The *ab initio* model potential method: Third-series transition metal elements

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In this paper we present nonrelativistic and relativistic core *ab initio* model potentials (AIMPs) and valence basis sets for La and the third-series transition metal elements. The relativistic AIMPs are derived from atomic Cowan–Griffin calculations; they are made of a spin-free part and a one-electron spin-orbit operator according to Wood and Boring. The core potentials correspond to the 62-electron core $[Cd,4f]$. The valence basis sets are optimized and spin-orbit corrected. We present monitoring spin-free calculations on the atoms, singly ionized ions and monohydrides of the ten elements, which show a good performance overall. A spin-free-state-shifted spin-orbit-configuration interaction calculation on Pt, which uses empirical spin-free data and which is expected to be essentially free from spin-free deficiencies, points out that the quality of the spin-orbit operators is very good. © *1999 American Institute of Physics.* [S0021-9606(99)30301-9]

I. INTRODUCTION

Effective core potential (ECP) methods are widely accepted as efficient tools for reducing the computational demands of molecular and solid state *ab initio* calculations without damaging the quality of the calculated valence properties.[1,2] ECP methods are especially indicated for the heavy elements of the Periodic Table, since they have a large number of core electrons which can be safely frozen and, in addition, they demand the consideration of relativistic effects, which can be handled with economy and precision by means of ECP methods.[3] In particular, several sets of ECPs exist for the third-series transition metal elements. Some of them are ultimately based upon the Phillips–Kleinman equation[4] and rely on the pseudo-orbital transformation that produces nodeless valence pseudo-orbitals; this is the case of the *pseudopotentials* produced by Bachelet *et al.*,[5] Hay and Wadt,[6,7] Ross *et al.*,[8] and Andrae *et al.*[9] Some others are based on the Huzinaga–Cantu equation[10] and lead to valence orbitals with the same nodal structure as the all-electron orbitals; this is the case of the *model potentials* produced by Sakai *et al.*[11]

Also based on the Huzinaga–Cantu equation, the *ab initio* model potential (AIMP)[12] method resulted from the implementation of two ideas which contrast with the basics of all the other ECP methods: (i) the core model potentials are obtained directly from the frozen core orbitals, without resorting to parametrization procedures based on the valence orbitals, and (ii) the components of the core model potentials must mimic the operators that they substitute as much as possible, while reducing the computing time. Accordingly, nonrelativistic AIMPs (NR-AIMP) and spin-free relativistic AIMPs derived from atomic Cowan–Griffin[13] calculations (CG–AIMP) have been produced and successfully moni-

tored for the main-group elements,[12,14,15] and for the first-series and second-series transition metal elements,[14,16,17] but they are not available for the third-series transition metal elements. Along a parallel line, spin-free relativistic AIMPs aimed to be used with the no-pair Douglas–Kroll[18] Hamiltonian (NP-AIMP) have been produced for the third-series transition metal elements by Wittborn and Wahlgren,[19] as well as for the transition metal elements from Sc to Hg, altogether with optimized valence basis sets, by Rakowitz *et al.*[20]

The ability of the spin-free CG-AIMPs to represent genuine relativistic effects in a consistent manner down to a group of the Periodic Table was shown in Ref. 15. An extension of the CG-AIMP method to include spin-orbit effects according to Wood–Boring's ideas[21] was proposed and implemented (WB-AIMP),[22,23] and the corresponding spin-orbit operators and spin-orbit-corrected valence basis sets were produced for the main-group elements as well as for the first- and second-series transition metal elements.[23,24] Also, a simple and efficient spin-free-state-shifting technique (sfss) was proposed to be used in spin-orbit-configuration interaction (CI) calculations in a basis of double-group symmetry adapted functions, as a practical means to decouple electron correlation and spin-orbit interactions, while including a significant amount of spin-orbit polarization.[25] The use of the sfss technique with empirical spin-free spectra allows us to perform spin-orbit-CI calculations, essentially free of deficiencies in the treatment of correlation, which are ideal for monitoring the quality of spin-orbit operators; sfss-spin-orbit-CI calculations on Ir^+ pointed out the very good quality of the WB-AIMP spin-orbit operators.[26]

In this work, we produced the ingredients of nonrelativistic NR-AIMP and of relativistic spin-free CG-AIMP and spin-orbit WB-AIMP calculations for La and the third-series transition metal elements: core model potentials, spin-orbit-corrected valence basis sets, and spin-orbit operators. We

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monitored their performance in spin-free calculations on the atoms, singly ionized ions, and monohydrides of the ten elements and in a spin-free-state-shifted spin-orbit CI calculation on the even spectrum of Pt. The overall quality of the results is good.

II. METHOD: MODEL POTENTIALS AND VALENCE BASIS SETS

The detailed procedures to follow in order to obtain the nonrelativistic AIMPs (NR-AIMP), the spin-free relativistic AIMPs derived from Cowan–Griffin atomic calculations (CG-AIMP), and the Wood–Boring one-electron spin-orbit operators which are added to the CG-AIMP Hamiltonian in order to produce the spin-dependent WB-AIMP Hamiltonian, as well as the corresponding valence basis sets, are fully described in Refs. 12, 17, and 23. Here we will only outline very briefly the procedure of the relativistic version.

A. WB-AIMP Hamiltonian

The spin-dependent relativistic WB-AIMP Hamiltonian of a molecule $H^{\text{WB-AIMP}}$ is the sum of a spin-free relativistic Hamiltonian $H^{\text{CG-AIMP}}$ and a pure spin-orbit Hamiltonian H^{SO}:

$$H^{\text{WB-AIMP}} = H^{\text{CG-AIMP}} + H^{\text{SO}}. \tag{1}$$

For a molecule with N_{val} valence electrons and N_{nuc} nuclei (each with nuclear charge Z^I and number of core electrons Z^I_{core}), the spin-free Hamiltonian reads

$$H^{\text{CG-AIMP}} = \sum_i^{N_{\text{val}}} h^{\text{CG-AIMP}}(i) + \sum_{i<j}^{N_{\text{val}}} \frac{1}{r_{ij}}$$
$$+ \sum_{I<J}^{N_{\text{nuc}}} \frac{(Z^I - Z^I_{\text{core}})(Z^J - Z^J_{\text{core}})}{R_{IJ}}, \tag{2}$$

with $h^{\text{CG-AIMP}}(i)$, the one-electron spin-free relativistic Cowan–Griffin *ab initio* model potential operator, defined by

$$h^{\text{CG-AIMP}}(i) = -\frac{1}{2}\nabla_i^2 + \sum_I^{\text{nuclei}} \left[-\frac{Z^I - Z^I_{\text{core}}}{r_i} \right.$$
$$+ \sum_k \frac{C_k^I \exp(-\alpha_k^I r_i^2)}{r_i}$$
$$+ \sum_l \sum_{m=-l}^{+l} \sum_{a,b} |\chi^I_{alm}\rangle A^{I,\text{MP}}_{l;ab} \langle \chi^I_{blm}|$$
$$\left. + \sum_c^{\text{core}} (-2\varepsilon_c^I) |\phi_c^I\rangle \langle \phi_c^I| \right]. \tag{3}$$

The terms in Eq. (3) are the nonrelativistic kinetic energy operator and a sum over the atoms in the molecule, which includes the operators of the nuclear attraction, core Coulomb and exchange interactions, and mass velocity plus Darwin interactions, as well as a term resulting from the linear-independency conditions between core and valence orbitals. For each atom I, the first term is the nuclear attraction fully shielded by the core electrons and the rest are the AIMP terms. They are obtained as follows: A numerical all-electron spin-free relativistic Cowan–Griffin–Hartree–Fock

calculation[13] is performed on a given state of atom I (usually the ground state, see Table II). From this calculation, several atomic orbitals are arbitrarily chosen to be the *core* orbitals; they are represented by analytical Gaussian expansions which are obtained by a maximum overlap criterium[27] ($\phi_{1s}-\phi_{5s}, \phi_{2p}-\phi_{4p}, \phi_{3d}-\phi_{4d}$, and ϕ_{4f} for the third-series transition metal elements in this paper, which we will call in short [Cd,4f]), and they and their orbital energies ($\varepsilon_{1s}-\varepsilon_{5s}, \varepsilon_{2p}-\varepsilon_{4p}, \varepsilon_{3d}-\varepsilon_{4d}, \varepsilon_{4f}$) are conveniently stored in libraries. With the core orbitals, the core Coulomb potential $2\Sigma\hat{J}_c(r)$ is calculated, the nuclear attraction corresponding to the core electrons $-Z^I_{\text{core}}/r$ is added to it ($-62/r$ here), and the result is represented with a local potential $1/r\Sigma_k C_k\exp(-\alpha_k r^2)$ by means of a least-squares fitting and it is stored. This is the third term on the right hand side of Eq. (3). The mass-velocity and Darwin radial numerical operators of Cowan–Griffin (not to be confused with Pauli's mass velocity and Darwin operators)[13] which correspond to the valence orbitals are also stored [$V_{\text{MD},5p}(r), V_{\text{MD},5d}(r)$ and $V_{\text{MD},6s}(r)$, here]. In a given atomic or molecular calculation, these scalar relativistic operators are added to the core exchange operator $-\Sigma\hat{K}_c$ and the result is spectrally represented in the space defined by the set of (Gaussian) primitive functions used for atom I, $\{\chi^I_{alm}\}$, which results in the fourth term on the right hand side of Eq. (3). In consequence, the $A^{I,\text{MP}}_{l;ab}$ coefficients are the elements of the product matrix $S^{I-1}V_{\text{EMD}}S^{I-1}$; here, S^I is the overlap matrix in the basis of primitives $\{\chi^I_{alm}\}$ and V_{EMD} is the matrix of the operator $-\Sigma\hat{K}_c + \hat{O}_p V_{\text{MD},5p}\hat{O}_p + \hat{O}_d V_{\text{MD},5d}\hat{O}_d + \hat{O}_s V_{\text{MD},6s}\hat{O}_s$ of atom I in the same basis ($\hat{O}_l = \Sigma^{+l}_{m=-l}|lm\rangle\langle lm|$). Since the set of primitives $\{\chi^I_{alm}\}$ is likely to change from one molecular calculation to another and it would not be efficient to tabulate the $A^{I,\text{MP}}_{l;ab}$ coefficients, they are instead calculated during the input processing part of every single molecular calculation.[28] The last term on the right hand side of Eq. (3), which results from the linear-independency conditions between core and valence orbitals[10] is calculated with the core orbitals and orbital energies. All this defines the spin-free CG-AIMP Hamiltonian, which is obtained without resorting to any parametrization procedure based on the use of the valence orbitals.

