrapolation techniques are presented.

Keywords Pseudopotential · Core-polarization potential · Transition metals · Transition metal oxides · Spectroscopic constants

1 Introduction

The effective core potential (ECP) method is almost as old as quantum mechanics [1, 2] and has developed during the last three decades into one of the most efficient tools for electronic structure calculations on heavy element compounds [3–18], where relativistic effects [19–30] are large. Among the two varieties of the ECP valence-only approach, i.e., the model potential (MP) approach working with valence orbitals conserving the correct nodal structure of the all-electron (AE) valence orbitals and the pseudopotential (PP) approach using pseudo-valence orbitals exhibiting a simplified radial nodal structure, the latter appears to be more popular.

The PPs currently used most frequently, in traditional molecular quantum chemistry, were derived either by the shape-consistent or the energy-consistent approach. In the former, the PP is extracted for a single atomic reference state by inversion of the radial Hartree–Fock (HF) equation, keeping the one-particle energy fixed and using an a priori constructed nodeless pseudo-valence orbital which is smoothed in the spatial core region and agrees exactly with the AE valence orbital in the spatial valence region. In contrast to this, the energy-consistent approach proposed by the Stuttgart group of Stoll and coworkers about 20 years ago does not use one-electron quantities as orbitals and orbital energies as reference data, but rather uses total valence energies of a multitude of electronic states of the neutral atom and not too highly charged ions. The development of the Stuttgart PP approach during the last decades is characterized mainly by changes in the choice of the AE reference data. The original so-called energy-adjusted scalar-relativistic PPs for 3d-transition metals were derived at the HF level and simple relativistic correction potentials extracted from Dirac–Hartree–Fock (DHF) data for the one-valence electron systems and the core electron system have been added [31]. Later, the quasirelativistic Wood–Boring HF scheme allowed a direct adjustment to scalar-relativistic reference data [32, 33] and also the derivation of approximate spin-orbit operators [34]. Finally, the switch to state-averaged multi-configuration Dirac–Hartree–Fock (MCDHF) reference data, based on the Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) Hamiltonian, and a two-component adjustment of the PPs in the intermediate coupling scheme was performed [35]. The latter approach was used more recently to extract PPs for heavy main group elements [15, 36–38] as well as transition metals with closed *d*-shell [39, 40]. Results for atoms as well as for ScO obtained with a preliminary set of such PPs for Sc to Ni have been published recently [41]. The present work introduces a slight modification of the fitting procedure which leads to significant improvements of the accuracy and allows to incorporate a much larger range of ionization levels, including those with ionization from semi-core orbitals resulting also in an improved description of these. In addition the improvements

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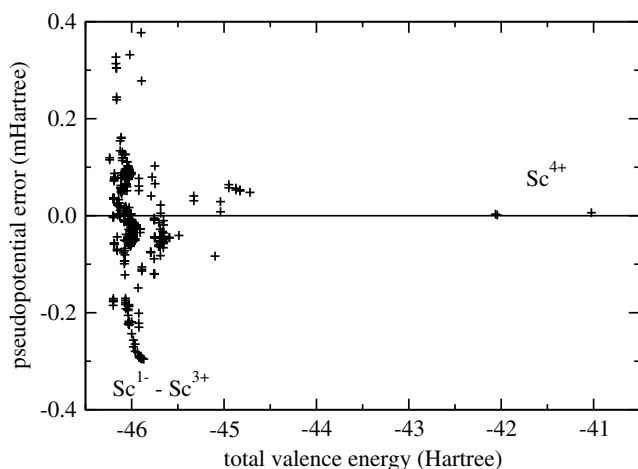


Fig. 1 Errors in energy differences between individual J-levels and the neutral atom ground-state J-level of Sc and its ions Sc^{1-} to Sc^{4+} (393 J-levels arising from 34 nonrelativistic configurations) obtained from finite-difference multi-configuration calculations in the intermediate coupling scheme with respect to corresponding AE MCDHF data obtained with the DCB Hamiltonian

obtained by adding a core-polarization potential (CPP) are investigated. The new scheme is tested for the atoms Sc to Ni and the diatomic molecules ScO and FeO.

