Spin-free relativistic no-pair *ab initio* core model potentials and valence basis sets for the transition metal elements Sc to Hg. Part I

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Relativistic one-component *ab initio* core model potentials are presented for first-, second-, and third-row transition elements; corresponding valence spaces comprise the ns, $(n-1)d$, and $(n-1)p$ shells. Direct relativistic effects on the valence electrons are explicitly taken into account by using one-component relativistic kinetic energy and Douglas–Kroll transformed no-pair nuclear attraction interaction operators. The Coulombic part of the atomic core–valence interaction has been fitted to the corresponding all-electron mean-field operators whereas a matrix representation has been chosen for the exchange part. While not involved in the fitting process, all-electron orbital energies and radial expectation values of the valence orbitals are very well reproduced in atomic model potential calculations. Molecular test calculations have been performed on selected transition metal oxides. Employing a $[4s,4p,4d]$ contraction of the valence basis, excellent agreement between core model potential and all-electron no-pair results is achieved for bond distances, harmonic frequencies, and dissociation energies. © *1999 American Institute of Physics.* [S0021-9606(99)30708-X]

I. INTRODUCTION

The use of one-component relativistic core potentials has become a common means to include spin-independent kinematic relativistic effects in molecular calculations. In most cases these relativistic core potentials have been generated by parameterizing nonrelativistic effective valence Hamiltonians such that they—in a least squares sense—reproduce eigenvalues or eigenvectors of a one-component relativistic atomic reference calculation. In this way relativistic effects are included solely by means of the core–valence interaction. This approximation works reasonably well because a large percentage of the relativistic effects in the valence shell is caused indirectly by a change of inner shell energies and shapes. Often, large-component Dirac–Fock[1] orbitals have served as a reference to which the core potentials were fitted. Commonest in this group are the two-component relativistic effective potentials by Ermler, Ross, Christiansen, and coworkers,[2] from which averaged and spin–orbit relativistic effective potentials have been extracted. Alternatively, one-component relativistic Hamiltonians have been used in all-electron reference calculations. The pseudopotentials by Hay and Wadt,[3] Barthelat and Durand,[4] the effective core potentials by the Stuttgart group,[5] and the *ab initio* model poten-

tials (AIMP) by Barandiarán and Seijo[6,7] are well-known representatives of the latter derived from atomic Cowan–Griffin[8] calculations.

Recently, Wittborn and Wahlgren presented relativistic AIMPs for third-row transition elements that include only the indirect relativistic effects in the core potentials.[9] Direct relativistic effects on the valence electrons are treated explicitly by using the relativistic kinetic energy and electron–nuclear interaction expressions of the Douglas–Kroll (DK) Hamiltonian. The latter is a spin-free relativistic Hamiltonian resulting from a transformation of a four-component no-pair Hamiltonian containing projectors to the positive energy spectrum of an electron in the (external) field of a nucleus.[10]

The Douglas–Kroll operator is a variationally stable one-component relativistic Hamiltonian that can be employed in all-electron treatments of molecular systems.[11] This offers the possibility of testing the performance of a core model potential by direct comparison with molecular all-electron results. The same applies to the Chang–Pelissier–Durand operator.[12] By contrast, the variational solution of the Cowan–Griffin equations is restricted to atoms. The corresponding mass–velocity and Darwin terms are unbounded from below and special boundary conditions at the nucleus are imposed on the atomic orbitals in order to handle this problem. In molecules, the all-electron Cowan–Griffin operator must be used in first-order perturbation theory in which the atomic relativistic potentials are fixed.[8]

We report on no-pair relativistic AIMPs and valence basis sets for the first-, second-, and third-row transition ele-

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ments. The number of primitive functions to describe the valence region is considerably smaller than in the primitive sets used by Wittborn and Wahlgren for the third-series transition elements.[9] For all transition elements we compare valence orbital energies and radial expectation values from all-electron and AIMP atomic calculations to provide a quality check for the model potentials and valence basis sets. Molecular test calculations have been carried out for the electronic ground states of the group 5 and group 10 monoxides. A comparison of spectroscopic parameters obtained from either type of calculation enables us to decide whether the core–valence partition and the basis set structure have been properly chosen for molecular calculations or not.

II. METHOD

A. All-electron spin-free Douglas–Kroll transformed no-pair Hamiltonian

The all-electron Hamiltonian used in this work is of the Douglas–Kroll type for the one-electron terms.[10] Following Samzow and Hess[13] who observed that relativistic corrections to the electron–electron interaction are of minor importance in the valence shell and may thus be neglected, the electron–electron interaction is described by the plain Coulomb interaction. For a molecule with nel electrons and NUC nuclei the Hamiltonian reads as

$$H_+^{sf1} = \sum_i^{nel} E_i + \sum_i^{nel} V^{sf}(i) + \sum_{i<j}^{nel} \frac{1}{r_{ij}} + \sum_{I<J}^{NUC} \frac{Z_I Z_J}{R_{IJ}}. \quad (1)$$

The first term,

$$E_i = \sqrt{p_i^2 + m^2}, \quad (2)$$

represents the relativistic kinetic energy. The second accounts for the relativistically corrected interaction between nuclei and electrons,

$$V^{sf}(i) = -A_i(V_{ext}(i) + \vec{R}_i V_{ext}(i) \vec{R}_i) A_i$$
$$- W_1^{sf}(i) E_i W_1^{sf}(i) - \frac{1}{2} \{(W_1^{sf}(i))^2, E_i\}. \quad (3)$$

Herein, $V_{ext}(i)$ describes the (nonrelativistic) Coulomb attraction between electron i and all nuclei, E_i is the kinetic energy as defined above, and

$$\vec{R}_i = \frac{\vec{p}_i}{E_i + m}, \quad (4)$$

$$A_i = \sqrt{\frac{E_i + m}{2E_i}}, \quad (5)$$

are factors resulting from the Douglas–Kroll transformation. According to a proposal by Hess, these factors are evaluated in momentum space employing the primitive molecular basis to resolve the identity.[11] The same applies to $W_1^{sf}(i)$ which represents an integral operator with kernel

$$W_1^{sf}(\vec{p}_i, \vec{p}_i') = A_i(\vec{R}_i - \vec{R}_i') A_i' \frac{V_{ext}(\vec{p}_i, \vec{p}_i')}{E_i + E_i'}. \quad (6)$$

This Hamiltonian is bounded from below[14] and may thus be employed in variational procedures.