The ingredients of the spin-free relativistic CG-AIMPs corresponding to the frozen-core [Cd,4f] of the third-series transition metal elements have been produced in this work ([Cd] frozen-core for La): The sets of $\{C_k, \alpha_k\}$ parameters, the core orbitals $\phi_{1s}-\phi_{5s}$, $\phi_{2p}-\phi_{4p}$, $\phi_{3d}-\phi_{4d}$, ϕ_{4f}, their orbital energies $\varepsilon_{1s}-\varepsilon_{5s}$, $\varepsilon_{2p}-\varepsilon_{4p}$, $\varepsilon_{3d}-\varepsilon_{4d}$, ε_{4f}, and the radial mass-velocity plus Darwin operators $V_{MD,5p}(r)$, $V_{MD,5d}(r)$ and $V_{MD,6s}(r)$. The corresponding nonrelativistic NR-AIMPs, which are necessary in order to study the size of the relativistic effects, have been produced as well (in this case the mass velocity and Darwin operators are suppressed). All these data are available from the authors.[29] Valence basis sets, Coulomb model potentials and core orbitals are presented in a PAPS document.[30]

The spin-orbit contribution in Eq. (1) is

$$H^{SO} = \sum_i^{N_{val}} \sum_I^{nuclei} h_{SO}^I(i), \qquad (4)$$

with the atomic one-electron spin-orbit terms,

$$h_{SO}^I(i) = \lambda^I \sum_{nl}^{valence} V_{SO,nl}^{I,MP}(r_i) \, \hat{O}_l^I \hat{l}^I \hat{s} \, \hat{O}_l^I. \qquad (5)$$

Herein, $\hat{l}^I$ and $\hat{s}$ are the usual vector angular momentum and spin operators, respectively; the projectors $\hat{O}_l^I$ (defined in terms of the spherical harmonics as $\hat{O}_l^I = \sum_{m=-l}^{+l} |lm,I\rangle\langle lm,I|$) are used in the form proposed by Pitzer and Winter.[31] The radial components are chosen to be analytical functions,

$$V_{SO,nl}^{I,MP}(r_i) = \sum_k \frac{B_k^{nl,I} \exp(-\beta_k^{nl,I} r_i^2)}{r_i^2}, \qquad (6)$$

whose parameters $\{B_k^{nl,I}, \beta_k^{nl,I}\}$ are determined through weighted least-squares fitting to the radial part of the Wood–Boring spin-orbit operator[21] which reads

$$V_{SO,nl}(r) = \frac{\alpha^2}{\{2 + \alpha^2[\epsilon_{nl} - V(r)]\}r} \frac{dV(r)}{dr}. \qquad (7)$$

Herein, α is the fine-structure constant, ϵ_{nl} are the orbital energies of the spin-free relativistic equations of Cowan and Griffin, and $V(r)$ is an $X\alpha$ approximation to the Hartree–Fock (HF) one-electron potential.[13] This effective one-electron spin-orbit operator includes an average of two-electron contributions through the use of the $X\alpha$ Hartree–Fock potential $V(r)$, although its detailed relationship to a mean-field spin-orbit operator is unknown. Also, an atomic scaling factor λ^I is included in Eq. (5) which was first empirically parametrized[23] and later found to be unnecessary;[26] in consequence, we use $\lambda^I = 1$. The $\{B_k, \beta_k\}$ parameters for the third-series transition metal elements have been produced here and they are presented in Table I.

B. Spin-free-state-shifted WB-AIMP Hamiltonian

The spin-free relativistic $H^{CG\text{-}AIMP}$ Hamiltonian [Eq. (2)] is used in standard nonrelativistic methods. The spin-dependent $H^{WB\text{-}AIMP}$ Hamiltonian [Eq. (1)] is used in spin-orbit CI calculations, e.g., in a basis of double-group symmetry-adapted functions with HF or complete active space self-consistent field (CASSCF) orbitals produced with the spin-free $H^{CG\text{-}AIMP}$ Hamiltonian. In order to treat electron correlation and spin-orbit interactions at the highest possible level, the sfss Hamiltonian $H_{sfss}^{WB\text{-}AIMP}$ was introduced:[25,26]

$$H_{sfss}^{WB\text{-}AIMP} = H^{WB\text{-}AIMP} + \sum_{iSM_S\Gamma\gamma} \delta(iS\Gamma)|\Phi^{\mathcal{P}}(iSM_S\Gamma\gamma)\rangle$$

$$\times\langle\Phi^{\mathcal{P}}(iSM_S\Gamma\gamma)|, \qquad (8)$$

with

$$\delta(iS\Gamma) = [E^{\mathcal{G}}(iS\Gamma) - E^{\mathcal{G}}(GS)] - [E^{\mathcal{P}}(iS\Gamma) - E^{\mathcal{P}}(GS)]. \qquad (9)$$

Here, $\mathcal{P}$ and $\mathcal{G}$ are two CI spaces of, respectively, small and large relative size; $\mathcal{P}$ is supposed to be good enough for the calculation of the spin-orbit couplings but not for the electron correlation effects, for which the much larger $\mathcal{G}$ space is necessary. $\Phi^{\mathcal{P}}(iSM_S\Gamma\gamma)$ are spin-free CI wave functions in the small space. GS refers to the ground state, but it can be any given spin-free state. This sfss Hamiltonian is a practical means to take advantage of the fact that electron correlation is handled with a much larger efficiency with spin-free Hamiltonians than with spin-dependent Hamiltonians. Its use is based on the assumption that correlation and spin-orbit can be decoupled to a large extent. A sfss spin-orbit calculation requires performing correlated spin-free calculations with the $H^{CG\text{-}AIMP}$ Hamiltonian using the $\mathcal{G}$ and $\mathcal{P}$ spaces and one final spin-orbit CI calculation with the $H_{sfss}^{WB\text{-}AIMP}$ Hamiltonian using the $\mathcal{P}$ space. A $\mathcal{P}$ space made of the significant reference configurations plus single excitations which can partially take care of spin-orbit polarizations has been proven to be very efficient in Ir^+.[26]

C. Atomic valence basis sets

The $H^{CG\text{-}AIMP}$ Hamiltonian [Eq. (2)] is used in atomic valence-only Hartree–Fock calculations and the valence basis sets (exponents and coefficients) are optimized by minimization of the valence SCF energy using standard all-electron methods.[32] The resulting valence atomic orbitals are spin-orbit corrected by changing the value of the innermost coefficient (and renormalizing) in such a way that the spin-orbit valence orbital coupling constants (ζ_{5p} and ζ_{5d} here) have the same value when they are evaluated using the numerical Cowan–Griffin–Hartree–Fock atomic orbitals and using the analytical spin-orbit-corrected valence orbitals.[23] This procedure has been shown to significantly improve the spin-orbit dependent properties at the same time that the quality of the bonding related properties is maintained.[23] Following this procedure, we obtained in this work the spin-orbit-corrected relativistic valence basis sets for the third-series transition metal elements. We obtained as well the nonrelativistic ones. All of them are available from the authors.[29] The basis sets obtained in this work are minimal valence basis sets made of $13s9p8d$ primitive Gaussian functions ($13s9p7d$ for La) contracted as $[1/1/1]$. When they are used in atomic and molecular calculations their flexibility can be enhanced with the release of the outermost primitives and the addition of appropriate functions, such as polarization (p and f) and diffuse (d) functions. Furthermore, artificial effects in molecules due to insufficient two-center orthogonality between the molecular orbitals and the $4f$ core orbital of the transition metal elements can be eliminated by extending the valence basis set in molecular calculations with the fully contracted $4f$ core orbital itself;[12] a single split of this orbital provides polarization of the $5d$ orbital and makes unnecessary the addition of polarization f functions. As we will see in Sec. IV, a recommended valence basis set results in s and d double-split, p single-split, the addition of one p-polarization primitive function (from Ref. 32), one diffuse d primitive function (from extrapolation of the lowest exponents), and the $4f$ core orbital (a five-primitive con-

TABLE I. Radial components of the spin-orbit operators [Eq. (6)].