2 Method

The method of relativistic energy-consistent ab initio pseudopotentials is described in detail elsewhere [15, 17] and will be outlined here only briefly. The valence-only model Hamiltonian for a system with n valence electrons and N cores/nuclei is given as

$$\mathcal{H}_v = -\frac{1}{2} \sum_i \Delta_i + \sum_{i<j}^n \frac{1}{r_{ij}} + V_{cv} + V_{cpp} + \sum_{\lambda<\mu}^N \frac{Q_\lambda Q_\mu}{r_{\lambda\mu}}. \quad (1)$$

Here i and j are electron indices, λ and μ core/nucleus indices. The nonrelativistic kinetic energy expression and the unmodified Coulomb repulsion are used for the valence electrons. The terms V_{cv} and V_{cpp} stand for core-valence interaction and core polarization potentials, respectively. It is hoped that a suitable parametrization of V_{cv} and V_{cpp} is able to compensate all errors resulting from the restriction of the quantum mechanical treatment to the valence electrons, thus reducing the computational effort when compared to AE calculations of similar quality.

Relativistic contributions result mainly from the parametrization of the ECP V_{cv} , which describes the interactions of the valence electrons with all cores/nuclei present in the system, and to a lesser extent from the parametrization of V_{cpp} , which accounts for static and dynamic core-polarization effects.

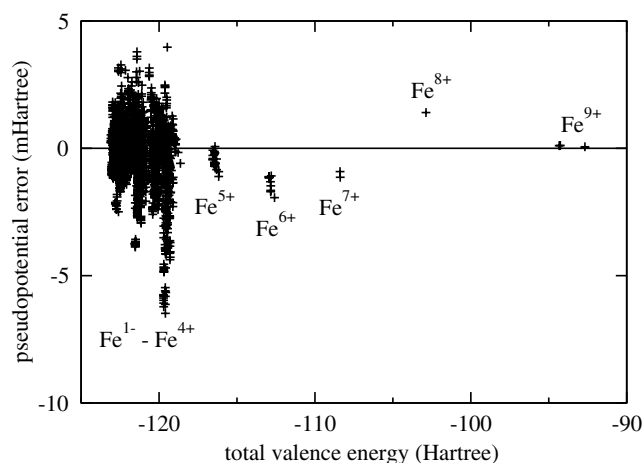


Fig. 2 As Fig. 1, but for Fe^{1-} to Fe^{9+} (3895 J-levels arising from 40 nonrelativistic configurations)

2.1 Pseudopotentials

The molecular ECP is assumed to be a superposition of atomic ECPs centered at the N nuclei λ , with the Coulomb attraction between point charges as the leading term

$$V_{cv} = \sum_i^n \sum_\lambda^N \left(-\frac{Q_\lambda}{r_{\lambda i}} + \Delta V_{cv}^\lambda(\vec{r}_{\lambda i}) \right) + \dots \quad (2)$$

Clearly, for elements treated without ECP approximation $\Delta V_{cv}^\lambda = 0$ and Q_λ equals the nuclear charge Z_λ . For the 3d-transition metal PPs presented here $Q_\lambda = Z_\lambda - 10$, i.e., a [Ne] core is adapted (small-core PPs). Although 3d-transition metal PPs with an [Ar] core can be derived, their reliability is weaker than for those with a [Ne] core [42]. The point charge approximation for the interaction between the nuclei/cores adopted in Eq. (1) is usually sufficiently accurate for such small-core 3d-Ps.

For modern quasirelativistic PPs, i.e., including spin-orbit coupling, a semilocal ansatz in two-component form was found to be a reasonable compromise between accuracy and efficiency

$$\Delta V_{cv}^\lambda(\vec{r}_{\lambda i}) = \sum_{l=0}^{L-1} \sum_{j=|l-1/2|}^{l+1/2} (V_{lj}^\lambda(r_{\lambda i}) - V_L^\lambda(r_{\lambda i})) P_{lj}^\lambda(i) + V_L^\lambda(r_{\lambda i}). \quad (3)$$

The operator P_{lj}^λ projects onto spinor spherical harmonics centered at the core λ

$$P_{lj}^\lambda(i) = P_{l, |l \pm 1/2|}^\lambda(i) = P_\kappa^\lambda(i) = \sum_{m_j=-j}^j |\lambda l j m_j(i)\rangle \langle \lambda l j m_j(i)|. \quad (4)$$

The PPs presented here have $L = 4$ and $V_L^\lambda = 0$. If spin-orbit coupling is neglected, i.e., for scalar-quasirelativistic calculations, a one-component form may be derived by averaging over spin, i.e., for $l > 0$

$$V_l^\lambda(r_{\lambda i}) = \frac{(l+1)V_{l+1/2} + lV_{l-1/2}}{2l+1} \quad (5)$$

