

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

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This is the second part of a report on spin-free relativistic no-pair *ab initio* core model potentials for the transition elements Sc to Hg. In the first part [J. Chem. Phys. **110**, 3678 (1999)], we introduced the no-pair *ab initio* model potential method and supplied model potentials for [Mg], [Zn], and [Cd,4f] cores of first-, second-, and third-row transition metals, respectively. At the Hartree–Fock level excellent agreement between all-electron and model potential results was observed for late transition metal oxides, whereas the performance of the model potentials was slightly less satisfactory for early transition metal oxides. In this paper we will present small-core model potentials corresponding to [Ne], [Ar,3d], and [Kr,4d,4f] cores, respectively. The performance of the model potentials is tested extensively in calculations on the diatomic oxides VO, NbO, TaO, NiO, PdO, and PtO, both at the Hartree–Fock level and when electron correlation is included by means of coupled-pair functional methods. Further we investigate the requirements on valence and intermediate basis sets used to represent the exchange and no-pair operators. © 1999 American Institute of Physics. [S0021-9606(99)30347-0]

I. INTRODUCTION

This is the second part of a report on no-pair one-component relativistic *ab initio* model potentials (AIMPs) and valence basis sets for the first-, second-, and third-row transition metal (TM) elements. In the first part¹ we presented AIMPs with [Mg], [Zn], and [Cd,4f] cores, respectively, corresponding to valence spaces comprising the ns , $(n-1)d$, and $(n-1)p$ shells where n is the principal quantum number of the outermost valence shell. In the following we shall refer to these model potentials as *medium-core* AIMPs. Employing these *medium-core* AIMPs, atomic all-electron (AE) orbital energies and radial expectation values of the valence orbitals were very well reproduced. Molecular one-component relativistic AE calculations were utilized as further benchmarks to test the performance of the AIMPs. At the Hartree–Fock (HF) level AIMP and AE results for the group 10 TM monoxides were in excellent agreement, while the performance of the AIMPs was slightly less satisfactory for the group 5 TM monoxides. In particular, the dissociation energies of VO and TaO were overestimated w. r. t. the corresponding AE values whereas bond distances and vibrational frequencies were in good accord. In these cases agreement with the AE values can be improved by including the $(n-1)s$ shell in the valence space and by enhancing the representation of the exchange and no-pair model potential

operators. For convenience, we shall call the latter representation basis sets *intermediate basis sets* in the following.

In the current paper, we present the details of these new model potentials and the corresponding valence and intermediate basis sets. We analyze how an improvement of the resolution of the identity affects the spectroscopic parameters of the group 5 and 10 TM monoxides. For third-row elements we also investigate the demands on f-valence basis sets. Further, we shall discuss the performance of the *small- and medium-core*-valence partitionings in HF and electron correlation calculations. Finally, we compare our data obtained at the correlated level with other theoretical and experimental work.

II. METHOD

The general features of the spin-free no-pair AIMP method have already been introduced in Ref. 1. For convenience, we would like to discuss here the methods for evaluating the exchange model potential and the relativistic no-pair operators in more detail. In both cases intermediate basis sets are involved.

A. The exchange model potential

In the AIMP method the exchange interaction between valence and core electrons V_{exch} is approximated by the exchange model potential $V_{\text{exch}}^{\text{MP}}$. The molecular $V_{\text{exch}}^{\text{MP}}$ is composed of atomic HF exchange potentials