Lanthanum		Hafnium		Tantalum	
$V_{SO}(5p)$		$V_{SO}(5p)$		$V_{SO}(5p)$	
β_k	B_k	β_k	B_k	β_k	B_k
1 062 434.0	0.316 284 351	828 377.0	0.298 838 027	840 608.0	0.295 090 740
1 139 43.8	0.259 445 609	92 047.30	0.259 885 928	93 875.00	0.260 778 075
17 362.70	0.143 824 809	14 720.05	0.158 482 339	14 929.95	0.161 947 106
2937.296	0.076 265 260	2519.611	0.084 861 639	2519.611	0.086 167 150
408.8461	0.034 413 499	386.8130	0.039 569 368	386.8130	0.040 070 293
49.682 97	0.013 636 063	54.446 65	0.016 299 951	54.676 35	0.016 448 812
5.182 618	0.003 714 795	6.581 837	0.005 417 598	6.722 247	0.005 539 299
0.492 503 9	0.000 558 879	0.707 144 1	0.000 729 291	0.707 758 1	0.000 748 354
$V_{SO}(5d)$		$V_{SO}(5d)$		$V_{SO}(5d)$	
β_k	B_k	β_k	B_k	β_k	B_k
648 783.0	0.356 649 850	348 937.0	0.366 814 713	349 416.0	0.364 827 965
62 450.70	0.246 617 397	32 404.40	0.241 792 838	32 681.90	0.243 007 244
8133.880	0.122 464 582	4061.380	0.114 948 612	4131.870	0.116 489 903
1160.066	0.052 313 001	546.6730	0.048 181 516	561.3760	0.049 178 174
171.0242	0.021 397 030	74.731 60	0.018 693 068	77.425 50	0.019 185 962
24.930 41	0.008 620 685	10.544 20	0.006 313 701	11.010 60	0.006 553 580
3.023 650	0.002 413 158	1.733 970	0.001 565 644	1.828 700	0.001 630 219
.321 065 5	0.000 321 494	0.1491 84 0	0.000 104 793	0.177 0230	0.000 127 945

Tungsten		Rhenium		Osmium	
$V_{SO}(5p)$		$V_{SO}(5p)$		$V_{SO}(5p)$	
β_k	B_k	β_k	B_k	β_k	B_k
840 410.0	0.292 284 394	922 982.0	0.281 975 229	1 009 680.0	0.271 456 538
94 870.30	0.259 941 525	104 721.7	0.263 327 714	116 787.0	0.262 151 089
15 148.14	0.165 055 520	16 373.70	0.173 618 991	18 740.30	0.179 499 356
2519.611	0.087 553 721	2634.738	0.091 390 804	3041.200	0.098 671 823
386.8130	0.040 559 331	399.0759	0.041 813 094	448.7360	0.045 308 897
54.686 35	0.016 648 257	56.339 63	0.017 068 254	61.888 80	0.018 306 087
6.772 687	0.005 616 782	7.062 068	0.005 810 721	7.638 500	0.006 213 038
0.703 6291	0.000 758 001	0.731 489 1	0.000 807 641	0.781 950 0	0.000 890 679
$V_{SO}(5d)$		$V_{SO}(5d)$		$V_{SO}(5d)$	
β_k	B_k	β_k	B_k	β_k	B_k
349 596.0	0.362 893 222	349 585.0	0.360 991 782	351 666.0	0.358 665 412
32 920.90	0.244 148 559	33 134.30	0.245 228 476	33 589.80	0.246 486 326
4196.500	0.117 967 330	4257.350	0.119 397 667	4356.250	0.121 139 567
575.2550	0.050 147 739	588.6360	0.051 101 293	608.0600	0.052 268 725
79.991 00	0.019 670 568	82.478 30	0.020 151 892	85.908 00	0.020 728 011
11.444 80	0.006 791 469	11.856 60	0.007 029 825	12.452 10	0.007 309 680
1.911 340	0.001 686 669	1.982 920	0.001 737 394	2.094 200	0.001 820 379
0.204 235 0	0.000 150 781	0.230 714 0	0.000 172 843	0.262 283 0	0.000 201 494

Iridium		Platinum		Gold	
$V_{SO}(5p)$		$V_{SO}(5p)$		$V_{SO}(5p)$	
β_k	B_k	β_k	B_k	β_k	B_k
882 208.0	0.280 937 582	938 208.0	0.273 778 825	917 162.0	0.273 090 953
101 270.3	0.260 624 153	107 472.2	0.263 432 589	105 793.0	0.262 044 288
16 368.63	0.172 573 920	17 116.37	0.177 544 734	17 107.55	0.177 122 614
2730.553	0.093 356 420	2830.690	0.095 918 641	2876.224	0.096 774 473
421.5071	0.043 691 874	437.5741	0.044 861 087	450.9637	0.045 667 731
60.063 78	0.017 976 984	62.811 86	0.018 533 717	65.823 22	0.019 027 479
7.658 918	0.006 217 620	8.084 998	0.006 485 347	8.649 507	0.006 772 759
0.790 591 0	0.000 912 627	0.836 348 0	0.000 986 817	0.918 923 0	0.001 100 221

TABLE I. (*Continued.*)

Iridium		Platinum		Gold	
$V_{SO}(5d)$		$V_{SO}(5d)$		$V_{SO}(5d)$	
β_k	B_k	β_k	B_k	β_k	B_k
351 444.0	0.356 798 362	352 227.0	0.354 828 824	522 618.0	0.321 613 769
33 772.00	0.247 464 382	34 052.30	0.248 520 440	55 150.30	0.259 216 658
4412.710	0.122 498 426	4483.450	0.123 985 135	8094.750	0.146 062 835
621.0900	0.053 200 728	636.3300	0.054 206 909	1304.760	0.069 573 800
88.397 00	0.021 209 766	91.275 00	0.021 727 345	221.7660	0.029 945 002
12.867 40	0.007 551 498	13.361 50	0.007 811 745	41.542 80	0.012 869 195
2.161 890	0.001 871 219	2.244 970	0.001 935 926	6.959 130	0.005 412 024
0.288 264 0	0.000 224 480	0.317 000 0	0.000 250 328	0.820 868 0	0.000 930 658

Mercury	
$V_{SO}(5p)$	
β_k	B_k
932 177.0	0.269 394 517
108 157.3	0.261 683 193
17 571.02	0.179 717 150
2948.894	0.098 863 660
461.5352	0.046 780 200
67.105 45	0.019 465 947
8.823 955	0.006 938 324
0.922 818 0	0.001 127 373

$V_{SO}(5d)$	
β_k	B_k
353 312.0	0.350 677 226
34 598.30	0.250 421 955
4626.050	0.126 897 965
667.3400	0.056 246 575
97.078 00	0.022 780 150
14.350 10	0.008 338 649
2.401 020	0.002 066 076
0.373 786 0	0.000 301 015

tracted function) single-split, that is a $13s10p9d5f$ primitive set contracted as $[3/3/4/2]$. Further uncontraction leads to even more flexible basis sets. For Lanthanum, the d splitting is a single one and the f function has only one primitive from Ref. 33, that is a $13s10p8d1f$ primitive set contracted as $[3/3/3/1]$.

III. ATOMIC CALCULATIONS

A. Spin-free calculations

In Table II we present spin-free relativistic Cowan–Griffin–Hartree–Fock valence energies and $5p$, $5d$ and $6s$ orbital energies and radial expectation values of the third-series transition metal elements. We show the results of the CG-AIMP calculations corresponding to the uncorrected and the spin-orbit corrected valence basis sets, together with the all-electron numerical Cowan–Griffin–Hartree–Fock calculations.[13] We present as well the $5p$ and $5d$ spin-orbit coupling constants, defined as $\zeta_{nl} = \langle \phi_{nl} | V_{SO,nl} | \phi_{nl} \rangle$; the all-electron numerical ones are calculated with the numerical spin-orbit operators [Eq. (7)] and the CG-AIMP ones with the analytical approximations of them [Eq. (6)]. It is observed that the spin-orbit correction of the basis sets, de-

signed to produce correct orbital spin-orbit coupling constants, significantly improves the expectation value of $1/r^3$, very much related to spin-orbit coupling, at a time that keeps essentially unaffected the orbital energies and the other radial expected values, which are bond-related properties. The overall agreement between the CG-AIMP results which use spin-orbit-corrected basis sets and the all-electron calculations is very good. We should note that, in contrast with pseudopotential methods, neither these properties nor the orbital shapes enter fitting procedures in the AIMP method; this agreement does simply reflect the facts that the model potentials efficiently mimic the operators substituted by them and that the valence basis sets are of good quality. A similar agreement is reached as well in the nonrelativistic case.