Table 1 Parameters (in a.u.) for the PPs of Sc ($Q = 11$) and Fe ($Q = 16$)

l	j	A_{lj}	a_{lj}	A_{lj}	a_{lj}
0	1/2	103.39636451	11.40346291	239.74474466	22.14297277
0	1/2	22.49320935	5.29646042	46.15501318	9.284655032
1	1/2	68.58037955	10.89458017	131.26794703	22.28449301
1	3/2	61.10485326	10.51320358	111.90692883	22.16423924
1	1/2	10.78318086	4.58180753	34.05612421	9.38245156
1	3/2	12.40791536	4.76544377	38.96853335	9.46218842
2	3/2	-31.43223769	17.03883955	-21.95819141	26.69705846
2	5/2	-36.78241045	18.83835552	-21.97341392	26.89933437
2	3/2	0.23197752	3.89174427	-1.27506048	8.97801127
2	5/2	0.12374551	3.69203788	-1.21589680	8.94834948
3	5/2	-4.13501446	7.65260834	-7.52149105	16.16577847
3	7/2	-5.80750904	8.80518896	-12.76642956	20.57989729

leading to a scalar-relativistic PP

$$\Delta V_{\text{cv,av}}^\lambda(\vec{r}_{\lambda i}) = \sum_{l=0}^{L-1} (V_l^\lambda(r_{\lambda i}) - V_L^\lambda(r_{\lambda i})) P_l^\lambda(i) + V_L^\lambda(r_{\lambda i}). \quad (6)$$

Now the operator P_l^λ projects onto the spherical harmonics centered at the core λ

$$P_l^\lambda(i) = \sum_{m_i=-l}^l |\lambda m_l(i)\rangle \langle \lambda m_l(i) |. \quad (7)$$

The potentials V_{lj}^λ , V_l^λ and V_L^λ are as usual represented as linear combinations of Gaussians, i.e., after dropping the indices l , j and L these expansions are of the type

$$V^\lambda(r_{\lambda i}) = \sum_k A_k^\lambda \exp(-a_k^\lambda r_{\lambda i}^2). \quad (8)$$

Usually in the energy-consistent PP approach the free parameters in the above ansätze were determined by minimizing the sum S of weighted-squared errors in the total valence energies E_J^{PP} of J-levels [Eq. (3)] [35] or LS-states [Eq. (6)] [31] with respect to the unmodified AE reference energies E_J^{AE} , i.e., $\Delta E = 0$ in

$$S = \sum_I (w_I [E_I^{\text{PP}} - E_I^{\text{AE}} + \Delta E]^2) := \min \quad (9)$$

In the present work the weights w_I were chosen to be equal for all J-levels arising from a nonrelativistic configuration and all nonrelativistic configurations were assigned to have equal weights. For the adjustment of the parameters with $l \leq 2$ a total of 34 configurations (Sc⁻ to Sc⁴⁺) with 393 J-levels and 40 configurations (Fe⁻ to Fe⁹⁺) with 3895 J-levels were chosen for Sc and Fe, respectively. Note that the number of reference states/configurations is considerably larger than for previously published PPs, e.g., the old scalar-relativistic PPs for Sc and Fe used only 7 and 13 reference energies of LS-states of the neutral atom and the monocation [31]. The relativistic PPs for Sc and Fe described recently used already 112 and 992 J-levels, respectively, arising from 13 configurations of the neutral metal, the monocation and the dication [41]. In contrast to this earlier work a global valence

Table 2 Atomic spinor energies (Hartree) from state-averaged finite difference PP and AE MCDHF/DC calculations of Sc [Ar] $3d^1 4s^2$ and Fe [Ar] $3d^6 4s^2$