B. Spin-free no-pair AIMP method

The spin-free no-pair model potential (MP) Hamiltonian for a molecule comprising $nval$ valence electrons and NUC nuclei may be written as a sum of effective one-electron operators, the two-electron interactions in the valence space and the internuclear repulsion,

$$H^{MP} = \sum_{i=1}^{nval} h(i) + \sum_{i<j}^{nval} \frac{1}{r_{ij}} + \sum_{I<J}^{NUC} V_{IJ}(R_{IJ}). \quad (7)$$

The first two terms in the effective Hamiltonian for electron i,

$$h(i) = E_i + V^{sf}(i) + \sum_I^{NUC} \frac{Z_{core}^I}{r_{Ii}} + \sum_I^{NUC} V_{Coul}^I(i)$$
$$+ \sum_I^{NUC} V_{exch}^I(i) + \sum_I^{NUC} P^I(i), \quad (8)$$

are identical to all-electron terms in Eq. (3). $V_{Coul}^I(i)$ is a radial operator representing the relativistically corrected Coulomb interaction of valence electron i with the core of atom I,

$$V_{Coul}^I(i) = V_{Coul}^I(r_{Ii}) = -\frac{Z_{core}^I}{r_{Ii}} + 2 \sum_c^{core(I)} J_c(i). \quad (9)$$

The operators J_c are defined in a completely analogous manner to the effective Coulomb operators in Hartree–Fock theory. Here, they are calculated using the no-pair relativistic atomic core orbitals. Note that we have added a zero to the one-electron Hamiltonian [Eq. (8)] by adding and subtracting Z_{core}^I/r_{Ii}. In this way, $V_{Coul}^I(i)$ asymptotically converges to zero much faster and can therefore more easily be approximated by a sum of Gaussians,

$$V_{Coul}^I(i) \approx V_{Coul}^{I;MP}(i) = \sum_k C_{Ik} \frac{\exp(-\alpha_{Ik} r_{Ii}^2)}{r_{Ii}}. \quad (10)$$

In this work, the parameters C_{Ik}, α_{Ik} are determined through a least-squares fit to a representation of the potential $V_{Coul}^I(i)$ [Eq. (9)] in the AE basis at center I.

Following the idea of Huzinaga *et al.*[15] which has originally been proposed for nonrelativistic AIMPs, a nonlocal representation is employed for the exchange potential,

$$V_{exch}^I(i) = -\sum_c^{core(I)} K_c(i) \approx V_{exch}^{I,MP}(i)$$

$$= \sum_l \sum_{m=-l}^l \sum_{a,b} |alm;I\rangle S^{-1} K S^{-1} \langle blm;I|. \quad (11)$$

The set of functions $|alm;I\rangle$ constitutes the intermediate basis at center I; each function is chosen to be a product of a radial primitive Gaussians and a spherical harmonic. S is the overlap matrix and K the matrix of V_{exch} in this intermediate basis. In the present case we have chosen the set $|alm;I\rangle$ to consist of all valence primitives at least. With this choice,

atomic calculations give identical results, regardless of whether V_{exch} or V_{exch}^{MP} are employed. Finally, the last term in Eq. (8) is a level shifter,

$$P^I(i) = - \sum_c^{core(I)} 2\epsilon_c |\phi_c\rangle \langle \phi_c |, \qquad (12)$$

with the core orbitals (ϕ_c) expanded in the all-electron basis. The P^I operators shift the core orbitals to positive energies (ϵ_c), that is to the virtual space, and give a positive contribution to a valence orbital energy as long as the corresponding orbital is not fully orthogonal to the core; in this way, the resulting valence orbitals have an overlap with the core orbitals as small as the basis set allows.

Like in all core potential methods, the internuclear repulsion is reduced to the interaction of two effective charges:

$$V_{IJ}(R_{IJ}) = \frac{(Z^I - Z_{core}^I)(Z^J - Z_{core}^J)}{R_{IJ}}. \qquad (13)$$

Atomic no-pair relativistic all-electron calculations were performed using the program AT35[16]. For the all-electron molecular calculations modified versions of either the MOLECULE-SWEDEN[17] or the MOLCAS[18] packages have been employed. AIMP integrals were computed using the ECPAIMP[19] code.

III. MODEL POTENTIALS, BASIS SETS, AND ATOMIC RESULTS

In this section we present model potentials and valence basis sets for the transition elements Sc–Hg. Further, we compare properties of valence orbitals obtained from AIMP and all-electron calculations on the atomic systems.

For the transition elements all-electron basis sets by Fægri[20,21] have been employed. The nonrelativistically optimized $16s11p8d$ Gaussian type functions (GTFs) for the first-row transition metals (TMs) and the $20s14p11d$ sets for the second-row elements have been used without changes; the relativistic shrinkage or expansion of the orbitals is taken into account through the contraction coefficients. Each basis set has been augmented by a diffuse d function required for a proper description of $s^1 d^{x+1}$ and $s^0 d^{x+2}$ configurations. Exponents for the first- and second-row elements were taken from the work of Hay[22] and Walch *et al.*,[23] respectively. The third-row TM $22s16p13d8f$ sets, on the other hand, were modified; for these elements the changes in orbital shapes, in particular, those of the valence orbitals, due to relativistic effects require an adjustment of the exponents: The two outermost s exponents were scaled by a factor of 1.4 and the subsequent two—describing the $5s$ node—by 1.25. Furthermore, two diffuse p, one d, and one f primitive were added according to the scheme described in detail by Wittborn and Wahlgren[9] giving rise to a total of $22s18p14d9f$ primitive GTFs.