In Table III we present $6s \rightarrow 5d$ excitation energies and $6s$ ionization energies, calculated at the Hartree–Fock level, which are useful to compare AIMP and all-electron results. The all-electron calculations are numerical. The basis sets used in the AIMP calculations result in triple-s, single-p and double-d split of the atomic orbitals and the addition of one polarization p function[32] and one diffuse d function required for a proper description of the configurations with different $6s$ and $5d$ population[34] (obtained by extrapolation from the

TABLE II. Spin-free relativistic valence energy, orbital energies and radial expectation values (in a.u.) and orbital spin-orbit coupling constants ζ_{nl} (in cm^{-1}). First entry: CG-AIMP calculations with the uncorrected valence basis sets. Second entry: CG-AIMP calculations with spin-orbit-corrected valence basis sets. Third entry: All-electron numerical Cowan–Griffin–Hartree–Fock calculations.

| | E(val) | $-\epsilon(6s)$ | $\langle 1/r\rangle_{6s}$ | $\langle r\rangle_{6s}$ | $-\epsilon(5d)$ | $\langle 1/r^3\rangle_{5d}$ | $\langle 1/r\rangle_{5d}$ | $\langle r\rangle_{5d}$ | ζ_{5d} |
					$-\epsilon(5p)$	$\langle 1/r^3\rangle_{5p}$	$\langle 1/r\rangle_{5p}$	$\langle r\rangle_{5p}$	ζ_{5p}
La $(s^2d^1)^2D$	−19.662 512	0.176 97	0.259	4.763	0.234 93	2.139	0.452	2.819	568
	−19.662 220	0.177 02	0.259	4.763	0.234 92	2.126	0.452	2.819	563
		0.179 57	0.263	4.723	0.235 46	2.119	0.447	2.891	563
					1.052 11	38.527	0.714	1.810	11 454
					1.052 04	39.239	0.715	1.810	11 663
					1.053 79	39.534	0.714	1.810	11 663
Hf $(s^2d^2)^3F$	−31.027 574	0.234 83	0.335	3.729	0.262 55	4.298	0.562	2.323	1478
	−31.008 169	0.234 84	0.335	3.729	0.262 56	4.272	0.562	2.323	1467
		0.237 03	0.337	3.712	0.263 42	4.268	0.560	2.339	1467
					1.603 64	105.407	0.965	1.352	38 209
					1.600 48	96.195	0.964	1.352	35 010
					1.605 65	98.023	0.957	1.353	35 012
Ta $(s^2d^3)^4F$	−37.893 064	0.247 43	0.351	3.574	0.320 09	5.485	0.617	2.109	1918
	−37.868 447	0.247 44	0.351	3.574	0.320 12	5.453	0.617	2.109	1907
		0.249 95	0.353	3.556	0.321 10	5.449	0.615	2.120	1907
					1.770 56	118.030	1.004	1.304	43157
					1.766 50	106.998	1.002	1.304	39 391
					1.772 46	109.139	0.995	1.305	39 393
W $(s^2d^4)^5D$	−45.777 679	0.258 79	0.365	3.443	0.372 74	6.683	0.665	1.956	2378
	−45.748 083	0.258 80	0.365	3.443	0.372 78	6.647	0.664	1.956	2364
		0.261 52	0.368	3.424	0.373 63	6.643	0.663	1.964	2363
					1.939 89	131.364	1.043	1.259	48 684
					1.935 05	118.493	1.040	1.259	44 118
					1.941 22	120.989	1.032	1.260	44 120
Re $(s^2d^5)^6S$	−54.769 587	0.268 12	0.378	3.335	0.433 94	7.944	0.710	1.829	2872
	−54.733 532	0.268 13	0.378	3.335	0.433 98	7.917	0.710	1.829	2861
		0.271 15	0.381	3.315	0.434 53	7.914	0.709	1.834	2861
					2.108 88	145.690	1.081	1.218	54 565
					2.102 97	130.623	1.078	1.218	49 174
					2.109 44	133.519	1.069	1.219	49 177
Os $(s^2d^6)^5D$	−64.748 472	0.280 84	0.391	3.219	0.451 71	9.191	0.747	1.746	3376
	−64.704 751	0.280 86	0.391	3.219	0.451 75	9.103	0.747	1.746	3340
		0.284 94	0.397	3.193	0.451 91	9.097	0.745	1.751	3340
					2.295 74	161.331	1.119	1.178	61 047
					2.288 63	143.792	1.116	1.178	54721
					2.295 55	147.143	1.106	1.179	54 723
Ir $(s^2d^7)^4F$	−75.946 399	0.291 90	0.404	3.120	0.484 57	10.522	0.785	1.666	3924
	−75.893 611	0.291 92	0.404	3.120	0.484 62	10.405	0.785	1.665	3876
		0.296 68	0.411	3.092	0.484 54	10.398	0.783	1.670	3876
					2.481 41	177.955	1.158	1.142	68 014
					2.472 84	157.615	1.154	1.142	60 621
					2.480 52	161.477	1.143	1.143	60 624
Pt $(s^2d^8)^3F$	−88.397 200	0.304 72	0.422	3.014	0.518 53	11.929	0.822	1.594	4515
	−88.334 019	0.304 74	0.422	3.014	0.518 58	11.789	0.822	1.594	4457
		0.307 50	0.424	3.001	0.521 19	11.783	0.820	1.597	4457
					2.667 28	193.634	1.196	1.109	75 503
					2.657 04	172.184	1.192	1.109	66 917
					2.667 61	176.616	1.180	1.110	66 921
Au $(s^1d^{10})^2S$	−102.257 448	0.285 77	0.411	3.088	0.449 90	12.627	0.836	1.579	4844
	−102.184 158	0.285 80	0.411	3.088	0.449 98	12.499	0.835	1.579	4792
		0.290 55	0.415	3.066	0.453 50	12.494	0.834	1.583	4792
					2.744 68	212.006	1.228	1.082	82 611
					2.732 77	185.500	1.224	1.082	72 832
					2.746 96	190.517	1.211	1.083	72 836
Hg $(s^2d^{10})^1S$	−117.306 043	0.323 99	0.446	2.859	0.602 50	14.999	0.895	1.468	5842
	−117.217 593	0.324 03	0.446	2.859	0.602 58	14.803	0.895	1.468	5759
		0.327 17	0.449	2.846	0.604 29	14.797	0.893	1.469	5759
					3.050 05	234.348	1.272	1.048	92 166
					3.035 76	203.650	1.267	1.048	80 765
					3.049 56	209.432	1.252	1.049	80 769

TABLE III. Atomic excitation and ionization energies with respect to the lowest atomic terms of the configu-rations $5d^n6s^2$: All-electron (first entry) and AIMP (second entry) nonrelativistic Hartree-Fock and spin-free relativistic Cowan–Griffin–Hartree–Fock results. No-pair spin-free relativistic results from Ref. 19 are in-cluded for comparison. All numbers in eV.

	NR-HF[a]	CG-HF[b]	NP-HF[c]	Exp.[d]		NR-HF[a]	CG-HF[b]	Exp.[d]
→La $(s^1d^2)^4F$	−0.98	−0.30	−0.31	0.36	→La$^+(s^1d^1)^3D$	4.30[e]	4.49[e]	5.87
	−0.94	−0.30	−0.38			4.32	4.50	
→Hf $(s^1d^3)^5F$	−0.38	0.95	0.94	1.69	→Hf$^+(s^1d^2)^4F$	5.07	5.61	—
	−0.36	0.95	0.91			5.10	5.62	
→Ta $(s^1d^4)^6D$	−1.28	0.21	0.18	1.04	→ Ta$^+(s^1d^3)^5F$	5.13	5.71	7.90
	−1.27	0.19	0.16			5.16	5.72	
→W $(s^1d^5)^7S$	−2.95	−1.29	−1.31	−0.18	→W$^+(s^1d^4)^6D$	5.17	5.77	7.94
	−2.93	−1.26	−1.35			5.21	5.81	
→Re $(s^1d^6)^6D$	−0.04	1.76	1.71	1.76	→Re$^+(s^1d^5)^7S$	5.19	5.79	7.88
	−0.03	1.73	1.69			5.24	5.80	
→Os $(s^1d^7)^5F$	−1.63	0.55	0.54	0.75	→Os$^+(s^1d^6)^6D$	5.58	6.40	8.77
	−1.61	0.52	0.50			5.62	6.41	
→Ir $(s^1d^8)^4F$	−2.43	0.09	0.07	0.40	→ Ir$^+(s^1d^7)^5F$	5.94	6.97	—
	−2.41	0.07	0.00			5.96	6.97	
→Pt $(s^1d^9)^3D$	−3.15[e]	−0.40	−0.45	−0.64	→Pt$^+(s^1d^8)^4F$	6.26	7.51	9.22
	−3.17	−0.41	−0.56			6.28	7.51	
→Au $(s^1d^{10})^2S$	−5.13	−1.86	⋯	−1.74	→Au$^+(s^1d^9)^3D$	6.56	8.03	9.76
	−5.27	−1.88	⋯			6.64	8.09	
	⋯	⋯	⋯	⋯	→Hg$^+(s^1d^{10})^2S$	6.83	8.51	10.43
	⋯	⋯	⋯	⋯		6.84	8.47	

[a]Nonrelativistic Hartree–Fock calculations. AE results from Ref. 58.
[b]Spin-free relativistic Cowan–Griffin–Hartree–Fock calculations (see Ref. 13). AE results from Ref. 58.
[c]No-pair spin-free relativistic Hartree–Fock calculations (Ref. 18) performed in Ref. 19.
[d]Reference 58, averages over experimental spin-orbit components of Ref. 37.
[e]This work. This result is not coincident with that of Ref. 58.

two outermost exponents). The contraction used in the AIMP calculations is [4/3/4] ([4/3/3] for La upon single-d split only). Table III reveals that the deviations brought about by the AIMP approximations are small and that they are very similar in the nonrelativistic and in the spin-free relativistic calculations. The all-electron relativistic effects are, in con-sequence, very well reproduced in the AIMP calculations. The results of the spin-free relativistic Douglas–Kroll no-pair calculations[18] on the $6s→5d$ excitation energies of Ref. 19 have been included in Table III; one can observe that the ability of the AIMP approach to mimic the all-electron (AE) results is similar in this case, too. Also, the results of spin-free relativistic approximations of Douglas–Kroll and Cowan–Griffin are remarkably close, both at the all-electron and at the AIMP levels.