AS	Sc		Fe	
	PP	AE	PP	AE
$3s_{1/2}$	-2.5916	-2.5861	-4.2823	-4.2697
$3p_{1/2}$	-1.5884	-1.5854	-2.8321	-2.8156
$3p_{3/2}$	-1.5682	-1.5659	-2.7715	-2.7549
$3d_{3/2}$	-0.3361	-0.3361	-0.5967	-0.5975
$3d_{5/2}$	-0.3353	-0.3355	-0.5913	-0.5915
$4s_{1/2}$	-0.2114	-0.2113	-0.2638	-0.2637

energy shift ΔE is now introduced as an additional adjustable parameter. Whereas the restriction to $\Delta E = 0$ in the original method implied that, e.g., the ground-state valence energy equals the sum of all ionization potentials leading from the neutral atom to the core-electron system, this is not the case for the new fitting procedure. Here only the sum of all ionization potentials leading from the neutral atom to the most highly ionized system included in the fit is reproduced correctly, i.e., in case of the present 3d-PPs all charge states between the anion and the cations with [Ne] $3s^2 3p^5$ and [Ne] $3s^1 3p^6$ configurations are considered. Despite the fact that in the present work ΔE amounts to only about 0.5 % of the neutral atom total valence energy, it is found that the value of the above sum S can be reduced by one or two orders of magnitude when it is treated as an adjustable parameter.

The terms for $l = 3$ were adjusted to the four energetically lowest [Ne] nf^1 configurations with eight J-levels of the one-valence electron ions Sc¹⁰⁺ and Fe¹⁵⁺. Since the results are only less affected by the $f_{5/2}$ and $f_{7/2}$ potentials, this simple fitting procedure is sufficient.

2.2 Core-polarization potentials

The use of CPPs together with large-core PPs was also proposed by Stoll and coworkers more than 20 years ago [43, 44]. The form of the CPP accounting for both static and dynamic polarization of the PP core was adopted from AE work of Meyer and coworkers [45, 46], i.e.,

$$V_{\text{CPP}} = -\frac{1}{2} \sum_{\lambda} \alpha_D^\lambda \mathbf{f}_{\lambda}^2 \quad (10)$$

with

$$\mathbf{f}_{\lambda} = \sum_i^n \frac{\mathbf{r}_{i\lambda}}{r_{i\lambda}^3} \omega(r_{i\lambda}) - \sum_{\mu \neq \lambda}^N Q_{\mu\lambda} \frac{\mathbf{r}_{\mu\lambda}}{r_{\mu\lambda}^3} \omega(r_{\mu\lambda}) \quad \text{and} \quad (11)$$

$$\omega(r) = (1 - \exp(-\delta r^2)).$$

Here α_D^λ is the dipole polarizability of the TM [Ne]-core λ and \mathbf{f}_{λ} is the electric field generated at the site of this core by the valence electrons (at relative positions $\mathbf{r}_{i\lambda}$) and the other cores or nuclei ($Q_{\mu\lambda}$, at relative positions $\mathbf{r}_{\mu\lambda}$). The cutoff parameter δ in the cutoff factor ω was adjusted at the coupled cluster level with single and double as well as perturbative

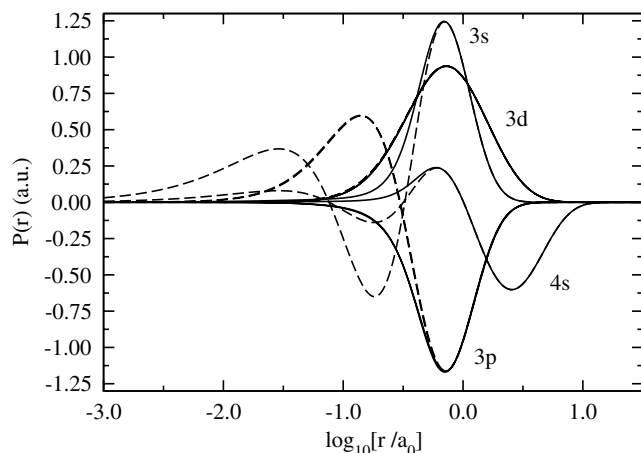


Fig. 3 Radial spinors of Fe in the [Ar] $3d^6 4s^2$ configuration from AE MCDHF (dashed lines) and energy-consistent PP (solid lines) finite difference calculations. Note that the difference between the $j = l - 1/2$ and $j = l + 1/2$ spinors is too small to be visible here

triple excitations (CCSD(T)) [47–49] after extrapolation to the basis set limit to the experimental first, second and third ionization potentials of the Sc atom. Since the higher ionization potentials for many transition metals are not accurate enough to serve as reference data, the same cutoff factor was used for Sc through Ni.