The orbitals obtained from relativistic atomic no-pair Hartree–Fock calculations serve as a reference for the construction of the Coulomb and exchange operators. In the AIMP calculations only the outermost ns, $(n-1)p$, and $(n-1)d$ shells are treated explicitly. For all transition elements, with the exception of Pd, ground state wavefunctions

have been generated. In the case of Pd the first excited $s^1 d^9$ state has been chosen because the d^{10} ground state does not provide meaningful contraction coefficients for the outermost s shell. The parameters of the local Coulomb potentials for the two kinds of model potentials are presented in Tables X–XII.[24] The exponents of the valence basis sets have been taken from earlier work, relativistically optimized in Cowan–Griffin Hartree–Fock calculations.[6,7,25] The valence basis sets of the transition elements were augmented by the same diffuse d functions as were the all-electron bases. Using these primitives, we have determined contraction coefficients in atomic relativistic no-pair CASSCF calculations with $x+2$ active electrons in the active ns and $(n-1)d$ shells where x denotes the d shell occupation in an atomic configuration with a closed valence s shell. Exponents and contraction coefficients of the valence basis sets are shown in Tables XIII–XV.[24] The nonlocal spectral representation of the exchange operator is actually computed during the input processing step of the molecular calculations. Since the exchange operator is represented in the complete set of valence primitives a tabulation of the matrix elements of the exchange model potential V_{exch}^{MP} is not necessary. Core orbital energies ϵ_c and generalized contracted core orbitals required for the construction of the level shifting operators and for the calculation of the coefficients in the nonlocal representation of the exchange potential [Eq. (11)] are given in Tables XVI–XVIII.[24]

As a first check of the quality of the model potentials, we have computed properties of the atomic wavefunctions. In these cases we employed the basis sets in their completely uncontracted form. Energies ϵ and radial expectation values ($\langle r^{-1} \rangle$, $\langle r \rangle$, and $\langle r^2 \rangle$) of the valence orbitals obtained in AIMP-CASSCF calculations are compared with all-electron Hartree–Fock results in Tables I–VI. Note that neither the orbital energies nor the orbital shapes directly enter the fitting process. For most of the transition elements very good agreement is observed. At first glance, the results seem to be less satisfactory for some of the early elements. They turned out to be genuine multi-configuration cases as indicated in Tables I–VI by the weights of their main configurations. For test purposes we also carried out AIMP-HF calculations in these cases. The results show that the observed deviations between AIMP-CASSCF and AE-HF are not caused by an improper AIMP but are due to the different treatment of the valence shell. For the complete first-, second-, and third-row transition series ns and $(n-1)d$ orbital energies from AIMP-HF and AE-HF calculations differ by less than $0.004 E_H$ or 0.01 eV. Radial expectation values are of comparable quality. Particularly noteworthy is the good agreement of the $1/r$ expectation values since they are dominated by contributions from the inner region of the radial coordinate.

IV. MOLECULAR CALCULATIONS

Molecular test calculations have been performed for the oxides of groups 5 and 10. The oxygen basis comprise $(10s5p2d)$ primitive functions contracted to $[4s3p2d]$ according to a Raffenetti scheme.[26,27] Each of the TM basis

TABLE I. Valence orbital energies $[E_H]$ of the first-row transition elements.

	Wavefunction	%[a]	Configuration	$-\varepsilon(3p)$	$-\varepsilon(4s)$	$-\varepsilon(3d)$
Sc	AIMP-CAS[b]	99.0	$4s^2 3d^1 - {}^2D$	1.5710	0.2115	0.3310
	AIMP-HF[c]	100.0		1.5706	0.2103	0.3343
	AE-HF[d]	100.0		1.5746	0.2113	0.3356
Ti	AIMP-CAS	99.9	$4s^2 3d^2 - {}^3F$	1.7926	0.2218	0.4298
	AIMP-HF	100.0		1.7926	0.2214	0.4305
	AE-HF	100.0		1.7970	0.2223	0.4315
V	AIMP-CAS	99.9	$4s^2 3d^3 - {}^4F$	2.0185	0.2317	0.4981
	AIMP-HF	100.0		2.0185	0.2315	0.4984
	AE-HF	100.0		2.0233	0.2324	0.4992
Cr	AIMP-CAS	100.0	$4s^1 3d^5 - {}^7S$	2.0555	0.2246	0.3638
	AE-HF	100.0		2.0619	0.2260	0.3664
Mn	AIMP-CAS	100.0	$4s^2 3d^5 - {}^6S$	2.4835	0.2496	0.6251
	AE-HF	100.0		2.4892	0.2505	0.6255
Fe	AIMP-CAS	100.0	$4s^2 3d^6 - {}^5D$	2.7498	0.2605	0.6321
	AE-HF	100.0		2.7558	0.2614	0.6324
Co	AIMP-CAS	100.0	$4s^2 3d^7 - {}^4F$	3.0180	0.2703	0.6593
	AE-HF	100.0		3.0256	0.2713	0.6570
Ni	AIMP-CAS	100.0	$4s^2 3d^8 - {}^3F$	3.2945	0.2798	0.6895
	AE-HF	100.0		3.3010	0.2806	0.6893
Cu	AIMP-CAS	100.0	$4s^1 3d^{10} - {}^2S$	3.3502	0.2425	0.4758
	AE-HF	100.0		3.3607	0.2443	0.4789
Zn	AIMP-CAS	100.0	$4s^2 3d^{10} - {}^1S$	3.8682	0.2974	0.7615
	AE-HF	100.0		3.8757	0.2982	0.7610

[a]The weight of a Hartree–Fock configuration.
[b]AIMP $3p$-,$4s$-,$3d$-valence calculation at the CASSCF level.
[c]AIMP $3p$-,$4s$-,$3d$-valence calculation at the Hartree–Fock level.
[d]All-electron calculation at the no-pair Hartree–Fock level.

sets described so far was augmented by a single p polarization function[28] and f polarization functions. The f polarization function added to the first- and second-row TM bases consists of a single contraction of three GTFs.[29] For the third-row transition elements the most diffuse primitive of the AE $4f$ basis served as a polarization function. The corresponding AIMP basis sets have been augmented by a contraction of five primitive f functions to maintain the orthogonality of the valence shells to the $4f$ core.[25] For a more flexible representation of the transition metal valence shells some of the most diffuse exponents in each Raffenetti contraction were added as primitives. The particular contraction scheme for the first-, second-, and third-row elements are apparent from Tables VII and VIII.