Once we know that the AIMP results resemble the AE ones within reasonable limits, and taking into account that electron correlation effects are necessary for a correct de-scription of the atomic excitations under consideration, we performed CASSCF calculations[35] where the active orbital space included the $5d$ and $6s$ orbitals, followed by average coupled-pair functional (ACPF) calculations[36] in which the previous CASSCF space was used as a multireference for single and double excitations. In all these CASSCF and ACPF calculations, we double split rather than triple split the s atomic orbital and we augmented the basis set with the $4f$ core orbital singly split, which resulted in a final contraction [3/3/4/2], except for La where a [3/3/3] contraction was used. In a first set of ACPF calculations labeled ACPF-ds, we cor-related only the $5d$ and $6s$ electrons; in a second set labeled

ACPF-[p]ds, we also allowed for single and double excita-tions from the $5p$ closed shell. We performed all these cal-culations with the nonrelativistic and the spin-free relativistic Hamiltonians, NR-AIMP and CG-AIMP. The results are shown in Table IV. One can see that the correlation effects are significant in general. The relativistic effects are, how-ever, crucial to reproduce the experimental values of these transitions. This is evident in Fig. 1, where the overall good quality of the CG-AIMP ACPF-[p]ds results is also clear.

B. Spin-orbit calculations

A realistic check of the quality of any spin-orbit operator can only be achieved through calculations that do not show any deficiencies in the treatment of spin-free effects. In par-ticular, contaminations associated with insufficient treatment of electron correlation must be avoided. Recent calculations of Ir$^+$ (Ref. 26) have shown that electron correlation and spin-orbit effects can be effectively decoupled to a large ex-tent by means of the *spin-free-state-shifting* technique [Eqs. (8) and (9)] and pointed out an unambiguous, systematic way to ascertain the accuracy of any spin-orbit operator based on the use of spin-free empirical information[26] (or, alternatively, benchmark spin-free calculations). Here we monitored the quality of the spin-orbit operator of Pt accordingly, that is in a sfss-WB-AIMP multireference CI [MRCI(S)] spin-orbit calculation, as we describe next.

We used the $H_{\text{sfss}}^{\text{WB-AIMP}}$ Hamiltonian [Eqs. (8) and (9)] with empirical data for the spin-free spectrum $E^{\mathcal{G}}(iS\Gamma) - E^{\mathcal{G}}(\text{GS})$ in a spin-orbit MRCI(S) calculation on the basis

TABLE IV. Atomic excitation energies with respect to the lowest atomic terms of the configurations $5d^n6s^2$. Nonrelativistic (first entry) and spin-free Cowan–Griffin relativistic (second entry) *ab initio* model potential CASSCF and ACPF results. All numbers in eV.

		CASSCF[a]	ACPF-ds[b]	ACPF-[p]ds[c]	Exp.[d]
→ La $(s^1d^2)^4F$	NR-AIMP	−0.35	—	0.22	
	CG-AIMP	0.13	—	0.73	0.36
→Hf $(s^1d^3)^5F$	NR-AIMP	−0.24	0.34	0.36	
	CG-AIMP	1.13	1.59	1.58	1.69
→Ta $(s^1d^4)^6D$	NR-AIMP	−1.11	−0.54	−0.46	
	CG-AIMP	0.38	0.82	0.86	1.04
→W $(s^1d^5)^7S$	NR-AIMP	−2.70	−1.99	−1.85	
	CG-AIMP	−1.05	−0.54	−0.43	−0.18
→Re $(s^1d^6)^6D$	NR-AIMP	−0.03	0.01	0.22	
	CG-AIMP	1.73	1.85	1.93	1.76
→Os $(s^1d^7)^5F$	NR-AIMP	−1.61	−1.40	−1.25	
	CG-AIMP	0.53	0.66	0.80	0.75
→Ir $(s^1d^8)^4F$	NR-AIMP	−2.40	−2.35	−2.18	
	CG-AIMP	0.07	0.06	0.23	0.40
→Pt $(s^1d^9)^3D$	NR-AIMP	−3.17	−3.25	−3.04	
	CG-AIMP	−0.41	−0.55	−0.34	−0.64
→Au $(s^1d^{10})^2S$	NR-AIMP	−5.27	−5.45	−5.18	
	CG-AIMP	−1.88	−2.07	−1.79	−1.74

[a]The active orbital space consists of the $5d$ and $6s$ orbitals.
[b]ACPF calculation with a multireference which is the previous CASSCF. Only $5d$ and $6s$ electrons are correlated.
[c]ACPF calculation with a multireference which is the previous CASSCF. $5p$, $5d$ and $6s$ electrons are correlated.
[d]Reference 58, averages over experimental spin-orbit components of Ref. 37.

FIG. 1. $6s\rightarrow5d$ transitions of the third-series transition metal elements: (full line) experimental data (averages over experimental spin-orbit components); (dashed line) spin-free relativistic CG-AIMP ACPF-[p]ds calculations of this work; (dotted line) nonrelativistic NR-AIMP ACPF-[p]ds calculations of this work.

of double-group symmetry-adapted functions which resulted after allowing single excitations from a multireference made of the relevant configurations: 21 configurations corresponding to the distribution of ten electrons in the $5d$ and $6s$ orbitals. (The orbitals were optimized in CG-AIMP HF calculations on $5d^86s^2-{}^3F$. We used $\bar{D}_{2h}$ double-group symmetry but obtained degeneracies with energy separations below 10^{-6} hartree for the components of a given J quantum number.) In order to produce the empirical spin-free spectrum, we performed a generalized least-squares fitting of all the parameters in the interaction matrices to the experimental even spectrum of Pt (Ref. 37) using the programs of Cowan[38] and following the procedure described by Kleef and Metsch;[39] then, we diagonalized the interaction matrices which resulted from using all the spin-free parameters and setting all the spin-dependent ones to zero. The empirical spin-free spectrum that we obtained is shown in Table V. The results of the spin-free CG-AIMP MRCI(S) calculation performed in the same CI space used in the corresponding spin-orbit MRCI(S) and the corresponding shifting constants $\delta(iS\Gamma)$ [Eq. (9)] are also shown.

In Table VI we compare the results of the sfss-WB-AIMP MRCI(S) spin-orbit calculation described above with the experiment. We can see that the quality of the results is very high, in line with what has already been observed in Ir$^+$.[26] This should be taken as an indication of two things: first, the quality of the spin-orbit operator is very high, and second, the spin-orbit and correlation effects can be decoupled to a large extent so that the latter can be handled in a separate spin-free calculation. We included in Table VI the
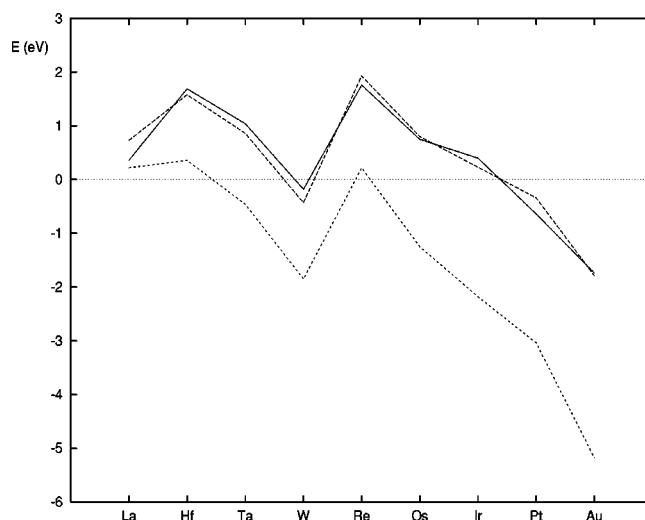
results of an (unshifted) WB-AIMP MRCI(SD) calculation, in which a much larger CI space including also double excitations from the same reference was used,[40] as well as the results of a Dirac–Hartree–Fock plus four-component CI (singles and doubles) calculation of Visscher *et al.*[41] of a comparable level in the treatment of correlation. The results of both of them are quite close and show a reasonable agreement with the experiment, but significantly poorer than the sfss-WB-AIMP MRCI(S) calculation; what emerges from the comparison is that the main source of the deviations from the experiment in the two unshifted calculations is not the treatment of the spin-orbit effects but the treatment of the correlation effects, which indirectly contaminates the spin-orbit splittings.

IV. MOLECULAR CALCULATIONS

A. Details of the calculations

In this section we present the results of monitoring molecular calculations on MH monohydrides of the third-series transition metal elements. We performed CASSCF calculations in which the outermost M–$5d$ and M–$6s$ electrons and the H–$1s$ electron are distributed in all possible ways among the σ, σ', σ'', π and δ molecular orbitals with main character of the above mentioned atomic orbitals. Using the CASSCF molecular orbitals we performed two sets of ACPF calculations (multireference single and double CI with size-consistency corrections)[36] with the CASSCF multireference: ACPF-ds, with single and double excitations from the active molecular orbitals, and ACPF-[p]ds, in which we correlated as well the M–$5p$ electrons by including all single and double excitations from the closed-shell of main character M–$5p$. Except when otherwise indicated, we have used for the metals the [3/3/4/2] valence basis set as explained below. For hydrogen, we used the [6s] set of Huzinaga[42] augmented with two p functions and contracted as [4/2]. We calculated dissociation energies with separate atomic calculations on

TABLE V. Spin-free spectrum of Pt and parameters of the sfss spin-orbit Hamiltonian [Eqs. (8) and (9)]. All numbers in cm^{-1}.