2.3 Valence basis sets and extrapolation

Even-tempered valence basis sets (15s15p15d13f11g9h) have been generated by minimizing the sum of the CISD energies of the lowest LS states arising from the TM [Ar] $3d^n 4s^2$, $3d^{n+1} 4s^1$, $3d^{n+2}$ and $M^+ 3d^n 4s^1$, $3d^n$ configurations ($n = 1$ to 8 for Sc to Ni). Similar to previous work on lanthanides [50,51] and actinides [52,53], the nearly linear behavior of the total valence energy in $1/l^3$ for $l > 2$ was used for the atomic calculations to extrapolate the results to the basis set limit. Here l denotes the largest angular quantum number present in the valence basis set. For molecules it was found that l has to refer to the TM basis set in order to get a good fit. The basis set superposition error was eliminated by the counter-poise correction [54]. After successful calibration of the new PPs it is planned to supplement them with correlation consistent valence basis sets of different sizes, e.g., as previously done for heavy main group elements [38].

2.4 Programs

AE reference and PP adjustment atomic calculations in intermediate coupling within the finite difference scheme were carried out with a modified version of the relativistic MCDHF atomic structure code GRASP [55]. The PP parameters were optimized with the quasi-Newton procedure of Murtagh and Sargent [56]. The dipole polarizabilities α_D^λ of the [Ne] cores

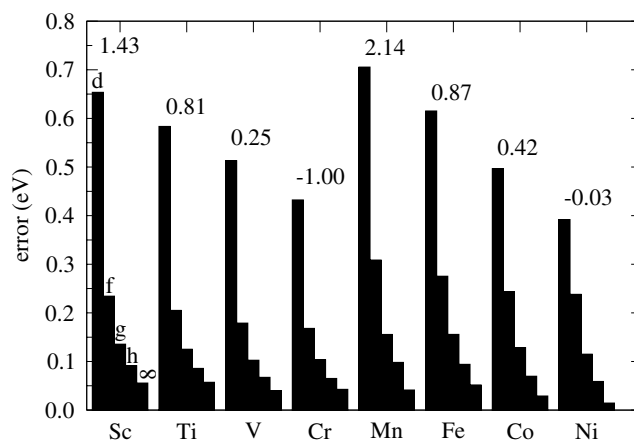


Fig. 4 Excitation energies $s^2 d^n \rightarrow s^1 d^{n+1}$ of Sc to Ni from CCSD(T) calculations with 15s15p15d13f11g9h valence basis sets with respect to spin-orbit averaged experimental data [59]. The experimental values are listed over the error bars (in eV)

were calculated within a coupled DHF scheme using the atomic finite difference program of Kolb and Johnson [57]. All scalar-relativistic and spin-orbit configuration interaction calculations using finite basis sets reported here were performed with the MOLPRO program package [58].

3 Results and discussion

A selection of results for Sc and Fe will be presented here in order to demonstrate the accuracy of the new PPs. The parameters to be used in connection with Eqs. (3), (5), (6) and (8) are listed in Table 1. Experimental data has been taken from the tables of Moore [59] and the book of Huber and Herzberg [60], unless otherwise noted.

3.1 Atoms

The accuracy of the fit of the s -, p - and d -terms of the PPs can be judged from the errors in the energy difference between all J-levels considered as reference data in the fit and the ground-state J-level of the neutral atom. Figures 1 for Sc and Figure 2 for Fe reveal that the PP errors amount to at most a few milli-Hartree. In case of Sc the maximum deviations are -8 meV and 10 meV for the 9th J-level of the Sc^{2+} [Ar] $3d^2$ and the 11th J-level of the Sc^{1+} [Ar] $3d^1 4s^1 4p^1$ configuration, respectively. For Fe the maximum deviations are -176 meV and 108 meV for the 43rd and 135th J-level arising from the [Ar] $3d^3 4s^1 4p^1$ configuration of Fe^{3+} . As discussed elsewhere, these errors are partly due to the frozen-core approximation, partly due to the overestimation of intershell exchange interaction when using pseudo-valence orbitals. The maximum deviations of the the average energies of the nonrelativistic configurations are -6 meV and 3 meV for Sc and -60 meV and 38 meV for Fe. In contrast