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$$V_{\text{exch}}^{\text{MP}} = \sum_I \sum_T \sum_{m=-l}^l \sum_{a,b} |alm;I\rangle \times (S_I^{-1} K_I S_I^{-1})_{alm,blmI} \langle blm;I|, \quad (1)$$

where S_I is the overlap matrix and K_I the matrix representation of the exchange potential of the core at center I in the intermediate basis $\{|alm;I\rangle\}$. In this work two different types of intermediate basis sets are used. One of them comprises all primitives of the molecular valence basis set and will be labeled *val* in the following. So far, this kind of resolution of the identity has been recommended for use in AIMP calculations because one-center contributions to the HF exchange potential are represented exactly in this basis.² In the course of this work it turned out, however, that in certain cases a more complete resolution of the identity is indicated. In order to improve the intermediate basis one might, therefore, think of employing the all-electron basis instead. In this case considerable errors in the calculation of the one-center exchange potentials are introduced. From this experience we conclude that the primitives of the molecular valence basis set should be a subset of the representation basis set. The second set, denoted by the label *aug.val*, therefore, starts with the valence set *val* but is augmented by selected primitives from the AE transition metal basis. In order to avoid singularity problems in matrix inversion operations we have chosen the augmentation functions such that their exponents are not too close to those of the basis set *val*. These additional primitives are tabulated in Tables XII–XIV for all TM elements.³

B. The spin-free relativistic no-pair operators

The relativistic no-pair operators which have to be considered in the spin-free no-pair AIMP method are the relativistic kinetic energy operators for the valence electron i

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

and the relativistically corrected interaction between the nuclei and electron i

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

Herein, $V_{\text{ext}}(i)$ 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.⁴ Let us consider, for instance, the calculation of the matrix element M of a single one-electron term of Eq. (3)

$$M = \langle al_a(i) | A_i \vec{R}_i V_{\text{ext}}(i) \vec{R}_i A_i | bl_b(i) \rangle. \quad (6)$$

M is calculated by the insertion of several intermediate basis sets $\{|\alpha_p(i)\rangle\}$ and $\{|kl_k(i)\rangle\}$.⁵

$$M = \sum_{\alpha, \beta, \gamma, \delta, k, n} \langle al_a(i) | \alpha_p(i) \rangle \langle \alpha_p(i) | \frac{A_i}{E_i + m} | \beta_p(i) \rangle \times \langle \beta_p(i) | kl_k(i) \rangle \langle kl_k(i) | (-i\nabla_i) V_{\text{ext}}(i) \times (-i\nabla_i) | nl_n(i) \rangle \times \langle nl_n(i) | \gamma_p(i) \rangle \langle \gamma_p(i) | \frac{A_i}{E_i + m} | \delta_p(i) \rangle \times \langle \delta_p(i) | bl_b(i) \rangle, \quad (7)$$

where the $\{\alpha_p(i)\}$ are functions of momentum space and $\{|kl_k(i)\rangle\}$ is the intermediate basis defined in ordinary space. The basis functions $\{\alpha_p(i)\}$ are obtained by diagonalizing the matrix of the nonrelativistic kinetic energy $p^2/2m$ represented in the original intermediate basis set. Note that integrals of type $\langle al_a(i) | \alpha_p(i) \rangle$ are not just simple overlap integrals, but represent Fourier transforms between real and momentum space. As for the exchange model potential, we will use intermediate basis sets of types *val* and *aug.val*, respectively.

III. MODEL POTENTIALS, BASIS SETS, AND ATOMIC RESULTS

In this section we present model potentials and valence basis sets for the TMs which we will refer to as *small-core* AIMPs. They correspond to the [Ne], [Ar,3d], and [Kr, 4d,4f] cores, respectively. The exponents of the primitive Gaussian functions used to describe the ns , $(n-1)d$, $(n-1)p$, and $(n-1)s$ valence shells are the same as in Ref. 1. Atomic AIMP calculations were carried out with a modified MOLECULE-SWEDEN⁶ package and the ECPAIMP⁷ code. We have determined contraction coefficients in atomic relativistic no-pair CASSCF (complete active space self-consistent field) 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. The actual atomic configurations and the newly optimized coefficients are presented together with the corresponding exponents in Tables IX–XI.³ The level shifters can be constructed from the data already presented in Ref. 1 by removing the part corresponding to the $(n-1)s$ shell from the AIMP Hamiltonian. The *small-core* Coulomb model potentials for the TMs are displayed in Tables VI–VIII.³ The *small-core* AIMP valence orbital energies and radial expectation values show the same good quality and agreement with AE results as we already observed for the *medium-core* AIMPs.