Term	Empirical	CG-AIMP MRCI(S)	$\delta(iS\Gamma)^a$
^3D	0	0	0
a ^1S	2 435	797	1 638
a ^1D	1 632	2 143	−511
^3F	3 944	5 591	−1 647
^3P	12 457	17 007	−4 550
b^1D	16 646	20 538	−3 892
^1G	17 030	22 118	−5 088
b^1S	39 846	48 402	−8 556

[a]See Eq. (9).

TABLE VI. Atomic spectrum of Pt. All numbers in cm^{-1}.

J	Main term	DHF+CI[a]	WB-AIMP MRCI(SD)[b]	sfss-WB-AIMP MRCI(S)	Experiment[c]
3	^3D	0	0	0	0
2	^3D	1 170	1 040	885	776
4	^3F	2 113	1 266	795	824
0	a ^1S	14 695	9 162	6 079	6 140
2	^3P	7 469	7 735	6 929	6 566
3	^3F	11 114	11 292	10 590	10 117
1	^3D	9 727	10 993	10 563	10 132
2	a ^1D	—	15 260	13 517	13 496
2	^3F	—	17 793	16 068	15 502
0	^3P	—	20 382	17 402	—
1	^3P	21 704	22 083	19 159	18 567
4	^1G	25 648	26 100	22 440	21 967
2	b ^1D	28 729	29 883	27 757	26 639
0	b ^1S	—	52 636	48 738	—

[a]Dirac–Hartree–Fock (DHF) plus four-component CI (singles and doubles) calculation from Ref. 41.
[b]Reference 40.
[c]Reference 37.

the ground states of H and M, at the same level of wave function and basis set as the corresponding molecular calculation.

B. Results

First, in order to decide upon a recommendable pattern of the valence basis set, we compare the spectroscopic constants of the $^2\Sigma^+$ state of PtH calculated with CASSCF wave functions at the all-electron and AIMP levels in Table VII. These calculations were done nonrelativistically since variational all-electron Cowan–Griffin calculations cannot be performed in molecules, but the conclusions might be safely extended to the spin-free relativistic case. The basis sets used for Pt in the valence-only NR-AIMP calculations are different contraction schemes of the $13s10p9d5f$ primitive set described in Sec. II C and used in the CASSCF and ACPF calculations of Sec. III. The basis set used for Pt in the all-electron calculation was a $22s16p13d8f$ primitive set of Faegri[43] augmented with the same p-polarization and d-diffuse functions as the valence-only calculation and contracted as $[8/6/6/3]$. The basis set of hydrogen described above was used in all the calculations. We observe in Table VII that the NR-AIMP calculation with the AE basis set produces results essentially coincident with the AE ones; this fact supports the chosen core-valence partition and proves the high quality of the core potentials. The use of the valence basis set with a contraction $[3/3/4/2]$ leads to very good results; this contraction scheme reaches a good balance between the quality of the results and the economy of the calculations which are desirable when an ECP method is used and, in consequence, it is advisable. Besides, Table VII shows that if a larger agreement with the AE results is required, it can be accomplished by releasing the outermost primitives of the p, d, and s blocks (in this order). We will use a $[3/3/4/2]$ contraction in the rest of the paper.

In order to check the ability of the present core potentials to represent relativistic effects in molecules of third-series transition metal elements, we performed nonrelativistic and relativistic calculations on the $^2\Sigma^+$ ground state of AuH$^+$. The relativistic effects on the bond distance are known to be very large in this molecule and coupled to the electron correlation effects: the bond shortening due to relativistic effects is about 1 Å at noncorrelated levels of calculation[44] and about 0.4 Å when correlation is also taken into account.[45]

We show in Table VIII that the relativistic effects estimated from the CG-AIMP and NR-AIMP calculations reasonably agree with the results of noncorrelated Dirac–Fock and correlated no-pair spin-free relativistic all-electron calculations. In particular, the fact that the nonrelativistic potential energy curve of AuH$^+$ ($^2\Sigma^+$) is extremely flat while the relativistic one is not, which is the reason for the large relativistic effects on R_e, is well reproduced by the AIMP calculations. The coupling between the spin-free relativistic and correlation effects is well reproduced too.

In Table IX we show the results of our CG-AIMP calculations on the MH hydrides (M being a transition element of the third series) together with the very scarce experimental information available and other theoretical calculations from the literature in which different valence-only and all-electron spin-free relativistic Hamiltonians were used. In order to summarize, we included only calculations that handled correlation effects at a level which could be compared with our calculations. Most of them are more or less equivalent to our ACPF-ds calculations. In Table IX, MCPF stands for modified coupled pair functional calculations,[46] an approximately size-consistent single-reference CI procedure. SOCI stands for second-order CI, which corresponds to single and double excitations from a CAS multireference and uses, in consequence, the same CI space as our ACPF-ds calculations. MRCI(SD)+Q stands for multireference CI with single and double excitations (a CI space equivalent to those of the SOCI and ACPF calculations) with the size-consistency correction of Langhoff and Davidson.[47] MP4(SDTQ) stands for full fourth order Möller-Plesset perturbation theory calculations. CISD is singles and doubles CI with a size-consistency correction.

Our CASSCF, ACPF-ds and ACPF-[p]ds calculations along the series show a uniform, significant effect of the dynamical correlation of the d and s shells and a minor effect of the $5p$ correlation, this being more important at the beginning of the series where the participation of the $5p$ orbital in bonding is expected to be higher. The comparison with

TABLE VII. Spectroscopic constants of PtH $^2\Sigma^+$. Nonrelativistic CASSCF calculations. Distances in Å , vibrational frequencies in cm^{-1}, and dissociation energies in kcal/mol.

	Pt basis set	R_e	ω_e	D_e
All-electron calculation				
	AE-[8/6/6/3][a]	1.655	1 710	58.14
NR-AIMP calculations				
	AE-[8/6/6/3][a]	1.655	1 720	58.15
	VAL-[3/3/4/2][b]	1.662	1 690	56.07
	VAL-[3/3/4/3][b]	1.662	1 690	56.07
	VAL-[3/3/5/2][b]	1.659	1 700	56.35
	VAL-[3/4/4/2][b]	1.657	1 710	57.39
	VAL-[4/3/4/2][b]	1.660	1 730	56.91
	VAL-[4/4/4/2][b]	1.656	1 740	58.16
	VAL-[3/4/5/2][b]	1.655	1 720	57.70
	VAL-[4/4/5/2][b]	1.653	1 740	58.47

[a]AE stands for all-electron basis set from Ref. 43.
[b]VAL for valence basis set from this work.

TABLE VIII. Spectroscopic constants of the $^2\Sigma^+$ ground state of AuH$^+$. Distances in Å , vibrational frequencies in cm^{-1}, and dissociation energies in kcal/mol. Dissociation limit is Au$^+$ $(5d^{10}-{}^1S)$+H(^{2}S). Numbers in parentheses correspond to the relativistic effects.

Method	Reference	R_e	ω_e	D_e
All-electron nonrel. HF	44	2.57		
All-electron DHF[a]	44	1.56(−1.01)	2200	13.6
All-electron nonrel. CC	45	1.936	600	—
All-electron no-pair rel. CC[b]	45	1.531(−0.41)	2238	45[c]
EAPP[d] nonrel. HF	59	2.636	305	1.6
EAPP[d] rel. HF	59	1.549(−1.09)	2124	10.4
EAPP[d] rel. CISD+Q	59	1.501	2312	39.8
NR-AIMP CASSCF	⋯	2.469	690	1.4
CG-AIMP CASSCF	⋯	1.571(−0.90)	1960	24.1
NR-AIMP ACPF-ds	⋯	2.300	401	3.5
CG-AIMP ACPF-ds	⋯	1.541(−0.76)	2040	34.5
NR-AIMP ACPF-[p]ds	⋯	2.185	434	4.2
CG-AIMP ACPF-[p]ds	⋯	1.531(−0.65)	2082	39.6

[a]$\Gamma_{1/2}$ state.
[b]Coupled-cluster (CC) calculations starting from AuH reference.
[c]Coupled-cluster calculations starting from AuH^{++} reference.
[d]Energy-adjusted pseudopotentials from Ref. 9 corresponding to the core [Kr,4d,4f].

experiments is limited to WH, AuH and HgH, the only hydrides whose spectroscopic constants have been measured, to our knowledge. The agreement of our results with the measurements of Ref. 48 on AuH and HgH is good. Furthermore, in AuH, our ACPF-[p]ds results are very close to the no-pair all-electron coupled-cluster calculations of Ref. 45 in which the same degree of electron correlation had been included. We take these agreements as indications of the good performance of our core potentials. In HgH, the spectroscopic constants have been deduced from measurements in Ref. 49 as well: The bond distance shows some deviation from our results and from the experimental data of Ref. 48; we do not have an explanation for this.

The apparently very large deviations with respect to the experimental bond distance and vibrational frequency of WH deserve some comments. These data were deduced from the analysis of the emission spectra of a plasma generated by a discharge in Ref. 50. In those experiments the emissions to two different vibrational levels of the electronic ground state were not identified. Instead, the value of ω_e was obtained as a rough estimate from the effective rotational constant B_v and the effective centrifugal constant D_v, with v unknown. This means that very large deviations from the true vibrational constant are possible: The agreement between our calculations and those of Ref. 51 indicate that this should be the case. Also, the too low values of R_e obtained in all the available theoretical calculations, in contrast with what is usual and with the results on AuH and HgH, might indicate that the interpretation of the emission spectrum measurements in Ref. 50 is questionable. In particular, a large value of v for the effective rotational constant B_v has not been ruled out; if this were so, the R_e obtained from B_v in Ref. 50 would be significantly overestimated.