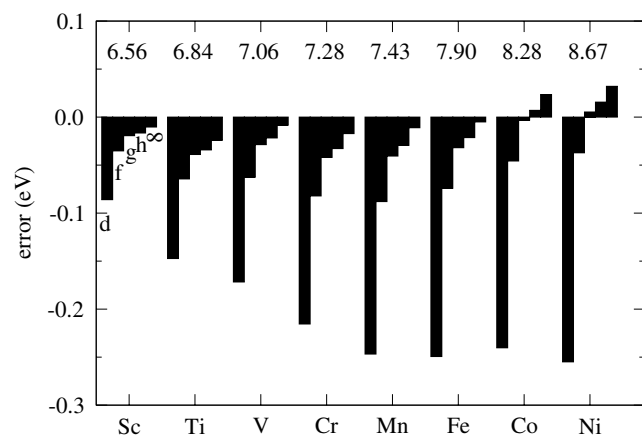


Fig. 5 As Fig. 4, but for the $s^2 d^n \rightarrow s^1 d^n$ ionization energies

Table 3 Ionization potentials IP_n ($n = 1-3$) of Sc from basis set extrapolated CCSD(T) results using a PP without and with CPP in comparison to experimental values averaged over fine structure components (in eV)

n	Exp.	PP	Error	PP+CPP	Error
1	6.56	6.55	-0.01	6.56	-0.02
2	19.36	19.38	0.02	19.35	-0.01
3	44.12	43.95	-0.17	44.12	0.00

Dipole polarizability $\alpha_D = 0.016357$;
Cutoff parameter $\delta = 12.0$ (in a.u.)

to the scalar-relativistic PPs published almost 20 years ago [31] as well as a recent set of relativistic MCDHF-adjusted PPs [41], the new PPs now can also describe quite accurately highly ionized states.

Since only total valence energies enter as reference data in the adjustment process, one might question the quality of the pseudo-valence orbitals/spinors. Figure 3 however demonstrates for the ground-state configuration of Fe that in the spatial valence region an excellent agreement is obtained with corresponding AE orbitals/spinors, whereas in the spatial core region the oscillations of the latter are eliminated. It is to be noted that the inclusion of highly excited configurations as $[\text{Ne}] 3s^2 3p^5$ and $[\text{Ne}] 3s^1 3p^6$ of Sc^{4+} and Fe^{9+} lead to a better (smoother) shape of the pseudo-valence orbitals in the spatial core region and also bring the one-particle electron energies closer to the corresponding AE values (Table 2).

Using the scalar relativistic PPs, two excitation energies ($3d^n 4s^2 \rightarrow 3d^{n+1} 4s^1, 3d^{n+2}$) and two ionization energies ($3d^n 4s^2 \rightarrow 3d^n 4s^1, 3d^{n+1} 4s^1$) have been calculated for all atoms at the CCSD(T) level using basis set extrapolation techniques. The results are consistently slightly better than those reported earlier for other PPs [41]. As an example the calculated data for the excitation $3d^n 4s^2 \rightarrow 3d^{n+1} 4s^1$ and ionization $3d^n 4s^2 \rightarrow 3d^n 4s^1$ energies of each element are graphically displayed in Figs. 4 and 5, respectively. Although the errors in the basis set extrapolated results are well below 0.1 eV, the values can still be further improved by adding the CPP to the PP. Figure 6 demonstrates this in the case of Sc.

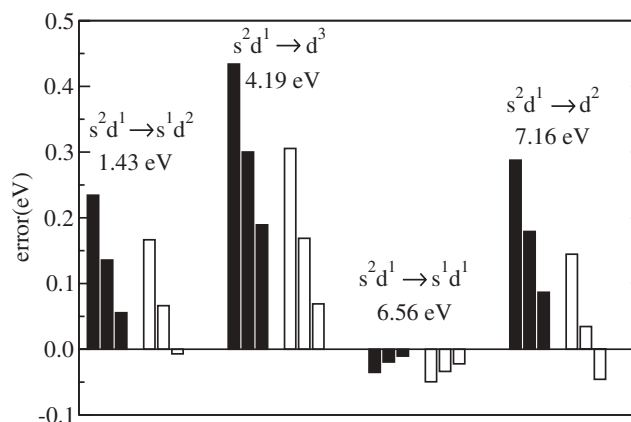


Fig. 6 Excitation and ionization energies of Sc from CCSD(T) PP (black bars) and PP+CPP (empty bars) calculations with respect to spin-orbit averaged experimental data [59]. Three neighboring bars correspond to results for $15s 15p 15d 13f$ and $15s 15p 15d 13f 11g$ valence basis sets as well as the basis set limit. The experimental values are listed over the error bars (in eV)

Table 4 As table 3, but for IP_n ($n = 1-8$) of Fe

n	Exp.	PP	Error	PP+CPP	Error
1	7.90	7.89	-0.01	7.89	-0.01
2	24.09	24.18	0.09	24.15	0.06
3	54.75	54.70	-0.05	54.72	-0.03
4	109.50	109.43	-0.07	109.57	0.07
5	184.61	184.65	0.04	184.95	0.34
6	283.73	283.57	-0.16	284.10	0.37
7	408.74	408.14	-0.60	408.97	0.23
8	559.78	558.65	-1.13	559.85	0.07

Dipole polarizability $\alpha_D = 0.005616$;
Cutoff parameter $\delta = 12.0$ (in a.u.)