IV. MOLECULAR CALCULATIONS

Molecular calculations are performed for the group 5 and 10 TM monoxides at the AE and AIMP levels employing the MOLCAS⁸ package. Transition metal AE basis sets, the *medium-core* TM AIMP basis sets, and the oxygen basis set have already been described in Ref. 1. The same polarization functions were used to augment the *medium-core* and *small-*

TABLE I. Comparison of spectroscopic parameters obtained from AE, *medium-core* and *small-core* AIMP calculations at the Hartree–Fock level (if not noted otherwise). The labels val and aug.val denote different intermediate basis sets (see text).

Molecule	State	Core	Representation		$R_e[\text{Å}]$	$\omega[\text{cm}^{-1}]$	$D_e[\text{eV}]$	
			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	$^3\Sigma^{-a}$	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

^aCASSCF calculation distributing six electrons in the π and π' orbitals.

core valence basis sets. For the first- and second-row TM elements the final contraction patterns for the *small-core* AIMP valence basis read $[5s/4p/4d/1f]$, whereas for the third-row elements a $[5s/4p/4d/2f]$ contraction is utilized. Unless noted otherwise all calculations at the correlated level were performed employing the modified coupled-pair functional (MCPF) method.⁹ For multi-reference cases the averaged coupled-pair functional (ACPF) approach was used.¹⁰ In either case single and double excitations from the set of ns and $(n-1)d$ orbitals were allowed, while restricting the replacements in the $(n-1)p$ shell of the TM to a single hole.

For a comparison of AE and AIMP results the same valence electron configuration ($\sigma^1\delta^2$, $^4\Sigma^-$) was chosen for VO, NbO, and TaO. For the lighter homologues VO and NbO this electron configuration corresponds to the ground state,^{11,12} whereas it yields a low-lying excited state in TaO.¹³ Due to the relativistic inert-pair effect the heavier TaO prefers a $\sigma^2\delta^1$ configuration leading to a $^2\Delta$ electronic ground state with $\Omega=3/2$ and $\Omega=5/2$ spin-orbit sublevels. In Sec. IV C, therefore, averaged spectroscopic parameters of these states are chosen as experimental reference.

The situation is different for NiO, PdO, and PtO. All

three diatomic oxides exhibit a $^3\Sigma^-$ ground state or fine-structure components hereof. Comparison with experiment is therefore made for this state with $\sigma^2\pi^2$ configuration. In PdO this state is not bound at the HF level, and we thus compare AE and AIMP results for the excited ($\sigma^1\pi^3$) $^3\Pi$ state of this molecule.

A. Discussion of AIMP and AE Hartree–Fock results

In Table I we list equilibrium distances, vibrational frequencies and dissociation energies of the ground or low-lying states of the group 5 and 10 TM monoxides. Unless stated otherwise, all calculations discussed in this section have been performed at the Hartree–Fock level.

The quality of the AIMP results can be estimated by comparison with corresponding AE values. Regardless of the core or intermediate basis set size, bond distances and vibrational frequencies are in excellent agreement with AE results. Concerning dissociation energies, deviations from AE results are within 0.2 eV, which can be accepted for any kind of effective core potential (ECP). Nevertheless some interesting trends in spectroscopic parameters are observed for the different types of AIMPs. When smaller AIMP cores are

TABLE II. Investigation of the representation basis set completeness of the exchange model potential and relativistic no-pair operators at the Hartree–Fock level using *small-core* AIMPs. The different sets of calculations were performed at the same interatomic distance close to the respective equilibrium distance of each molecule. Thus the dissociation energies D presented are only approximate. The labels val and aug.val denote different intermediate basis sets (see text).