Table VII displays equilibrium bond distances and harmonic frequencies of NiO obtained in AIMP-CASSCF calculations with various basis sets. If the full all-electron basis is retained in the AIMP calculations, i.e., if a $[6s/4p/4d/1f]$ contraction of the Fægri basis is used, only marginal deviations from the all-electron results occur. The third row in Table VII lists the values obtained from AIMP calculations in which the contractions representing the core orbitals have been deleted from the all-electron basis while the valence orbitals are left unchanged (Fægri $[3s/3p/4d/1f]$). In this case the results deteriorate markedly. The potential energy curve is too repulsive at short bond distances and too flat at large internuclear separations. The same is true for the corresponding $[911/511/6111/3]$ contraction of the valence basis by Casarrubios. The origin of these problems is clear cut: Since the Coulomb and exchange potentials and the level

TABLE II. Radial expectation values $[a_0]$ of the first-row transition elements.

	Wavefunction	%[a]	Configuration	3p $\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	4s $\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	3d $\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
Sc	AIMP-CAS[b]	99.0	$4s^2 3d^1 - {}^2D$	1.153	1.171	1.603	0.321	3.938	17.857	0.783	1.720	3.841
	AIMP-HF[c]	100.0		1.153	1.171	1.604	0.320	3.951	17.989	0.792	1.695	3.719
	AE-HF[d]	100.0		1.155	1.172	1.615	0.323	3.937	17.850	0.793	1.691	3.701
Ti	AIMP-CAS	99.9	$4s^2 3d^2 - {}^3F$	1.241	1.090	1.390	0.337	3.762	16.344	0.899	1.476	2.803
	AIMP-HF	100.0		1.241	1.090	1.390	0.337	3.766	16.384	0.901	1.473	2.790
	AE-HF	100.0		1.244	1.091	1.400	0.339	3.753	16.260	0.902	1.470	2.780
V	AIMP-CAS	99.9	$4s^2 3d^3 - {}^4F$	1.328	1.021	1.221	0.352	3.608	15.069	0.991	1.335	2.293
	AIMP-HF	100.0		1.328	1.021	1.221	0.352	3.610	15.089	0.992	1.334	2.288
	AE-HF	100.0		1.331	1.022	1.229	0.354	3.597	14.974	0.993	1.332	2.279
Cr	AIMP-CAS	100.0	$4s^1 3d^5 - {}^7S$	1.399	0.972	1.111	0.349	3.639	15.406	0.997	1.378	2.531
	AE-HF	100.0		1.402	0.974	1.121	0.352	3.622	15.249	0.998	1.378	2.541
Mn	AIMP-CAS	100.0	$4s^2 3d^5 - {}^6S$	1.497	0.909	0.969	0.379	3.358	13.117	1.160	1.139	1.668
	AE-HF	100.0		1.500	0.910	0.976	0.381	3.347	13.020	1.162	1.137	1.661
Fe	AIMP-CAS	100.0	$4s^2 3d^6 - {}^5D$	1.583	0.861	0.870	0.394	3.231	12.163	1.230	1.081	1.515
	AE-HF	100.0		1.587	0.862	0.876	0.397	3.220	12.076	1.232	1.079	1.509
Co	AIMP-CAS	100.0	$4s^2 3d^7 - {}^4F$	1.668	0.818	0.786	0.409	3.121	11.378	1.303	1.024	1.366
	AE-HF	100.0		1.671	0.820	0.792	0.411	3.111	11.292	1.304	1.023	1.362
Ni	AIMP-CAS	100.0	$4s^2 3d^8 - {}^3F$	1.752	0.780	0.715	0.423	3.023	10.694	1.376	0.972	1.236
	AE-HF	100.0		1.756	0.781	0.720	0.425	3.014	10.622	1.378	0.970	1.231
Cu	AIMP-CAS	100.0	$4s^1 3d^{10} - {}^2S$	1.824	0.750	0.661	0.391	3.267	12.534	1.383	0.998	1.352
	AE-HF	100.0		1.827	0.753	0.670	0.391	3.260	12.505	1.386	1.000	1.350
Zn	AIMP-CAS	100.0	$4s^2 3d^{10} - {}^1S$	1.918	0.714	0.599	0.448	2.854	9.569	1.523	0.881	1.022
	AE-HF	100.0		1.923	0.715	0.604	0.451	2.846	9.506	1.525	0.880	1.018

[a]The weight of the Hartree–Fock configuration.
[b]AIMP $3p$-,$4s$-,$3d$-valence calculation at the CASSCF level.
[c]AIMP $3p$-,$4s$-,$3d$-valence calculation at the Hartree–Fock level.
[d]The all-electron calculation at the no-pair Hartree–Fock level.

TABLE III. Valence orbital energies $[E_H]$ of the second-row transition elements.

	Wavefunction	%[a]	Configuration	$-\varepsilon(4p)$	$-\varepsilon(5s)$	$-\varepsilon(4d)$
Y	AIMP-CAS[b]	92.0	$s^2d^1-{}^2D$	1.2980	0.2086	0.2239
	AIMP-HF[c]	100.0		1.3033	0.2005	0.2302
	AE-HF[d]	100.0		1.3045	0.2012	0.2314
Zr	AIMP-CAS	97.5	$s^2d^2-{}^3F$	1.4930	0.2165	0.3109
	AIMP-HF	100.0		1.4954	0.2130	0.3160
	AE-HF	100.0		1.4954	0.2136	0.3161
Nb	AIMP-CAS	100.0	$s^1d^4-{}^6D$	1.5782	0.2284	0.2870
	AE-HF	100.0		1.5784	0.2287	0.2871
Mo	AIMP-CAS	100.0	$s^1d^5-{}^7S$	1.7501	0.2373	0.3422
	AE-HF	100.0		1.7506	0.2377	0.3423
Tc	AIMP-CAS	100.0	$s^2d^5-{}^6S$	2.0631	0.2399	0.5152
	AE-HF	100.0		2.0645	0.2407	0.5155
Ru	AIMP-CAS	100.0	$s^1d^7-{}^5F$	2.1398	0.2374	0.3929
	AE-HF	100.0		2.1414	0.2383	0.3932
Rh	AIMP-CAS	100.0	$s^1d^8-{}^4F$	2.3374	0.2370	0.4284
	AE-HF	100.0		2.3392	0.2379	0.4284
Pd	AIMP-CAS	100.0	$s^1d^9-{}^3D$	2.5382	0.2365	0.4660
	AE-HF	100.0		2.5404	0.2375	0.4658
Ag	AIMP-CAS	100.0	$s^1d^{10}-{}^2S$	2.7409	0.2358	0.5113
	AE-HF	100.0		2.7428	0.2367	0.5106
Cd	AIMP-CAS	100.0	$s^2d^{10}-{}^1S$	3.1153	0.2800	0.7217
	AE-HF	100.0		3.1180	0.2808	0.7211