Overall, our results are similar to those of other methods. In particular, the closeness between our CG-AIMP ACPF-ds results and the NP-AIMP MCPF results of Wittborn and Wahlgren,[19] which correspond to the spin-free no-pair Hamiltonian of Douglas–Kroll[18] is remarkable. Since both CG-AIMP and NP-AIMP methods have a common imple-

mentation of the frozen-core approximations involved, the previous agreement indicates that the Douglas–Kroll and Cowan–Griffin Hamiltonians are of similar quality for these molecular calculations, in spite of their different origins. The existence of systematic deviations with other methods is not apparent, except for a tendency to produce ω_e values slightly smaller than those of spin-free averaged relativistic ECP (AREP)[8] calculations. With respect to the disagreement in the ground state of the ReH molecule found by Wittborn and Wahlgren[19] ($^5\Sigma^+$) and Dai and Balasubramanian[52] ($^7\Sigma^+$), our calculations agree with the former result. We find another disagreement in the ground state of IrH according to our calculation ($^3\Delta$) and to those of Dai and Balasubramanian[53] ($^3\Sigma^-$) at an equivalent level of correlation; the energy difference between the two states is, however, small.

V. CONCLUSIONS

We produced and monitored the quality of the ingredients of relativistic spin-free CG-AIMP and spin-orbit WB-AIMP calculations with La and third-series transition metal elements. Starting from atomic Cowan–Griffin calculations, we generated the spin-free relativistic core AIMPs which correspond to the 62-electron core [Cd,4f]. Of those elements, we obtained their spin-orbit operators and their corresponding optimized, spin-orbit-corrected valence basis sets. We produced, as well, the nonrelativistic AIMPs and valence basis sets, since they are necessary for the explicit calculation of the relativistic effects. Also, we performed monitoring spin-free calculations on the atoms, singly ionized ions, and monohydrides of the ten elements, which revealed the good quality of the AIMPs. Finally, we carried out a spin-free-state-shifted spin-orbit-CI calculation on the

TABLE IX. Spectroscopic constants of third-series transition metal hydrides. Spin-free relativistic calculations and experimental results. Distances in Å , vibrational frequencies in cm^{-1}, and dissociation energies in kcal/mol.

Molecule	State	Method	Level	Reference	R_e	ω_e	D_e	Dissoc. limit
LaH[a]	$^1\Sigma^+$	CG-AIMP[b]	CASSCF	$\cdots$	2.11	1350	61.7	La (s^2d^1) ^2D
			ACPF-ds	$\cdots$	2.08	1380	63.2	
			ACPF-[p]ds	$\cdots$	2.06	1420	62.6	
		NP-AIMP[c]	MCPF	19	2.08	—	63.7	
		NP-AE[d]	MCPF	19	2.07	—	64.2	
		AREP[e]	SOCI	33	2.08	1433	60.0	
HfH	$^2\Delta$	CG-AIMP[b]	CASSCF	$\cdots$	1.84	1730	54.2	Hf (s^2d^2) ^3F
			ACPF-ds	$\cdots$	1.84	1680	64.2	
			ACPF-[p]ds[j]		1.82	1710	62.6	
		NP-AIMP[c]	MCPF	19	1.85	—	64.4	
		NP-AE[d]	MCPF	19	1.86	—	65.2	
		AREP[e]	SOCI	60	1.85	1702	66.2	
TaH	$^3\Phi$	CG-AIMP[b]	CASSCF		1.77	1730	43.8	Ta (s^2d^3) ^4F
			ACPF-ds		1.75	1800	56.7	
		NP-AIMP[c]	MCPF	19	1.76	—	55.2	
		NP-AE[d]	MCPF	19	1.76	—	57.8	
		AREP[e]	SOCI	61	1.75	1810	55.1	
WH	$^6\Sigma^+$	CG-AIMP[b]	CASSCF		1.76	1730	46.5	W (s^1d^5) ^7S
			ACPF-ds		1.72	1820	61.3	
			ACPF-[p]ds		1.71	1820	62.9	
		NP-AIMP[c]	MCPF	19	1.73	—	61.9	
		NP-AE[d]	MCPF	19	1.73	—	62.9	
		AREP[e]	SOCI	51	1.73	1897	62.0	
		Experiment[f]		50	1.79	531	—	
ReH	$^5\Sigma^+$	CG-AIMP[b]	CASSCF		1.67	1920	24.1	Re (s^2d^5) ^6S
			ACPF-ds		1.64	1970	43.7	
			ACPF-[p]ds		1.64	1950	46.2	
		NP-AIMP[c]	MCPF	19	1.64	—	45.3	
		NP-AE[d]	MCPF	19	1.64	—	44.8	
		AREP[e]	SOCI	52	1.63	2042	22.1	
	$^7\Sigma^+$	CG-AIMP[b]	CASSCF		1.82	1550	29.8	Re (s^2d^5) ^6S
			ACPF-ds		1.80	1520	36.6	
			ACPF-[p]ds		1.79	1550	36.1	
		NP-AIMP[c]	MCPF	19	1.81	—	24.8	
		AREP[e]	SOCI	52	1.82	1611	30.4	
OsH	$^4\Pi$	CG-AIMP[b]	CASSCF		1.63	1960	39.8	Os (s^2d^6) ^5D
			ACPF-ds		1.58	2130	58.2	
			ACPF-[p]ds		1.58	2160	59.5	
		NP-AIMP[c]	MCPF	19	1.59	—	61.5	
		NP-AE[d]	MCPF	19	1.59	—	60.5	
		AREP[e]	SOCI	62	1.58	2212	—	
		EAPP[g]	MRCI(SD)+Q	63	1.56	2327	62.7	
		HW-ECP[h]	MRCI(SD)+Q	63	1.56	2339	63.0	
IrH	$^3\Delta$	CG-AIMP[b]	CASSCF		1.60	2010	52.4	Ir (s^2d^7) ^4F
			ACPF-ds		1.55	2230	73.7	
			ACPF-[p]ds		1.54	2270	70.8	
		NP-AIMP[c]	MCPF	19	1.57	—	76.9	
		NP-AE[d]	MCPF	19	1.55	—	74.4	
		AREP[e]	MRCI(SD)	53	1.55	2316	58.3	
	$^3\Sigma^-$	CG-AIMP[b]	CASSCF		1.59	2030	48.3	Ir (s^2d^7) ^4F
			ACPF-ds		1.54	2230	69.6	
			ACPF-[p]ds		1.53	2210	69.4	
		AREP[e]	MRCI(SD)	53	1.56	2476	60.9	
PtH	$^2\Sigma^+$	CG-AIMP[b]	CASSCF		1.58	2050	55.2	Pt (s^1d^9) ^3D
			ACPF-ds		1.52	2290	77.5	
			ACPF-[p]ds		1.52	2310	78.0	
		NP-AIMP[c]	MCPF	19	1.52	—	74.0	

TABLE IX. (*Continued.*)

Molecule	State	Method	Level	Reference	R_e	ω_e	D_e	Dissoc. limit
		NP-AE[d]	MCPF	19	1.51	—	74.0	
		HW-ECP[h]	MP4(SDTQ)	64	1.50	2544	75.4	
		RECP[i]	MRCI(SD)	65	1.54	—	71.7	
	$\Omega = \frac{1}{2}$	4-comp. AE	DHF+CI[k]	41	1.53	2419	63.2	
AuH	$^1\Sigma^+$	CG-AIMP[b]	CASSCF	⋯	1.59	1910	49.1	Au $(s^1 d^{10})\ ^2S$
			ACPF-ds	⋯	1.55	2120	65.0	
			ACPF-[p]ds	⋯	1.53	2140	68.0	
		NP-AE[d]	CC [p]ds	45	1.52	2288	—	
		AREP[e]	CISD	66	1.59	2100	—	
		EAPP[g]	CISD	59	1.50	2288	68.2	
		Experiment		48	1.52	2303	74.3	
HgH	$^2\Sigma^+$	CG-AIMP[b]	CASSCF	⋯	1.81	1200	−8.8	Hg $(s^2 d^{10})\ ^1S$
			ACPF-ds	⋯	1.80	1110	9.8	
			ACPF-[p]ds	⋯	1.78	1270	10.4	
		AREP[e]	MRD-CI	67	1.78	1309	7.3	
		EAPP[g]	CISD	68	1.73	1185	2.8	
			QCI	⋯	1.79	1156	6.9	
		Experiment		48	1.77	1203	10.4	
				49	1.74	1387	10.6	

[a][Cd]-core and [3/3/3/1] valence basis set for La.
[b]Spin-free relativistic CG-AIMP calculations of this work corresponding to the core [Cd,4f].
[c]No-pair spin-free relativistic AIMP from Ref. 19 corresponding to the core [Ar,3d].
[d]No-pair spin-free relativistic all-electron calculations.
[e]Spin-free averaged relativistic ECP from Ref. 8 corresponding to the core [Kr,4d,4f].
[f]See text for a discussion.
[g]Spin-free relativistic energy-adjusted pseudopotential from Ref. 9 corresponding to the core [Kr,4d,4f].
[h]Spin-free relativistic ECP from Ref. 7 corresponding to the core [Kr,4d,4f].
[i]Spin-free relativistic ECP from Ref. 3.
[j]Here the reference space is a selection of the CAS: only configurations with coefficients with an absolute value larger than 0.05 are retained.
[k]Dirac–Hartree–Fock plus four-component CI calculations.

even spectrum of Pt which confirmed the conclusions of Ref. 26: The quality of the one-electron WB-AIMP spin-orbit operators is very high; thus, the quality of the spin-orbit splittings in WB-AIMP calculations is mainly limited by the treatment of the correlation effects, which can be handled at the spin-free level with standard *ab initio* techniques with a nonrelativistic structure.