In addition the higher ionization potentials up to the first ionization from the $3p$ semi-core orbitals were calculated. Tables 3 and 4 summarize the results of the extrapolation to the basis set limit. Note that the CPP cutoff parameter has been adjusted to the experimental values for Sc, and then used also for the other 3d transition elements. Figure 7 shows that without/with CPP the higher ionization potentials can be reproduced at the basis set extrapolation CCSD(T) level with errors of less than 2.5 eV (1.4%)/1.0 eV (0.8%) for all elements considered here.

3.2 Molecules

Two diatomic molecules in their electronic ground states, i.e., $\text{ScO}^2\Sigma^+$ (leading configuration $\text{Sc}^{2+} 4s\sigma^1 \text{O}^{2-}$) and $\text{FeO}^5\Delta$ (leading configuration $\text{Fe}^{2+} 4s\sigma^1 3d\delta^3 3d\pi^2 \text{O}^{2-}$), have been studied. ScO has been investigated very well both theoretically and experimentally and can serve to calibrate PPs for Sc [41,61]. In contrast to this, the situation for FeO appears to be less clear and both theoretical as well as experimental investigations encounter severe difficulties, e.g., the wave-

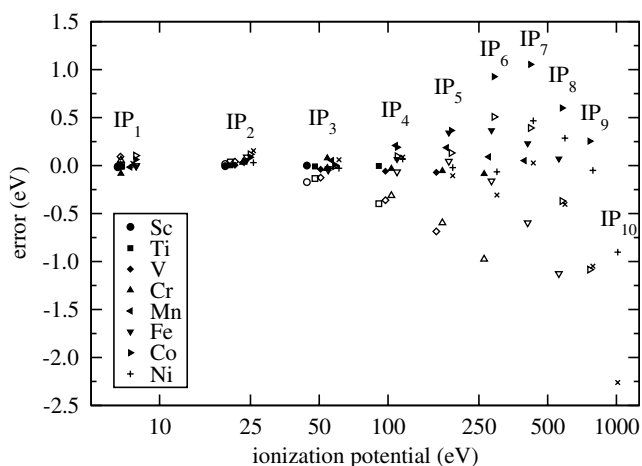
Table 5 Bond length R_e (Å), binding energy D_e (eV) and vibrational constant ω_e (cm^{-1}) for ScO $^1\Sigma^+$ and FeO $^5\Delta$ from CCSD(T) and CASSCF/AQCC calculations, respectively, in comparison to experimental data

basis sets	ScO			FeO		
	R_e	D_e (D_0)	ω_e	R_e	D_e (D_0)	ω_e
l	1.720/1.734	5.91/5.61	921/906	1.640/1.657	2.79/2.55	835/802
$l+1$	1.677/1.682	6.63/6.53	969/962	1.603/1.609	3.33/3.21	902/890
$l+2$	1.671/1.673	6.83/6.79	976/974	1.595/1.597	3.52/3.49	920/917
$l+3$	1.669/1.669	6.92/6.91	980/979	1.593/1.594	3.61/3.59	927/925
ext. ^a	1.666/1.666	7.00/7.00	983/983	1.590/1.589	3.68/3.69	934/935
exp.	1.668 ^b	7.02 (6.96) ^c 6.98 (6.92) ^d	973 ^b	(1.57) ^e 1.616 ^g	4.26 (4.20) ^e	965 ^e , 970 ^f 880 ^g , 882 ^h

The notation .../... refers to results without/with counter-poise correction of the basis set superposition error

The entries $l, l+1, \dots$ denote the maximum angular quantum number included in the basis sets of O ($l=1; 15s9p5d4f3g$) and Fe ($l=2; 15s15p15d13f11g9h$)^a basis set extrapolation