[a]The weight of the Hartree–Fock configuration.
[b]AIMP $4p$-,$5s$-,$4d$-valence calculation at the CASSCF level.
[c]AIMP $4p$-,$5s$-,$4d$-valence calculation at the Hartree–Fock level.
[d]The all-electron calculation at the no-pair Hartree–Fock level.

shifting operators are identical for different contractions of a given primitive basis, the errors must arise from an insufficient ability of the strongly contracted bases to keep the valence orbitals orthogonal to the core. The largest effect comes from the nonorthogonality w.r.t. the Ni $2p$ core: Since the $2p$ lobe of the Ni $3p$ orbital is represented by the three innermost GTFs, a considerable improvement is observed (line 5 in Table VII) by just altering the contraction scheme

TABLE IV. Radial expectation values $[a_0]$ of the second-row transition elements.

	Wavefunction	%[a]	Configuration	$4p$			$5s$			$4d$		
				$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle 1/r \rangle$	$\langle r \rangle$	$\langle r^2 \rangle$
Y	AIMP-CAS[b]	92.0	$s^2d^1-{}^2D$	0.899	1.461	2.443	0.302	4.145	19.602	0.499	2.682	8.887
	AIMP-HF[c]	100.0		0.898	1.461	2.443	0.296	4.223	20.389	0.529	2.523	7.832
	AE-HF[d]	100.0		0.901	1.462	2.451	0.298	4.210	20.247	0.531	2.513	7.773
Zr	AIMP-CAS	97.5	$s^2d^2-{}^3F$	0.958	1.376	2.169	0.316	3.966	17.939	0.607	2.185	5.816
	AIMP-HF	100.0		0.958	1.377	2.169	0.313	4.000	18.268	0.614	2.156	5.647
	AE-HF	100.0		0.961	1.376	2.168	0.315	3.993	18.249	0.616	2.152	5.625
Nb	AIMP-CAS	100.0	$s^1d^4-{}^6D$	1.009	1.312	1.971	0.323	3.852	16.978	0.635	2.117	5.546
	AE-HF	100.0		1.011	1.313	1.976	0.328	3.841	16.915	0.637	2.112	5.515
Mo	AIMP-CAS	100.0	$s^1d^5-{}^7S$	1.064	1.248	1.783	0.337	3.698	15.685	0.701	1.911	4.487
	AE-HF	100.0		1.067	1.248	1.788	0.343	3.684	15.573	0.703	1.907	4.467
Tc	AIMP-CAS	100.0	$s^2d^5-{}^6S$	1.126	1.182	1.595	0.353	3.578	14.751	0.803	1.646	3.251
	AE-HF	100.0		1.129	1.182	1.598	0.355	3.566	14.633	0.805	1.643	3.241
Ru	AIMP-CAS	100.0	$s^1d^7-{}^5F$	1.173	1.138	1.481	0.352	3.571	14.738	0.814	1.655	3.363
	AE-HF	100.0		1.177	1.138	1.484	0.356	3.558	14.626	0.816	1.653	3.358
Rh	AIMP-CAS	100.0	$s^1d^8-{}^4F$	1.226	1.091	1.362	0.358	3.527	14.424	0.869	1.553	2.961
	AE-HF	100.0		1.230	1.091	1.364	0.361	3.513	14.293	0.870	1.551	2.956
Pd	AIMP-CAS	100.0	$s^1d^9-{}^3D$	1.279	1.048	1.258	0.362	3.491	14.167	0.922	1.465	2.632
	AE-HF	100.0		1.283	1.048	1.260	0.365	3.473	14.004	0.923	1.464	2.628
Ag	AIMP-CAS	100.0	$s^1d^{10}-{}^2S$	1.331	1.010	1.166	0.365	3.463	13.984	0.971	1.387	2.355
	AE-HF	100.0		1.335	1.010	1.168	0.369	3.443	13.780	0.974	1.386	2.351
Cd	AIMP-CAS	100.0	$s^2d^{10}-{}^1S$	1.391	0.967	1.069	0.410	3.099	11.156	1.054	1.267	1.936
	AE-HF	100.0		1.396	0.967	1.071	0.412	3.088	11.052	1.056	1.266	1.931

[a]The weight of the Hartree–Fock configuration.
[b]AIMP $4p$-,$5s$-,$4d$-valence calculation at the CASSCF level.
[c]AIMP $4p$-,$5s$-,$4d$-valence calculation at the Hartree–Fock level.
[d]All-electron calculation at the no-pair Hartree–Fock level.

TABLE V. Valence orbital energies $[E_H]$ of the third-row transition elements.

	Wavefunction	%[a]	Configuration	$-\varepsilon(5p)$	$-\varepsilon(6s)$	$-\varepsilon(5d)$
Hf	AIMP-CAS[b]	97.7	$s^2d^2-{}^3F$	1.5980	0.2418	0.2609
	AIMP-HF[c]	100.0		1.6007	0.2357	0.2638
	AE-HF[d]	100.0		1.6038	0.2365	0.2630
Ta	AIMP-CAS	96.0	$s^2d^3-{}^4F$	1.7624	0.2540	0.3166
	AIMP-HF	100.0		1.7670	0.2485	0.3219
	AE-HF	100.0		1.7705	0.2493	0.3207
W	AIMP-CAS	93.0	$s^2d^4-{}^5D$	1.9273	0.2664	0.3651
	AIMP-HF	100.0		1.9351	0.2599	0.3746
	AE-HF	100.0		1.9391	0.2608	0.3733
Re	AIMP-CAS	100.0	$s^2d^5-{}^6S$	2.1028	0.2694	0.4356
	AE-HF	100.0		2.1072	0.2703	0.4342
Os	AIMP-CAS	100.0	$s^2d^6-{}^5D$	2.2883	0.2831	0.4532
	AE-HF	100.0		2.2932	0.2840	0.4517
Ir	AIMP-CAS	100.0	$s^2d^7-{}^4F$	2.4725	0.2946	0.4859
	AE-HF	100.0		2.4780	0.2957	0.4844
Pt	AIMP-CAS	100.0	$s^1d^9-{}^3D$	2.5553	0.2892	0.4147
	AE-HF	100.0		2.5621	0.2910	0.4138
Au	AIMP-CAS	100.0	$s^1d^{10}-{}^2S$	2.7372	0.2877	0.4547
	AE-HF	100.0		2.7445	0.2895	0.4538
Hg	AIMP-CAS	100.0	$s^2d^{10}-{}^1S$	3.0397	0.3240	0.6066
	AE-HF	100.0		3.0466	0.3257	0.6043