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APPENDIX

The numerical all-electron atomic nonrelativistic Hartree–Fock and spin-free relativistic Cowan–Griffin–Hartree–Fock calculations necessary to produce the core orbitals have been performed with the program MCHF72.[54] The optimization of the valence basis sets has been carried out with a modified version of the program ABS[55] adapted to handle AIMP integrals. The spin-free CASSCF and ACPF calculations have been performed with the MOLCAS.4 package.[28] We used a modified version of the COLUMBUS suite of programs[56] for the spin-orbit-CI calculations; the AIMP integrals are calculated with ECPAIMP[57] in this case.

[1] M. Krauss and W. J. Stevens, Annu. Rev. Phys. Chem. **35**, 357 (1984).
[2] S. Huzinaga, Can. J. Chem. **73**, 619 (1995).
[3] O. Gropen, in *Relativistic Effects in Atoms and Molecules*, Vol. 2 of *Methods in Computational Chemistry*, edited by S. Wilson (Plenum, New York, 1988), p. 109.
[4] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).
[5] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
[6] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 270 (1985).
[7] P. J. Hay and W. R. Wadt, J. Chem. Phys. **82**, 299 (1985).
[8] R. B. Ross, J. M. Powers, T. Atashroo, W. C. Ermler, L. A. LaJohn, and P. A. Christiansen, J. Chem. Phys. **93**, 6654 (1990).
[9] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, and H. Preuss, Theor. Chim. Acta **77**, 123 (1990).
[10] S. Huzinaga and A. A. Cantu, J. Chem. Phys. **55**, 5543 (1971).
[11] Y. Sakai, E. Miyoshi, M. Klobukowski, and S. Huzinaga, J. Comput. Chem. **8**, 226 (1987); **8**, 256 (1987).
[12] S. Huzinaga, L. Seijo, Z. Barandiarán, and M. Klobukowski, J. Chem. Phys. **86**, 2132 (1987).
[13] R. D. Cowan and D. C. Griffin, J. Opt. Soc. Am. **66**, 1010 (1976).
[14] Z. Barandiarán and L. Seijo, Can. J. Chem. **70**, 409 (1992).
[15] Z. Barandiarán and L. Seijo, J. Chem. Phys. **101**, 4049 (1994).
[16] L. Seijo, Z. Barandiarán, and S. Huzinaga, J. Chem. Phys. **91**, 7011 (1989).
[17] Z. Barandiarán, L. Seijo, and S. Huzinaga, J. Chem. Phys. **93**, 5843 (1990).
[18] M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974).
[19] C. Wittborn and U. Wahlgren, Chem. Phys. **201**, 357 (1995).
[20] F. Rakowitz, C. M. Marian, L. Seijo, and U. Wahlgren, J. Chem. Phys. (in press).
[21] J. H. Wood and A. M. Boring, Phys. Rev. B **18**, 2701 (1978).
[22] S. Katsuki and S. Huzinaga, Chem. Phys. Lett. **147**, 597 (1988).
[23] L. Seijo, J. Chem. Phys. **102**, 8078 (1995).

[24] M. Casarrubios and L. Seijo, J. Mol. Struct.: THEOCHEM **426**, 59 (1998).

[25] R. Llusar, M. Casarrubios, Z. Barandiarán, and L. Seijo, J. Chem. Phys. **105**, 1 (1996).

[26] F. Rakowitz, M. Casarrubios, L. Seijo, and C. M. Marian, J. Chem. Phys. **108**, 7980 (1998).

[27] E. Francisco, L. Seijo, and L. Pueyo, J. Solid State Chem. **63**, 391 (1986).

[28] K. Andersson *et al.* MOLCAS version 4, Lund University, Sweden, 1997.

[29] Detailed core AIMP and valence basis set data libraries in electronic format are available from the authors upon request or directly at the address http://www.qui.uam.es/Data/AIMPLibs.html. See also Ref. 28.

[30] See AIP Document No. PAPS JCPSA6-110-303901 for 32 pages of Valence Gaussian basis sets, Coulomb model potentials, and core orbitals. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 500 Sunnyside Boulevard, Woodbury, NY 11797-2999. Fax: 516-576-2223, e-mail: paps@aip.org. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.

[31] R. M. Pitzer and N. W. Winter, J. Phys. Chem. **92**, 3061 (1988).

[32] *Gaussian Basis Sets for Molecular Calculations*, edited by S. Huzinaga (Elsevier, Amsterdam, 1984).

[33] K. K. Das and K. Balasubramanian, Chem. Phys. Lett. **172**, 373 (1990).

[34] P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[35] B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, Chem. Phys. **48**, 157 (1980); P. E. M. Siegbahn, A. Heiberg, J. Almlöf, and B. O. Roos, J. Chem. Phys. **74**, 2384 (1981); P. E. M. Siegbahn, A. Heiberg, B. Roos, and B. Levy, Phys. Scr. **21**, 323 (1980).

[36] R. Ahlrichs, P. Scharf, and C. Ehrhardt, J. Chem. Phys. **82**, 890 (1985); R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Lett. **143**, 413 (1988).

[37] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D. C., 1952), circular 467, Vols 2 and 3 (1959).

[38] R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981).

[39] T. van Kleef and B. Metsch, Physica B & C **95**, 251 (1978).

[40] M. Casarrubios and L. Seijo, Chem. Phys. Lett. **236**, 510 (1995).

[41] L. Visscher, T. Saue, W. C. Nieuwpoort, K. Faegri, and O. Gropen, J. Chem. Phys. **99**, 6704 (1998).

[42] S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).

[43] K. Faegri (private communication).

[44] Y. Ishikawa, G. L. Malli, and N. C. Pyper, **194**, 481 (1992).

[45] U. Kaldor and B. A. Hess, Chem. Phys. Lett. **230**, 1 (1994).

[46] D. P. Chong and S. R. Langhoff, J. Chem. Phys. **84**, 5606 (1986).

[47] S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).

[48] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure of Diatomic Molecules* (Van Nostrand, New York, 1979).

[49] W. C. Stwalley, J. Chem. Phys. **63**, 3062 (1975).

[50] J. F. Garvey and A. Kuppermann, J. Phys. Chem. **92**, 4583 (1988).

[51] Z. Ma and K. Balasubramanian, Chem. Phys. Lett. **181**, 467 (1991).

[52] D. Dai and K. Balasubramanian, J. Mol. Spectrosc. **158**, 455 (1993).

[53] D. Dai and K. Balasubramanian, New J. Chem. **15**, 721 (1991).

[54] C. Froese-Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977); MCHF72 program, Version modified by M. Klobukowski and L. Seijo.

[55] S. Huzinaga, M. Klobukowski, and Y. Sakai, Comput. Phys. Commun. **30**, 311 (1983).

[56] R. M. Pitzer (principal author), COLUMBUS suite of programs (ARGOS, CNVRT, SCFPQ, LSTRN, CGDBG, and CIDBG); See: A. H. H. Chang and R. M. Pitzer, J. Am. Chem. Soc. **111**, 2500 (1989), and references therein for a description. CNVRT and LSTRN have been adapted to handle ECPAIMP integrals by L. Seijo. CIDBG has been modified for spin-free-state-shifted spin-orbit CI calculations by M. Casarrubios.

[57] ECPAIMP is an integral program for ECP and AIMP calculations written by L. G. M. Pettersson, L. Seijo, and M. A. Nygren.

[58] R. L. Martin and P. J. Hay, J. Chem. Phys. **75**, 4539 (1981).

[59] P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, and P. D. W. Boyd, J. Chem. Phys. **91**, 1762 (1989).

[60] K. Balasubramanian and K. K. Das, J. Mol. Spectrosc. **145**, 142 (1991).

[61] W. Cheng and K. Balasubramanian, J. Mol. Spectrosc. **149**, 99 (1991).

[62] M. Benavides-Garcia and K. Balasubramanian, J. Mol. Spectrosc. **150**, 271 (1991).

[63] D. Andrae, U. Häudßermann, M. Dolg, H. Stoll, and H. Preuss, Theor. Chim. Acta **78**, 247 (1991).

[64] C. M. Rohlfing, P. J. Hay, and R. L. Martin, J. Chem. Phys. **85**, 1447 (1986).

[65] O. Gropen, J. Almlöf, and U. Wahlgren, J. Chem. Phys. **96**, 8363 (1992).

[66] R. B. Ross and W. C. Ermler, J. Phys. Chem. **89**, 5202 (1985).

[67] A. B. Alekseyev, H.-P. Liebermann, R. J. Buenker, and G. Hirsch, J. Chem. Phys. **104**, 4672 (1996).

[68] U. Haussermann, M. Dolg, H. Stoll, H. Preuss, P. Schwerdtfeger, and R. M. Pitzer, Mol. Phys. **78**, 1211 (1993).