Molecule	State	d-occupation	Core	Representation		$D[\text{eV}]$ ΔD [eV]	TM state
				Exchange	Relativistic		
VO	$4\Sigma^-$	3.2	[Ne]	val	val	1.549	$4F(d^3s^2)$
				val	aug.val	+0.002	
				aug.val	aug.val	-0.046	
NbO	$4\Sigma^-$	3.3	[Ar,3d]	val	val	3.330	$6D(d^4s^1)$
				val	aug.val	-0.003	
				aug.val	aug.val	+0.184	
TaO	$4\Sigma^-$	3.2	[Kr,4d,4f]	val	val	4.362	$4F(d^3s^2)$
				val	aug.val	+0.005	
				aug.val	aug.val	-0.099	
NiO	$3\Sigma^-$	8.2	[Ne]	val	val	- 1.668	$3F(d^8s^2)$
				val	aug.val	+0.004	
				aug.val	aug.val	-0.040	
PdO	3Π	9.1	[Ar,3d]	val	val	0.776	$3D(d^9s^1)$
				val	aug.val	+0.005	
				aug.val	aug.val	+0.008	
PtO ^a	$3\Sigma^-$	8.7	[Kr,4d,4f]	val	val	0.905	$3D(d^9s^1)$
				val	aug.val	-0.005	
				aug.val	aug.val	-0.072	

^aCASSCF calculation distributing six electrons in the π and π' orbitals.

employed, typically equilibrium distances are increased, dissociation energies are decreased, while vibrational frequencies remain almost unchanged. As expected, the effects due to reducing the core size are more distinct for the early TM elements, because the radial extent of their cores is larger and the $(n-1)s$ shells are easier polarized. Further, the dissociation energies of the early TM oxides obtained at the AIMP level appear to be sensitive to the size of intermediate basis. The deviations from the corresponding AE results are diminished when the matrix representation of the exchange and relativistic operators is improved. Excellent agreement is observed when spectroscopic parameters obtained at the AE level are compared with the “best” type of AIMP calculations, i.e., when *small-core* AIMPs and intermediate basis sets of aug.val type are used.

In order to check the quality requirements on the intermediate basis sets we carried out three series of test calculations. In all cases we employed *small-core* AIMPs. In the first series both the exchange model potentials and the relativistic no-pair operators were represented by intermediate basis sets of type val, in the second we used aug.val no-pair basis sets and val exchange model potential basis sets and, finally, in the third series aug.val representation basis sets were used for both types of operators. For reasons of comparability, the different sets of calculations on a specific molecule were performed at the same interatomic distance close to the respective equilibrium distance. Thus the dissociation energies presented in Table II are only approximate. The inclusion of additional basis functions for the representation of the relativistic no-pair operators do not alter the results,

i.e., intermediate basis sets of type val are already approximately complete for this type of operator. A rationale of this result is the fact that the kinematic relativistic correction factors R and A [Eqs. (4) and (5)] affect mainly regions of high linear momentum, e.g., close to a nucleus. The most significant relativistic corrections affect the core electrons, which have already been incorporated in the model potential (MP). When the representation of the exchange model potential is improved as well (fifth entries in Table II), the changes in the dissociation energies are more distinct. This means that the val representation sets have some deficiencies in this case. Similar observations were made for nonrelativistic test calculations on first-row transition metal oxides, i.e., when the intermediate basis was used solely for resolving the identity in the exchange matrix elements. We can, therefore, safely assume that the changes in the dissociation energies mainly arise from the improved representation of the exchange model potential operator. As both types of intermediate basis sets—val and val.aug—allow for the exact calculation of one-center exchange model potential operator contributions (cf. Sec. II), the two-center exchange terms must be responsible for the observed changes. Very similar effects are found for *medium-core* and *small-core* AIMPs. We are, therefore, lead to the conclusion that the representation of the two-center exchange interaction of the valence shells with the semicore $(n-1)s$ is not critical but that rather inner core orbitals are involved.

Next, we tested the performance of different f valence basis sets for the third-row transition metal elements. This question is of technical interest since the calculation of inte-

TABLE III. Comparison of different *f* valence basis sets (*f*-VBS). For all cases the AIMP calculations were performed with the same aug.val representation basis set.