[a]The weight of the Hartree–Fock configuration.
[b]AIMP $5p$-,$6s$-,$5d$-valence calculation at the CASSCF level.
[c]AIMP $5p$-,$6s$-,$5d$-valence calculation at the Hartree–Fock level.
[d]All-electron calculation at the no-pair Hartree–Fock level.

of the p primitives from [511] to [521] without changing the number of contracted p orbitals. The decontraction of the fourth p primitive rectifies most of the remaining error. If, in addition, the expansion coefficient of a further s function is allowed to float, the results become nearly identical to both the results in the completely uncontracted valence basis and the all-electron results. Summarizing, we find that an AIMP calculation employing a $[4s/4p/4d/1f]$ valence basis on Ni yields excellent agreement with all-electron results on NiO; if, for reasons of efficiency, a smaller basis has to be used, a $[3s/3p/4d/1f]$ set with contraction scheme [911/521/6111/3] still gives reasonable agreement.

In the following, all calculations for first- and second-row TM oxides with AIMPs corresponding to [Mg] and [Zn] cores, respectively, have been carried out using a $[4s/4p/4d/1f]$ contraction of the valence basis. For the third-row element AIMPs with $[Cd,4f]$ core a $[4s/4p/4d/2f]$ contraction has been employed. In order to make the comparison between AIMP and AE results more transparent, we have repeated the AE calculations with the decontracted primitives replaced by the corresponding GTFs from the AIMP valence basis.

Table VIII displays equilibrium bond distances, harmonic vibrational frequencies, and dissociation energies of the ground or low-lying excited electronic states of the group 5 oxides VO, NbO, and TaO and the group 10 oxides NiO, PdO, and PtO. Unless noted otherwise, all calculations have been performed at the Hartree–Fock level. For the group 5 oxides we have chosen a ${}^4\Sigma^-$ state with electronic configuration $\sigma_{O2s}^2\sigma^2\pi^4\sigma'^1\delta^2$, the electronic ground state of VO[30] and NbO.[31] NiO exhibits a ${}^3\Sigma^-$ ground state with electron configuration $\sigma_{O2s}^2\sigma^2\pi^4\delta^4\sigma'^2\pi'^2$.[30] The corresponding state in PdO is not bound at the Hartree–Fock level. In this case the test calculations have been performed for the $\sigma_{O2s}^2\sigma^2\pi^4\delta^4\sigma'^1\pi'^3({}^3\Pi)$ state. Due to convergence prob-

TABLE VI. Radial expectation values $[a_0]$ of the third-row transition elements.

	Wavefunction	%[a]	Configuration	5p $\langle 1/r \rangle$	5p $\langle r \rangle$	5p $\langle r^2 \rangle$	6s $\langle 1/r \rangle$	6s $\langle r \rangle$	6s $\langle r^2 \rangle$	5d $\langle 1/r \rangle$	5d $\langle r \rangle$	5d $\langle r^2 \rangle$
Hf	AIMP-CAS	97.7	$s^2d^2-{}^3F$	0.958	1.355	2.083	0.340	3.684	15.527	0.552	2.380	6.905
	AIMP-HF[c]	100.0		0.958	1.355	2.084	0.336	3.725	15.897	0.561	2.342	6.675
	AE-HF[d]	100.0		0.963	1.354	2.086	0.339	3.705	15.678	0.560	2.343	6.682
Ta	AIMP-CAS	96.0	$s^2d^3-{}^4F$	0.996	1.306	1.935	0.355	3.533	14.301	0.610	2.146	5.554
	AIMP-HF	100.0		0.996	1.306	1.934	0.352	3.570	14.618	0.616	2.122	5.424
	AE-HF	100.0		1.001	1.305	1.936	0.355	3.549	14.401	0.616	2.123	5.428
W	AIMP-CAS	93.0	$s^2d^4-{}^5D$	1.033	1.262	1.803	0.371	3.340	13.235	0.657	1.986	4.731
	AIMP-HF	100.0		1.033	1.261	1.803	0.367	3.437	13.569	0.664	1.965	4.619
	AE-HF	100.0		1.039	1.261	1.804	0.369	3.418	13.374	0.664	1.966	4.622
Re	AIMP-CAS	100.0	$s^2d^5-{}^6S$	1.070	1.220	1.686	0.380	3.329	12.741	0.709	1.836	4.006
	AE-HF	100.0		1.076	1.219	1.686	0.383	3.309	12.555	0.709	1.836	4.009
Os	AIMP-CAS	100.0	$s^2d^6-{}^5D$	1.108	1.181	1.578	0.395	3.207	11.833	0.746	1.752	3.655
	AE-HF	100.0		1.115	1.180	1.578	0.398	3.188	11.666	0.746	1.753	3.656
Ir	AIMP-CAS	100.0	$s^2d^7-{}^4F$	1.146	1.145	1.483	0.409	3.105	11.106	0.784	1.671	3.321
	AE-HF	100.0		1.153	1.144	1.482	0.412	3.088	10.951	0.784	1.671	3.322
Pt	AIMP-CAS	100.0	$s^1d^9-{}^3D$	1.177	1.116	1.410	0.407	3.118	11.231	0.797	1.662	3.328
	AE-HF	100.0		1.185	1.115	1.410	0.411	3.099	11.066	0.797	1.662	3.326
Au	AIMP-CAS	100.0	$s^1d^{10}-{}^2S$	1.214	1.085	1.332	0.413	3.084	11.017	0.834	1.585	3.013
	AE-HF	100.0		1.222	1.084	1.331	0.416	3.066	10.851	0.835	1.584	3.012
Hg	AIMP-CAS	100.0	$s^2d^{10}-{}^1S$	1.256	1.050	1.246	0.445	2.864	9.479	0.894	1.470	2.560
	AE-HF	100.0		1.265	1.049	1.246	0.451	2.844	9.324	0.895	1.470	2.561

[a]The weight of the Hartree–Fock configuration.
[b]AIMP $5p$-,$6s$-,$5d$-valence calculation at the CASSCF level.
[c]AIMP $5p$-,$6s$-,$5d$-valence calculation at the Hartree–Fock level.
[d]All-electron calculation at the no-pair Hartree–Fock level.