^b ScO: R_0 instead of R_e given [60] ω_e derived from $\Delta G(1/2)$ and $x_e\omega_e$ [60]; ^c D_e derived from D_0^0 [69]; ^d D_e derived from D_0^0 [70]; ^e D_e derived from D_0^0 [60]; ^f Ref. [65,66]; ^g Ref. [67]; ^h Ref. [68]

**Fig. 7** Errors of ionization potentials derived from CCSD(T) PP (empty symbols; Ni: x) and PP+CPP (filled symbols; Ni: +) calculations extrapolated to the basis set limit in comparison to experimental data [59]

function exhibits a difficult multi-reference character [62] and the optical spectrum is ‘frankly a nightmare’ and ‘exhibits little regularity or beauty’ [63]. The results for basis set extrapolation studies at the CCSD(T) level for ScO and the complete active space self-consistent field/averaged coupled cluster (CASSCF/AQCC) [64] level for FeO are listed in Table 5. The basis set extrapolated results including a CPP for R_e , D_e and ω_e within 0.004 Å, 0.04 eV and 4 cm^{-1} with those without CPP and therefore will not be reported here. Spin-orbit effects have negligible influence on R_e and ω_e and only lead to a small lowering of D_e by ≈ 0.01 eV for both ScO and FeO.

Excellent agreement with the experimental values is obtained for ScO, i.e., the errors of the basis set extrapolated CCSD(T) results in the bond length, binding energy and vibrational constant are only -0.002 Å, 0.02 eV and 10 cm^{-1} , respectively.

A much more difficult multi-reference case is FeO in the $^5\Delta$ ground state, as already noted by Bauschlicher and Mai-

tre [62]. At the CASSCF level the Fe $3d$ and $4s$ as well as the O $2p$ orbitals were kept active, resulting in 12 electrons in 9 active orbitals and 270/260 CSFs in the A_1/A_2 irreducible representation of the C_{2v} point group. The AQCC expansions allowed for excitations from all orbitals except O $1s$ and comprised upto 18×10^6 contracted configurations (4.8×10^9 uncontracted configurations). Despite this large computational effort our best estimate for the binding energy (3.69 eV) is ≈ 0.6 eV lower than the experimental value (4.26 eV) [60], very similar to the result of the AE calculations of Bauschlicher and Maitre [62]. Compared to the vibrational frequency given by Huber and Herzberg (965 cm^{-1}) [60,65], which was confirmed in 1995 by Fan and Wang [66], our best value (935 cm^{-1}) is still too low by 30 cm^{-1} , whereas it is too high by ≈ 55 cm^{-1} compared to newer values given by Cheung et al. (880 cm^{-1}) [67] and Drechsler et al. (882 cm^{-1}) [68]. In addition, our best calculated bond length (1.589 Å) is 0.03 Å shorter than the most recent experimental value (1.616 Å) [67], but still 0.02 Å longer than the estimate given by Huber and Herzberg (1.57 Å) [57]. Unfortunately, more extensive correlation treatments (e.g., the inclusion of Fe $4p$ into the active space) were not feasible.

Our PP results (1.603 Å, 3.83 eV, 896 cm^{-1}) come into good agreement with the AE averaged coupled pair functional (ACPF) values of Bauschlicher and Maitre (1.609 Å, 3.65 eV, 885 cm^{-1}) [62] when we try to mimic their calculations, i.e., use their aug-cc-pVQZ basis sets for O and their (3f 2g) polarization set for Fe, include $\sigma(\text{Fe } 4p)$ in the active space (for evaluating R_e and ω_e), freeze besides the O $1s^2$ shell also the Fe $3s^2 3p^6$ shells at the ACPF level and do not apply the counter-poise correction for the basis set superposition error. We note however, that in contrast to the PP calculations, relativistic contributions have not been taken into account in the AE study, which might partly explain some of the remaining differences. Finally it is fair to state that the seemingly good agreement between some experimental values ($R_e = 1.616$ Å, $\omega_e = 880$ or 882 cm^{-1}) and theoretical results obtained at this level is most likely fortuitous.

4 Conclusions

A new fitting scheme based on modified total valence energies for energy-consistent PPs has been proposed and tested for the 3d-transition metals Sc to Ni adopting a small-core definition. Accurate results were obtained for atomic excitation and ionization energies, as well as for molecular constants of the diatomic test molecule ScO. It has further been shown that the addition of a core polarization potential improves especially the atomic results, despite the small ‘unpolarizable’ [Ne] cores used.

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