Molecule	State	Core	Representation			<i>f</i> -VBS	$R_e[\text{\AA}]$	$\omega[\text{cm}^{-1}]$	$D_e[\text{eV}]$
			Exchange	Relativistic					
TaO	$4\Sigma^-$	AE	ae	[9,1]	1.693	1070	4.21
		AIMP	[Cd,4f]	val	val	[5,1]	1.683	1068	4.42
		AIMP	[Cd,4f]	val	val	[1,1]	1.672	1058	4.54
		AIMP	[Cd,4f]	val	val	[-,1]	1.686	1078	4.52
		AIMP	[Cd,4f]	aug.val	aug.val	[5,1]	1.686	1061	4.33
		AIMP	[Cd,4f]	aug.val	aug.val	[1,1]	1.682	1059	4.34
		AIMP	[Cd,4f]	aug.val	aug.val	[-,1]	1.687	1057	4.26
PtO	$3\Sigma^-$	AE	ae	[9,1]	1.808	686	0.89
		AIMP	[Cd,4f]	val	val	[5,1]	1.799	706	0.92
		AIMP	[Cd,4f]	val	val	[1,1]	1.799	714	0.97
		AIMP	[Cd,4f]	val	val	[-,1]	1.793	720	0.99
		AIMP	[Cd,4f]	aug.val	aug.val	[5,1]	1.807	695	0.87
		AIMP	[Cd,4f]	aug.val	aug.val	[1,1]	1.810	692	0.84
		AIMP	[Cd,4f]	aug.val	aug.val	[-,1]	1.812	691	0.84

grals involving shells of angular momentum quantum number $l=3$ or higher are the most memory and disk consuming. The original AIMP *f* valence basis sets¹ comprise one five-primitive contracted function plus one *f* polarization primitive ([5,1]). Exponents and contraction coefficients of the former were fitted to the all-electron atomic 4*f* orbital.¹⁴ In a first step the four primitives exhibiting the largest exponents are removed from the contracted function resulting to [1,1] valence basis sets. In a second step the remaining single primitive is removed as well and just a single *f* polarization primitive remains in the valence basis set ([-,1]). This means that in case the valence basis (val) is employed for resolving the identity also the representation of the exchange and relativistic operators changes. By contrast, the intermediate basis remains the same in all (aug.val) calculations, i.e., in these cases always seven primitive *f* functions represent the MP Hamiltonian. Table III displays the results of AE and *medium-core* AIMP calculations at the HF or CASSCF levels, respectively. The changes of the TaO and PtO spectroscopic parameters are quite small when the *f* valence basis sets are reduced while retaining the enhanced representation basis (aug.val). In this case it appears, therefore, sufficient to keep just the *f* polarization function in the valence basis set. Since intermediate representation basis sets are involved in the calculation of one-electron integrals only the additional memory and disk requirements are negligible. In contrast, the use of reduced *f* valence basis sets saves considerable resources in the evaluation of the two-electron integrals. We would like to note that this procedure is not recommendable, if only the valence primitives are used as intermediate basis sets. In the latter case, the reduction of the *f* basis leads to a further increase of the dissociation energies enlarging the deviation from the AE result.

B. Correlation calculations

When correlation effects are included, the spectroscopic parameters are changed significantly compared to the HF level of calculation. The corresponding spectroscopic parameters are presented in Table IV. Not surprisingly, the most

distinct effect is observed for the dissociation energies which prove to be totally unrealistic at the HF level. At the correlated level the group 5 TM monoxides exhibit dissociation energies in the range of 6 to 7 eV while the group 10 TM monoxides show dissociation energies of approximately half this amount only.