TABLE VII. Equilibrium bond distance R_e, harmonic frequency ω_e, and dissociation energy D_e of NiO: Basis set dependence of AIMP-CASSCF values and comparison with all-electron results.

Core	Contracted basis set[a]	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
AE	F[16,16,16,16,1,1/11,11,1,1/9,1,1,1/3]	1.672	779	-1.66[b]
AIMP	F[16,16,16,16,1,1/11,11,1,1/9,1,1,1/3]	1.669	782	-1.64
AIMP	F[16,1,1/11,1,1/9,1,1,1/3]	1.694	730	-1.84
AIMP	V[9,1,1/5,1,1/6,1,1,1/3]	1.696	722	-1.81
AIMP	V[9,1,1/5,2,1/6,1,1,1/3]	1.684	737	-1.75
AIMP	V[9,1,1/5,1,1,1/6,1,1,1/3]	1.678	759	-1.68
AIMP	V[9,1,1,1/5,1,1,1/6,1,1,1/3]	1.673	769	-1.65
AIMP	V[1,1,1,1,1,1,1,1,1/1,1,1,1,1,1,1/1,1,1,1,1,1/3]	1.672	776	-1.63

[a]F denotes the Ni basis by Fægri;[20] V the Ni valence basis by Casarrubios and Seijo.[25]
[b]The negative value indicates that the $^3\Sigma^-$ state of NiO is metastable with respect to dissociation into Ni(^3F) and O(^3P) at the Hartree–Fock level.

lems of the single determinant representation of the $^3\Sigma^-$ state of PtO, we have carried out small CASSCF calculations for this state with six active electrons in the π and π' orbitals. Dissociation energies have been computed in a super-molecule approach i.e., as energy differences between (1) the molecular energies at equilibrium bond distance and (2) the energy of a high-spin state at the internuclear separation of $1000a_0$. The use of a super-molecule approach for the determination of dissociation energies is crucial for a balanced matrix representation of the momentum-dependent terms in the no-pair Hamiltonian [Eq. (3)]: Employing different resolutions of the identity for the molecule and the separated atom limit leads to completely unreasonable results.

Regarding bond distances, vibrational frequencies, and dissociation energies, excellent agreement between AIMP and AE results is observed for the late transition metal oxides. Equilibrium bond distances are reproduced by the AIMP treatment with deviations of less than 0.01 Å, and harmonic frequencies agree to within a few cm^{-1} ranging from complete agreement (best case) to 20 cm^{-1} (worst case). Dissociation energies differ by at most 0.07 eV. Somewhat larger errors are observed for the early transition metal oxides. Interestingly, the $^4\Sigma^-$ states of VO and TaO which correlate with V$^4F_g(4s^2d^3)$ and O^3P_g in the separated atom limit are slightly overbound in the AIMP treatment; the

overbinding is also apparent from the computed equilibrium bond distances which are too short. On the contrary the dissociation energy of the corresponding state in NbO which originates from O^3P_g and Nb in its $^6D_g(5s^1d^4)$ ground state is slightly underestimated. Several reasons may be thought of as being responsible for these deviations. The most obvious one is the neglect of the $(n-1)s$ shell polarization which is known to play an important role in compounds of the early transition metals but which is not taken into account in the AIMPs with [Mg], [Zn], and [Cd, $4f$] cores, respectively. A further approximation to be checked is the completeness of the matrix representation of the exchange operator [Eq. (11)] and the relativistic kinematic factors [Eqs. (4) and (5)]. For this purpose we have constructed a set of small-core ([Ne], [Ar, $3d$], and [Kr, $4d,4f$], respectively) AIMPs and corresponding basis sets. Technical details will be presented in a forthcoming publication.[32] Furthermore, we have designed a series of AIMP calculations with the intermediate bases $|alm;I\rangle$ augmented by a selection from the corresponding TM AE basis set. The latter type of basis set is denoted by the label *aug.val* in Table IX.

Let us focus on the $(n-1)s$ shell polarization effect first. Enlarging the valence space by including the $(n-1)s$ shell has a marked effect only on the dissociation energies of the early transition metal oxides. In all cases D_e is decreased

TABLE VIII. Equilibrium bond distances R_e, harmonic frequencies ω_e, and dissociation energies D_e of low-lying electronic states of the group 5 and 10 oxides obtained at the all-electron (AE) and AIMP valence Hartree–Fock levels.

Molecule	State	Calculation	Contracted TM basis set	R_e (Å)	ω_e (cm^{-1})	D_e (eV)
VO	$^4\Sigma^-(\sigma\delta^2)$	AE	[16,16,16,16,1,1,1/11,11,1,1,1/9,1,1,1/3]	1.555	1178	1.53
		AIMP	[9,1,1,1/5,1,1,1/6,1,1,1/3]	1.542	1199	1.72
NbO	$^4\Sigma^-(\sigma\delta^2)$	AE	[20,20,20,20,20,1,1,1/14,14,14,1,1,1/12,12,1,1,1/3]	1.658	1105	3.51
		AIMP	[11,1,1,1/7,1,1,1/7,1,1,1/3]	1.657	1080	3.46
TaO	$^4\Sigma^-(\sigma\delta^2)$	AE	[22,22,22,22,22,22,1,1,1/18,18,18,1,1,1/14,14,14,1,1,1/9,1]	1.693	1070	4.21
		AIMP	[13,1,1,1/9,1,1,1/9,1,1,1/5,1]	1.683	1068	4.42
NiO	$^3\Sigma^-(\sigma^2\delta^4\pi^2)$	AE	[16,16,16,16,1,1,1/11,11,1,1,1/9,1,1,1/3]	1.674	773	-1.72[a]
		AIMP	[9,1,1,1/5,1,1,1/6,1,1,1/3]	1.673	769	-1.65
PdO	$^3\Pi(\sigma^1\pi^1)$[b]	AE	[20,20,20,20,20,1,1,1/14,14,14,1,1,1/12,12,1,1,1/3]	1.981	549	0.75
		AIMP	[11,1,1,1/7,1,1,1/7,1,1,1/3]	1.980	549	0.80
PtO	$^3\Sigma^-(\sigma^2\delta^4\pi^2)$	AE	[22,22,22,22,22,22,1,1,1/18,18,18,1,1,1/14,14,14,1,1,1/9,1]	1.808	686	0.89
		AIMP	[13,1,1,1/9,1,1,1/9,1,1,1/5,1]	1.799	706	0.92

[a]The negative value indicates that the $^3\Sigma^-$ state of NiO is metastable with respect to dissociation into Ni(^3F) and O(^3P) at the Hartree–Fock level.
[b]The $\sigma^2\delta^4\pi^2-{}^3\Sigma^-$ state of PdO is not bound at the HF level.
[c]The CASSCF calculation distributing 6 electrons in the π and π' orbitals; HF calculations were not convergent.

TABLE IX. Comparison of spectroscopic parameters obtained from AE, large-core ([Mg], [Zn], and [Cd, $4f$] core, respectively) and small-core ([Ne], [Ar, $3d$], and [Kr, $4d$, $4f$] core, respectively) AIMP calculations. The labels *val* and *aug.val* denote different intermediate basis sets (see text).

| Molecule | State | Core | Representation | | R_e (Å) | ω_e (cm^{-1}) | D_e (eV) |
			Exchange	Relativistic			
VO	$^4\Sigma^-$	AIMP [Mg]	*val*	*val*	1.542	1199	1.72
		AIMP [Mg]	*aug.val*	*aug.val*	1.545	1187	1.63
		AIMP [Ne]	*val*	*val*	1.551	1191	1.59
		AIMP [Ne]	*aug.val*	*aug.val*	1.552	1185	1.54
		AE —	—	*ae*	1.555	1178	1.53
NbO	$^4\Sigma^-$	AIMP [Zn]	*val*	*val*	1.657	1080	3.46
		AIMP [Zn]	*aug.val*	*aug.val*	1.655	1099	3.59
		AIMP [Ar, $3d$]	*val*	*val*	1.665	1089	3.35
		AIMP [Ar, $3d$]	*aug.val*	*aug.val*	1.661	1110	3.53
		AE —	—	*ae*	1.658	1105	3.51
TaO	$^4\Sigma^-$	AIMP [Cd, $4f$]	*val*	*val*	1.683	1068	4.42
		AIMP [Cd, $4f$]	*aug.val*	*aug.val*	1.686	1061	4.33
		AIMP [Kr, $4d$, $4f$]	*val*	*val*	1.686	1074	4.36
		AIMP [Kr, $4d$, $4f$]	*aug.val*	*aug.val*	1.689	1066	4.26
		AE —	—	*ae*	1.693	1070	4.21
NiO	$^3\Sigma^-$	AIMP [Mg]	*val*	*val*	1.673	769	-1.65
		AIMP [Mg]	*aug.val*	*aug.val*	1.675	771	-1.68
		AIMP [Ne]	*val*	*val*	1.677	768	-1.66
		AIMP [Ne]	*aug.val*	*aug.val*	1.678	769	-1.70
		AE —	—	*ae*	1.674	773	-1.72
PdO	$^3\Pi$	AIMP [Zn]	*val*	*val*	1.980	549	0.80
		AIMP [Zn]	*aug.val*	*aug.val*	1.974	548	0.81
		AIMP [Ar, $3d$]	*val*	*val*	1.987	547	0.78
		AIMP [Ar, $3d$]	*aug.val*	*aug.val*	1.977	548	0.79
		AE —	—	*ae*	1.981	549	0.75
PtO	$^3\Sigma^-$	AIMP [Cd, $4f$]	*val*	*val*	1.799	706	0.92
		AIMP [Cd, $4f$]	*aug.val*	*aug.val*	1.807	695	0.87
		AIMP [Kr, $4d$, $4f$]	*val*	*val*	1.801	701	0.91
		AIMP [Kr, $4d$, $4f$]	*aug.val*	*aug.val*	1.812	685	0.83
		AE —	—	*ae*	1.808	686	0.89

bringing the values for VO and TaO into better agreement with the AE values. For NbO, which already in the AIMP [Zn] calculation exhibits too small a dissociation energy the deviation is seemingly increased. The latter results point to a cancellation of errors in the NbO large-core calculation. The remaining errors are essentially removed by improving the matrix representation of the exchange and relativistic operators (entry *aug.val* in Table IX).

V. CONCLUSIONS

In this work, we provide relativistic *ab initio* no-pair model potentials and valence basis sets for the transition elements Sc–Hg. A comparison of atomic properties obtained from AIMP Hartree–Fock and all-electron HF calculations shows that ns and $(n-1)d$ valence orbital energies differ by less than $0.004\,E_H$ (0.01 eV) for the complete first-, second-, and third-row transition series. Radial expectation values are of comparable quality.

AIMP calculations on late TM oxides with [Mg], [Zn], and [Cd,4f] cores, respectively, and employing a $[4s/4p/4d/1f]$ contraction of the TM valence basis are in excellent agreement with all-electron results; if, for reasons of efficiency, a smaller basis has to be used, a $[3s/3p/4d/1f]$

contraction still gives reasonable agreement. The performance of the AIMP method is slightly less satisfactory for the early transition metal oxides, if the high accuracy of the results on the late TM oxides is taken as a reference. The deviations from the corresponding all-electron values fall, however, well in the range of other types of effective core potentials. It is shown that also in these cases the spectroscopic parameters can be brought into excellent agreement with the AE values, if the $(n-1)s$ shell is included in the valence space and the intermediate basis sets—used for representing the exchange and no-pair operators—are improved.

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