Comparing the results of the AIMP and AE calculations at the correlated level we find that the effects of including the $(n-1)s$ shell are slightly more pronounced than at the HF level. Equilibrium distances of the group 5 TM monoxides increase by ~ 0.01 – 0.02 Å when *small-core* AIMPs are used instead of *medium-core* AIMPs. Concerning the augmentation of the intermediate basis, the same trends—both in direction and magnitude—are observed as in the HF calculations, in consistence with the fact that this augmentation improves the representation of the core exchange operator, which is an effective one-electron operator. Again, the *small-core* AIMP results, applying the aug.val representation basis sets, are in excellent agreement with the AE ones. The largest deviations occur for PtO, i.e., 0.013 Å in the bond length, 25 cm^{-1} in the harmonic vibrational frequency and 0.17 eV in the dissociation energy, which we consider to be still very good.

C. Comparison with other theoretical and experimental work

In Table V our results at the correlated level are compared with other theoretical and experimental work. For all group 5 TM monoxides, very good to excellent agreement with experimental results is found. Compared to the theoretical studies by Bauschlicher and Langhoff^{15,16} and Dolg *et al.*^{13,17} results of similar or better quality are obtained in the present study. Our calculated dissociation energies retain 91%–95% of the experimentally determined values, vibrational frequencies and equilibrium distances are reproduced to within an error of at most 23 cm^{-1} or 0.015 Å, respectively. Part of the remaining errors are due to deficiencies in the oxygen basis which is a [4s3p2d] set of generalized contracted Gaussians. In the diatomic oxides oxygen carries a

TABLE IV. Comparison of spectroscopic parameters obtained from AE, *medium-core* and *small-core* AIMP modified coupled-pair functional (if not noted otherwise) calculations. The labels val and aug.val denote different intermediate basis sets (see text).

Molecule	State	AIMP	Core	Representation		$R_e[\text{\AA}]$	$\omega[\text{cm}^{-1}]$	$D_e[\text{eV}]$
				Exchange	Relativistic			
VO	$^4\Sigma^-$	AIMP	[Mg]	val	val	1.565	1025	6.38
		AIMP	[Mg]	aug.val	aug.val	1.568	1017	6.31
		AIMP	[Ne]	val	val	1.585	1010	6.12
		AIMP	[Ne]	aug.val	aug.val	1.586	1008	6.09
		AE	ae	1.588	1003	6.06
NbO	$^4\Sigma^-$	AIMP	[Zn]	val	val	1.665	1012	7.31
		AIMP	[Zn]	aug.val	aug.val	1.662	1031	7.42
		AIMP	[Ar,3d]	val	val	1.685	998	7.05
		AIMP	[Ar,3d]	aug.val	aug.val	1.680	1022	7.21
		AE	ae	1.676	1022	7.23
TaO	$^4\Sigma^-$	AIMP	[Cd,4f]	val	val	1.692	992	7.33
		AIMP	[Cd,4f]	aug.val	aug.val	1.695	984	7.25
		AIMP	[Kr,4d,4f]	val	val	1.703	989	7.19
		AIMP	[Kr,4d,4f]	aug.val	aug.val	1.706	981	7.11
		AE	ae	1.710	990	7.03
NiO	$^3\Sigma^-$	AIMP	[Mg]	val	val	1.595	997	3.55
		AIMP	[Mg]	aug.val	aug.val	1.597	995	3.51
		AIMP	[Ne]	val	val	1.601	995	3.48
		AIMP	[Ne]	aug.val	aug.val	1.601	993	3.45
		AE	ae	1.599	1010	3.49
PdO	$^3\Pi$	AIMP	[Zn]	val	val	1.842	519	2.90
		AIMP	[Zn]	aug.val	aug.val	1.829	559	2.89
		AIMP	[Ar,3d]	val	val	1.856	461	2.85
		AIMP	[Ar,3d]	aug.val	aug.val	1.834	543	2.86
		AE	ae	1.836	542	2.80
PtO	$^3\Sigma^{-a}$	AIMP	[Cd,4f]	val	val	1.792	1027	2.88
		AIMP	[Cd,4f]	aug.val	aug.val	1.799	1020	2.78
		AIMP	[Kr,4d,4f]	val	val	1.797	1024	2.82
		AIMP	[Kr,4d,4f]	aug.val	aug.val	1.803	1014	2.73
		AE	ae	1.790	1039	2.90

^aACPF calculations with reference spaces obtained from distributing six electrons in the π and π' orbitals.

partial negative charge; for a proper description of the electron affinity at least one f polarization function is required.¹⁸

Somewhat larger errors in calculated spectroscopic parameters are found for the group 10 monoxides, in accord with the results of other theoretical studies.^{17,19} This is not too astonishing as large polarization basis sets are required to account for the differential electronic correlation in the late TM.^{20,21} Furthermore, spin-orbit interaction has a non-negligible influence on the spectroscopic parameters in the heavier compounds.

For NiO we underestimate the equilibrium distance by 0.03 Å, the vibrational frequency is overestimated by about 160 cm⁻¹ and we retain 88% of the experimental dissociation energy. Dolg *et al.*¹⁷ get a similar deviation for the equilibrium distance, perfect agreement for the vibrational frequency but they retain only 60% of the experimental dissociation energy. Multireference configuration interaction calculations by Bauschlicher *et al.*¹⁹ overestimate the equilibrium distance by 0.04 Å and underestimate the frequency by 140 cm⁻¹, while the single-reference results deviate considerably from experiment. It appears thus that both, large basis sets and a multireference treatment is required for NiO.

For PdO, to our knowledge, no reliable experimental spectroscopic parameters have been determined. Its dissociation energy, from which we retain 77%, was derived from thermochemical data.²² The only other theoretical study, which we know of, was performed by Bauschlicher *et al.*¹⁹ These authors did not include any kinematic relativistic effects, however. It is thus not astonishing that their results differ considerably from ours.

Even less is known about the properties of the heaviest homolog PtO. For a long time its ground state was erroneously identified as a state of $^1\Sigma^+$ symmetry.²²⁻²⁴ In 1983 Sassenberg *et al.*²⁵ concluded from their experimental spectral data that the lowest $\Omega=0^+$ and 1 states together correspond to a spin-orbit split $^3\Sigma^-$ state. They determined vibrational frequencies of 851 and 832 cm⁻¹ for the 0^+ and 1 states, respectively. Our calculated values of 1014 or 1039 cm⁻¹ at the AIMP or AE level of calculation, respectively, are substantially higher. However, as apparent from the substantial second-order splitting between the fine-structure components of the $^3\Sigma^-$ state, spin-orbit effects have a considerable influence on the spectroscopic parameters of PtO in this state. Although little is known about the excited elec-

TABLE V. Spectroscopic constants of group 5 and 10 transition metal monoxides. Spin-free relativistic calculations from our work, other theoretical and experimental results.

Molecule	State	Method	Level	Reference	R_e [\AA]	ω_e [cm^{-1}]	D_e [eV]
VO	$4\Sigma^-$	NP-AIMP ^a	MCPF	this work	1.586	1008	6.09
		NP-AE ^b	MCPF	this work	1.588	1003	6.06
		AE+R ^c	CPF	15	1.604	969	5.68 ^d
		PP ^e , nonrel.	CI(SD)+Q ^f	17	1.578	890	5.32
		Experiment		22	1.589	1011	6.41 ^d
		Experiment		26	...	1011	6.44±0.20
NbO	$4\Sigma^-$	NP-AIMP ^a	MCPF	this work	1.680	1022	7.21
		NP-AE ^b	MCPF	this work	1.676	1022	7.23
		RECP ^g	MCPF	16	1.697	977	6.83
		QRPP ^h	ACPF	13	1.675	1033	6.91
		Experiment		22	1.691	989	7.8 ^d
		Experiment		26	...	989	7.93±0.26
TaO	$4\Sigma^-$	NP-AIMP ^a	MCPF	this work	1.706	981	7.11
		NP-AE ^b	MCPF	this work	1.710	990	7.03
		QRPP ⁱ	ACPF	13	1.701	1004	6.91
	2Δ	NP-AIMP ^a	MCPF	this work	1.689	1026	7.53
		QRPP ⁱ	ACPF	13	1.691	1023	7.67
		Experiment		22	1.686	1030	8.2 ^d
Experiment		26	...	1030	8.24±0.13		
NiO	$3\Sigma^-$	NP-AIMP ^a	MCPF	this work	1.601	993	3.45
		NP-AE ^b	MCPF	this work	1.599	1010	3.49
		PP ^e , nonrel.	CI(SD)+Q ^f	17	1.591	848	2.33
		AE, nonrel.	CI(SD)+Q ^f	19	1.50	510	...
		AE, nonrel.	MRCI(SD)+Q ⁱ	19	1.67	690	...
		Experiment		22	3.87 ^d
		Experiment		26	...	838	3.91±0.18
		Experiment		27	1.627	839	3.81
PdO	3Π	NP-AIMP ^a	MCPF	this work	1.834	543	2.86 ^j
		NP-AE ^b	MCPF	this work	1.836	542	2.80 ^j
		AE, nonrel.	CI(SD)+Q ^f	19	1.95	480	...
	$3\Sigma^-$	NP-AIMP ^a	MCPF	this work	1.808	636	2.15
		AE, nonrel.	CI(SD)+Q ^f	19	1.70	380	...
		AE, nonrel.	MRCI(SD) ^k	19	1.95	470	...
		Experiment		22	2.87 ^d
		Experiment		26	...	810 ^l	...
PtO	$3\Sigma^-$	NP-AIMP ^a	ACPF	this work	1.803	1014	2.73
		NP-AE ^b	ACPF	this work	1.790	1039	2.90
		Experiment		25	...	851 ^m	...
		Experiment		25	...	832 ⁿ	...

^aSpin-free relativistic *small-core* NP-AIMP calculation using the intermediate basis sets of type aug.val for the representations of the exchange and no-pair operators.

^bSpin-free relativistic NP-AE calculation.

^cMass-velocity and Darwin contributions have been included using first-order perturbation theory.

^dA dissociation energy D_0 is given.

^eEnergy-adjusted pseudopotential method, SEFIT results are given for the R_e and ω_e ; D_e is taken from MEFIT calculations.

^fCI calculations with single and double excitations including Davidson correction.

^gRelativistic effective core potential method.

^hQuasirelativistic energy-adjusted pseudopotential method.

ⁱMRCI calculations with single and double excitations including Davidson correction.

^jDissociation to the s^1d^9 excited state of Pd.

^kMRCI calculations with single and double excitations.

^lEstimated value according to the authors' note.

^mHarmonic vibrational frequency of the $\Omega=0^+$ state.

ⁿHarmonic vibrational frequency of the $\Omega=1$ state.

tronic states of PtO, it can be deduced from the spectra of the lighter homologs NiO and PdO that a low-lying 3Π -state should exist in PtO which can interact with the ground state components via spin-orbit coupling.

V. CONCLUSIONS

In this work, we complement our previous study on relativistic no-pair *ab initio* model potentials and valence basis

sets for the transition elements Sc–Hg. AIMP and valence basis sets corresponding to valence spaces comprising the $ns, (n-1)d, (n-1)p$, and $(n-1)s$ shells are provided. Atomic properties obtained from AIMP Hartree–Fock calculations exhibit very good agreement with corresponding all-electron HF calculations. Excellent agreement between AIMP and AE results is obtained at the HF and the correlated levels for equilibrium distances and vibrational frequencies. As expected, the explicit inclusion of the $(n-1)s$ semicore into the valence space turns out to be more important for early than for late transition metal monoxides. Relativistic operators are sufficiently well represented in the valence basis. Augmenting the resolution of the identity for the exchange operator, on the other hand, improves dissociation energies, in particular of early TM monoxides, bringing them into close agreement with the AE results. In this case it is possible to reduce the third-row TM f valence basis sets without loss of accuracy which implies considerable savings in computational resources. For the group 5 TM monoxides our results agree very well with experiment, while for the group 10 TM monoxides inclusion of additional static and dynamic correlation effects and spin–orbit coupling seems to be indicated.

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